Nanoscale materials at work: Mapping emerging applications in energy, medicine, and beyond

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Abstract

Since their inception in the early 1960s, the use of nanoscale materials has progressed in leaps and bounds, and their role in diverse fields ranging from human health to energy is undeniable. In this report, we utilize the CAS Content Collection, a vast repository of scientific information extracted from journal and patent publications, to identify emerging topics in this field. This involves understanding trends, such as the growth of certain topics over time, as well as establishing relationships between emerging topics. We achieved this by using a host of strategies including a quantitative natural language processing (NLP) approach to identify 279 emerging topics and sub-topics across three major categories – materials, applications, and properties – by surveying roughly 3 million publications in the nanoscience landscape. This wealth of information has been condensed into several conceptual mind maps and other graphs that provide metrics related to the growth of identified emerging concepts, group them into hierarchical classes, and explore the connections between them. We delved deeper into four major emerging applications of nanoscale materials – drug delivery, sensors, energy, and catalysis – to provide a more comprehensive and detailed picture of the use of nanotechnology in these fields. In addition, we leveraged the CAS registry, consisting of over 250 million substances, to determine and discover substances across varied classes (such as polymers, elements, organic/inorganic molecules) and how they are utilized in the 4 major applications. Our extensive analysis taking advantage of an NLP-based approach along with robust CAS indexing provides valuable insights in the field that we hope can help to inform and drive future research efforts.

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Introduction

Nanoscience, the study of materials and phenomena at the nanometer scale, has emerged as a frontier discipline at the intersection of physics, chemistry, biology, and engineering, with profound implications for various industries and scientific disciplines.

Nanomaterials have dimensions on the scale of one billionth of a meter. Specifically, IUPAC has defined nanoparticles as those having sizes in the range of 1-100 nm.[1] Materials having at least one dimension, pores, film thickness, or surface features in the 1-100 nm range are also considered as nanomaterials.[2, 3] At the nanoscale, materials exhibit unique properties and behaviors that are distinct from their bulk counterparts, enabling innovative applications in areas such as electronics, medicine, energy, and environmental remediation. By synthesizing, manipulating, or combining matter at the nanoscale, researchers can tailor properties such as conductivity, catalytic activity, and optical properties to meet specific needs. Additionally, the ability to precisely control size, shape, and composition opens doors to unprecedented functionalities, paving the way for transformative technologies.[4] Some of the tunable properties are melting point, band gap, fluorescence, electrical conductivity, magnetic permeability, surface area, and chemical reactivity, to mention a few.[5]

The concept of nanotechnology emerged for the first time in the lecture "There's plenty of room at the bottom" delivered by the physicist and Nobel prize laureate Richard Feynman at the American Physical Society meeting in 1959.[6] This presentation is considered to be a seminal event in the history of nanoscience, as it inspired the conceptual beginnings of the field decades later.[7] In this lecture, Dr. Feynman aimed to draw the attention of the audience to the advancement of technologies to produce ultrasmall objects built of very few atoms or molecules. In the 1990s, with the rapid rise of the nanotechnologies, scientists recalled Feynman's lecture and found that much of what they were concerned with was actually envisaged 30-40 years previously. Since then, Richard Feynman has been considered the founder of this new area of science and technology. The interest in exploring the size-dependent properties and utilizing these properties to enhance or create applications led to rapid growth in the number of publications related to nanomaterials beginning in the 1990s. The initial years of nanoscale research were focused on synthesis methods and morphology. In recent years, the relentless pursuit of understanding and harnessing nanoscale phenomena has become a focal point for researchers worldwide. It has now reached a point where products using nanotechnology are commercially available.[8, 9]

The high surface to volume ratio of nanomaterials can significantly enhance the surface-related properties such as catalytic activity,[10] charge storage capacity,[11] ion storage capacity,[12] and gas storage capacity, which are important in multiple applications including energy conversion and storage[13] and environmental remediation.[14] Their small size, and ability to customize nanomaterials has made them valuable in life sciences applications such as drug delivery[15, 16] and diagnostics.[17] Nanoporous catalysts[18, 19] and membranes[20] help achieve high product selectivity and precise gas separation,[21] respectively. Due to their distinct properties, nanomaterials can be highly responsive to environmental variations, leading to their use in different types of sensors.[22-24] Due to their high strength, as well as low density relative to

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conventional materials, nanomaterials and their composites are preferred in engineering applications.[25-27]

Using data from the CAS Content Collection, the world's largest human expert-curated collection of scientific data, we present a landscape view of the current research in the field of nanoscience. Querying this database resulted in identifying roughly 3 million journal and patent documents in the field of nanoscience published since 2003. Using Natural Language Processing analysis[28] focused on recently published documents, we identified emerging and prevalent topics, and clustered/grouped them into categories such as applications, materials, and properties. Out of the most prevalent topics, four related to applications of nanoscience and nanotechnologies, namely drug delivery, sensors, catalysis, and energy-related applications were further analyzed to provide insights into emerging trends with respect to substances/materials used, applications, as well as nanostructure morphologies utilized in these areas. Since the use of artificial intelligence (AI) continues to proliferate across diverse fields, we chose to dedicate a small section to analyzing the role of AI in nanoscience which remains very much in its infancy/early stages but with a promising future.

The key figures in this document include mind maps presenting emerging applications, materials, and properties associated with nanoscience, as well as a mind map presenting the most frequently referenced applications. The in-depth analysis on the four prevalent topics includes publication trends, most prolific and influential commercial and non-commercial publishing institutions, and patent assignees, along with analysis of substances and scientific concepts indexed by CAS.

Nanotechnology: Emerging Topics and Trend Landscape

In this section, we identify and describe the most active areas of research and development within the broad landscape of nanoscale materials (nanotechnology). This will be done in three ways. First, quantitative journal and patent document data analysis will be used to build a conceptual mind map showing a hierarchy of active and emerging research concepts. We will then select key features (concepts) in the mind map and cite examples of the most influential research which is driving their emergence with recent literature examples. Finally, additional quantitative analysis will be used to explore connections between concepts in the mind map.

Figures 1, 2, and 3 are conceptual mind maps of emerging topics in nanoscience. These were made by first identifying journal and patent documents containing nanoscale material topics in the CAS Content Collection published since 2019. This resulted in a set of over 1.3 million documents. NLP analysis, guided by subject matter experts, was then used to extract, and group scientific concepts from these documents. The publication frequency and growth rate since 2019 for these concepts was calculated and used to select the topics in the map. A hierarchy of concepts was then built, breaking up the concepts between applications, materials, and property sections. Figure 1 is combined map illustrating only the 1st level branches in the application, properties, structure-based grouping of materials, and composition-based grouping of materials, along with the number of documents which mention each of these concepts. It is important to note that the ends of the branches in the map, and the individual data points in the graphs, represent groups of terms summarized by the label. For example, the term "food" includes concepts such

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as food safety, food processing, food additives, and food preservation. Similarly, terms with alternate forms such as “nanoenzyme”, “nano-enzyme”, and “nanozyme”, as well as singular and plural forms, have also been grouped.

Of the three sections in Figure 1, a detailed hierarchy of concepts in applications and materials are presented in Figure 2A and 3A respectively. In the applications section of Figure 1, the applications with most number of documents, which are taken up for in-depth analysis, are highlighted. The most prevalent properties in these documents are related to the major applications. Surface properties and porosity are important for catalytic, filtration/membrane and sensing applications. Applications such as sensors, energy storage, energy conversion and photonics depend on the electrical properties of the materials. The other prevalent properties are biomedical, mechanical, thermal, adsorption, and optical properties.

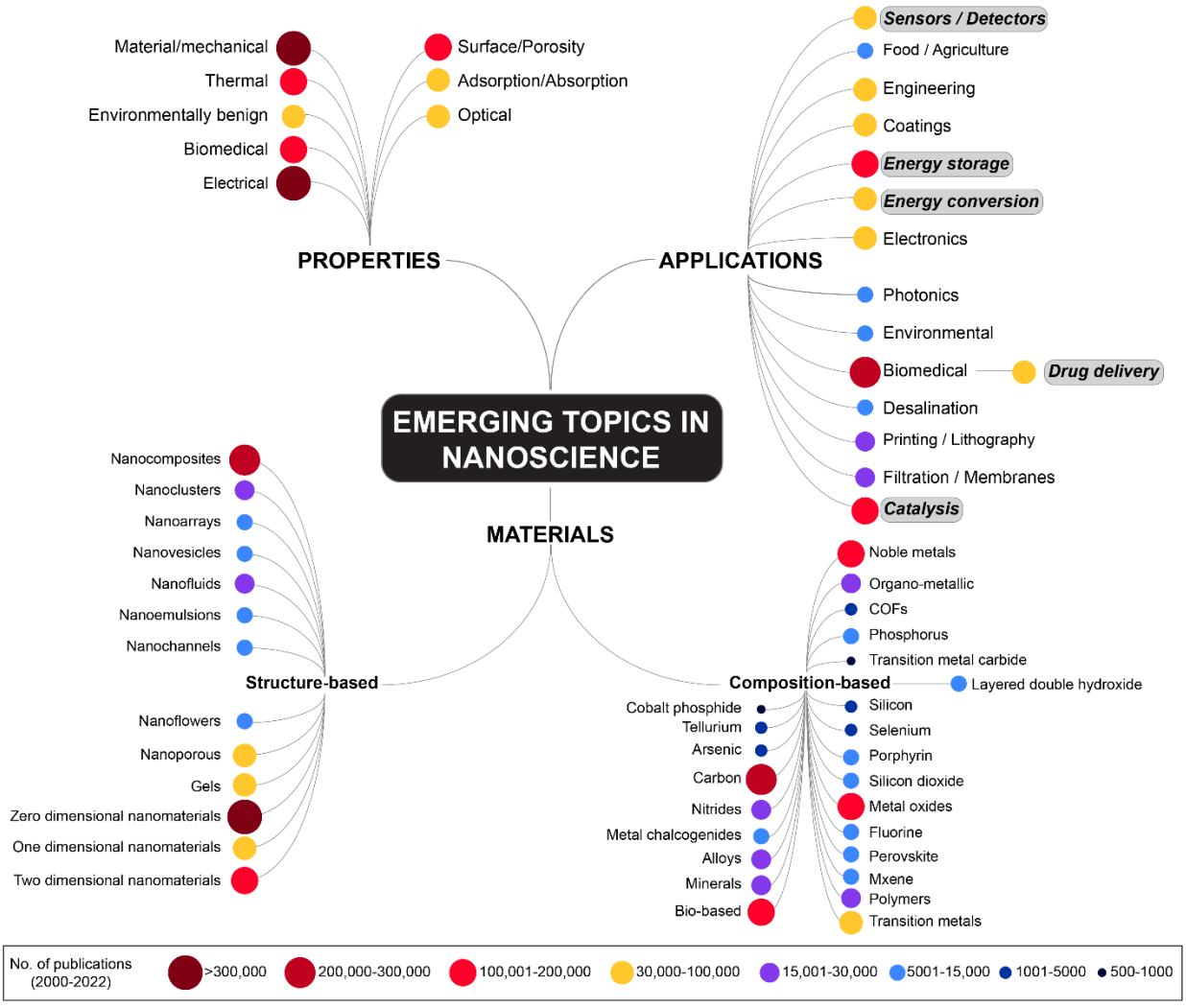

Figure 1: Mind map of the applications, materials, and properties in nanoscience which showed high growth in recent years.

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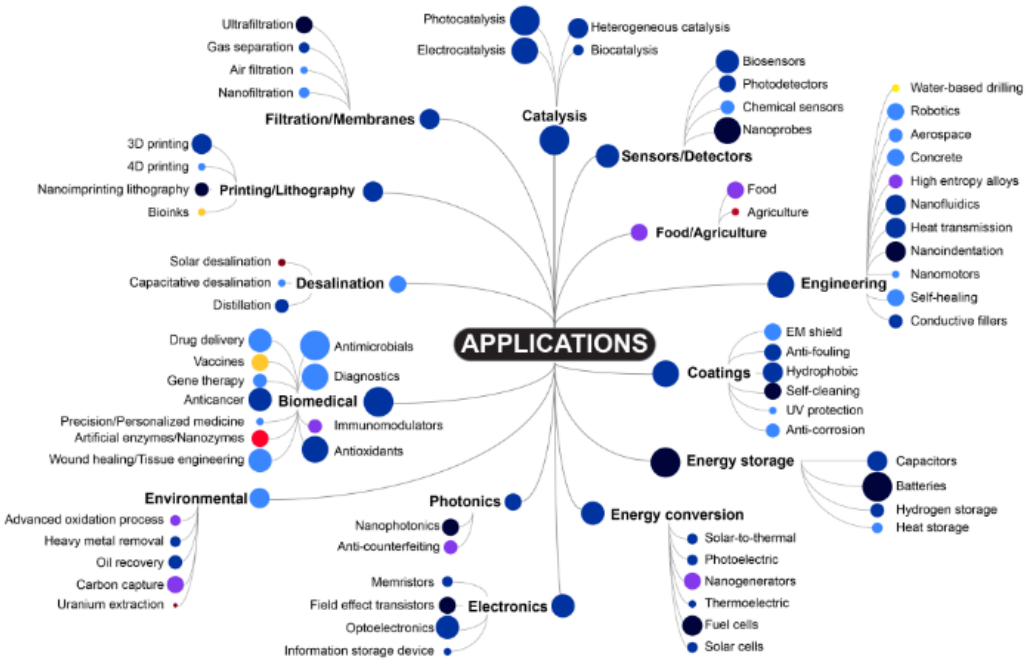
Panel B of both Figures 2 and 3 shows the total number of publications containing the concepts in the mind maps, and the average year-over-year growth rate of these publications from 2019 to 2022. Concepts that are referenced in a relatively low number of publications, but with a high growth rate, are found in the upper left section of the graphs, while more mature concepts with a relatively lower growth rate are found in the lower right section.

In the applications section of the map, the most prominent emerging branches are biomedical (driven largely by diagnostics, antimicrobials, antioxidant, and drug delivery), catalysis (electro- and photocatalysis), and energy storage. In the materials section, active areas of research include 0D and 2D nanomaterials, carbon-based materials, naturally derived materials including cellulose and lipids, and noble metals. In the section below, we will highlight concepts within the mind map of especially high growth from 2020-2023.



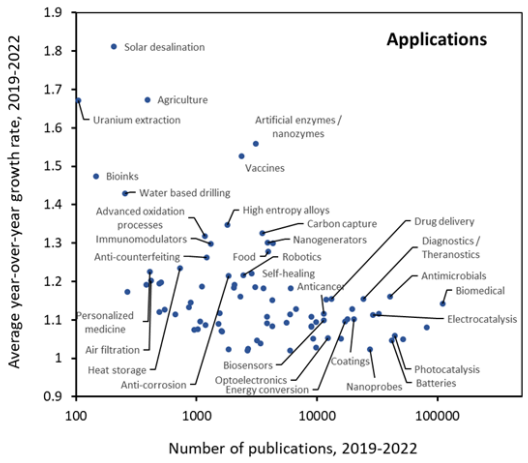


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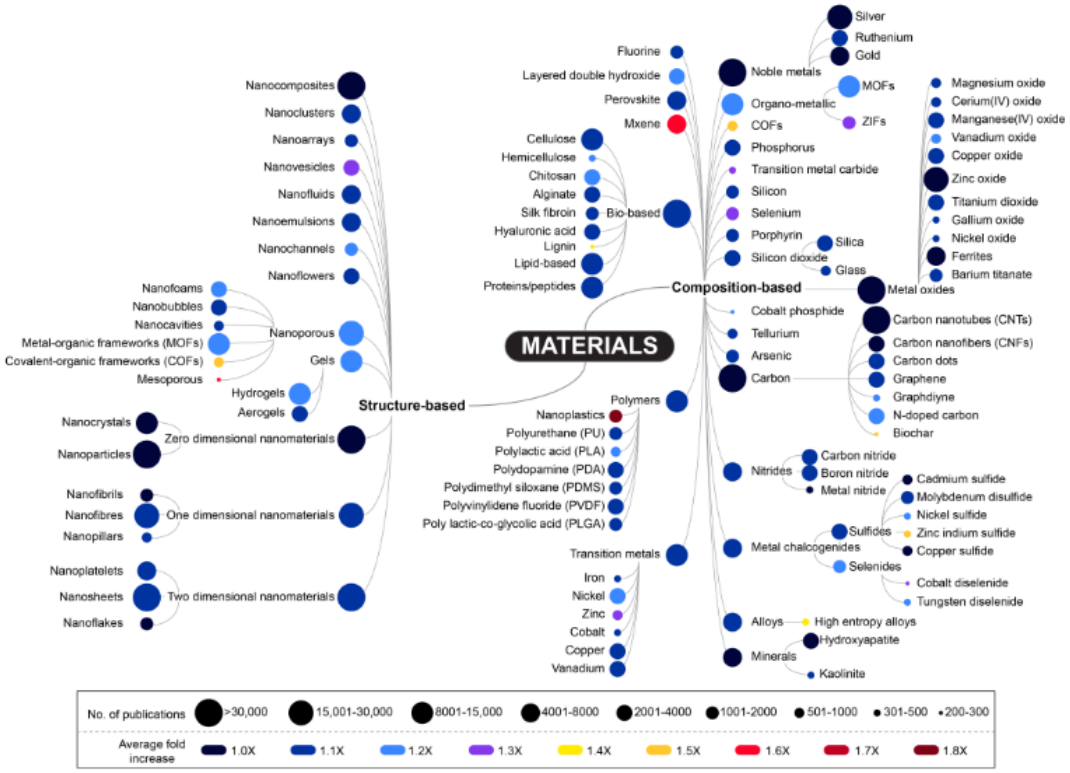
Figure 2: (A) conceptual mind map and (B) average 2019-2022 growth rate versus number of publications over that time period that reference applications involving nanoscale materials.



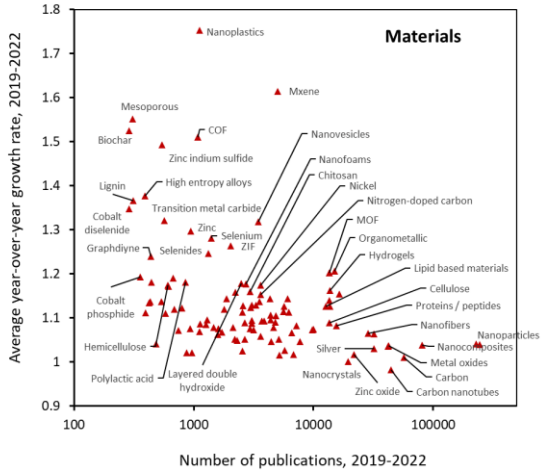


Figure 3: (A) conceptual mind map and (B) average 2019-2022 growth rate versus absolute number of publications that reference nanoscale materials.

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Applications

There are several emerging applications which are notable for their relative growth rate and overall number of publications in which they appear from 2019-2022. Nanogenerators are an example of such an application, specifically triboelectric and piezoelectric nanogenerators. These devices generate electrical energy from motion, through charge separation that takes place when two surfaces interact (tribo) or through deformation (piezo). Their growing frequency in publications appears to be driven by their use to power wearable devices such as human motion sensors[29, 30] and in human-machine interfaces.[31] We can further understand the context in which the term 'nanogenerator' is used in publications by plotting the growth rate and absolute number of co-occurrences of this term with other concepts in the mind maps in our document set. This is shown in Figure 4, where co-occurring terms are classified as material, application, or property-related.

Based on this analysis, the emerging materials most prominently associated with nanogenerators are nanofibers[32] and zinc oxide,[33] with hydrogels growing particularly quickly. Nanofibers are of interest to triboelectric nanogenerators because of their high surface area (improving the macroscopic charge density), flexibility, and the possibility of synthesizing customized nanofiber materials using electrospinning.[34] Polyvinylidene fluoride (PVDF) nanofibers have the additional advantage of a strong electrical dipole due to the presence of fluorine.[35] 1-dimensional ZnO nanomaterials are used in both types of nanogenerators, for its piezoelectric and mechanical properties.[36]

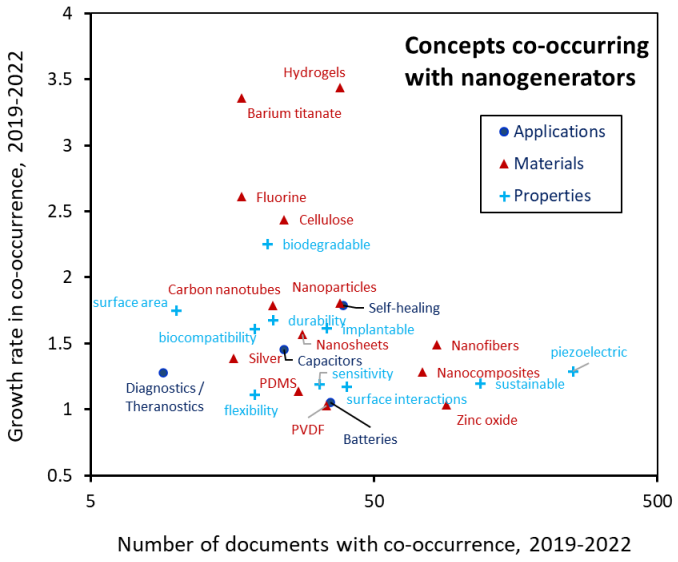

Figure 4: average 2019-2022 growth rate versus number of publications over that time period for terms co-occurring with nanogenerator applications.

Studies to decrease the presence of carbon dioxide in atmosphere and to capture and store it before release into the atmosphere are important due to its role in global warming. The use of nanomaterials for this purpose has grown in recent years since surface area and porosity play important roles in this process. More than 90% of the studies containing nanomaterials use them as catalysts for the reduction of CO_2 to useful chemicals, or the capture and storage of CO_2 using nanoporous materials. Reduction of CO_2 using nanocatalysts is carried out using electrocatalytic, photocatalytic and heterogeneous thermal catalysis,[37]

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in decreasing order of their contribution. Electrocatalytic reduction of CO_2 has been reported using transition metals[38] particularly copper[39] and tin, noble metals, post transition metals,[40] and carbon nanostructures. Thermal catalytic reduction of CO_2 is carried out using supported noble[41] and transition metal nanoparticles.[42] Nanoporous materials such as metal organic frameworks,[43] porous organic polymers,[44] covalent organic frameworks,[45] carbon nanotubes,[46] nanoporous carbon,[47] nanoporous silica[48] are used for capture and storage of CO_2.

Sustainable agriculture and nanofertilizers has the second highest growth rate in the Applications category and co-occurs primarily with nanoparticles.[49-51] Nanomaterials are of interest due to their potential to help address the world's food security and agricultural challenges such as those caused by pesticides, traditional fertilizers, climate change, irrigation difficulties, and poor soil quality. They are also considered a possible pathway to sustainable fertilizers.[52] A recent review by Shah *et. al.* discusses how nanotechnology can be applied for soil remediation, fertilizers/pesticides, drought stress, crop growth and seed germination (genetic engineering), water management, and nutrient delivery with a focus on sustainable agriculture.[53]

Life science and biomedical applications have driven a significant amount of growth in the use of nanoscale materials, as shown in Figure 2(a). Three notable examples include vaccines, nanozymes, and bioinks. Vaccines are biological preparations that render immunity to a particular infectious disease by stimulating the immune system to recognize the pathogenic agent. Nanoparticle-based vaccines are an emerging area of research that utilizes nanotechnology to enhance the effectiveness of vaccines.[54-56] These nanovaccines employ nanoscale materials, such as nanoparticles, liposomes, nanogels, micelles, and dendrimers, as delivery vehicles for antigens and adjuvants, aiming to improve immune responses and vaccine efficacy.[57, 58] Nanovaccines can advance targeted delivery, antigen presentation, stimulation of innate immunity, robust T cell response, combined with safety to combat infectious diseases and cancers. Moreover, nanovaccines can be highly valuable in generating effective immutherapeutic formulations against cancer.[59, 60]

Nanozymes are nanomaterials with enzyme-like catalytic activities.[61, 62] These synthetic nanostructures mimic the functions of natural enzymes but offer several advantages, such as better stability, tunable catalytic properties, cost-effectiveness, and easier large-scale production.[63] Some common types of nanozymes include metal-based nanoparticles such as gold, silver, platinum; metal oxide nanoparticles such as iron oxide, manganese oxide; and carbon-based nanostructures, e.g., graphene, carbon nanotubes.[64, 65] They have garnered significant interest in various fields, including biomedicine, environmental remediation, and industrial processes.[66] .[63] Some common types of nanozymes include metal-based nanoparticles such as gold, silver, platinum; metal oxide nanoparticles such as iron oxide, manganese oxide; and carbon-based nanostructures, e.g., graphene, carbon nanotubes.[64, 65] They have garnered significant interest in various fields, including biomedicine, environmental remediation, and industrial processes.[66]

The use of nanomaterials in bioinks is gaining popularity, especially for formulations used in 3D bioprinting. For instance, using nanomaterials such as clay, graphene carbon nanotubes, and silica particles can enhance the structural and rheological properties of bioinks and provide bioactive properties such as drug delivery capacity and antimicrobial effects.[67] Bioinks containing nanoparticles loaded with growth factors such as vascular endothelial growth factor (VEGF) or bone morphogenetic protein (BMP) can help to promote angiogenesis and osteogenesis within printed constructs.[68-70] In addition, bioinks incorporating polymer nanofibrils can be used to build cell culture scaffolds.[71] Furthermore, bioinks can be functionalized by incorporating luminescent optical sensor nanoparticles making them suitable for imaging cells while

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they grow.[70] Nanoparticle-containing bioinks can be used for printing 3D organs, for instance, gold nanorod-incorporated gelatin methacryloyl (GelMA)-based bioink is developed for printing 3D functional cardiac tissue constructs.[72] These examples highlight vast applications of nanoparticles containing bioinks in 3D printing.[67]

Materials

The data shown in Figure 3 refers to the use of prominently emerging material-related terms that appear in publications involving nanoscale materials. These material-related terms may be the nanoscale materials themselves, or materials that are often combined with nanoscale materials, or used to make them.

As can be seen in Figure 3(B), the term 'nanoplastics' has been growing rapidly in use since 2019. Nanoplastics are synthetic or modified natural polymers typically defined as being 1 µm or less in size, though some define them as being between 1 to 100 nm.[73, 74] These plastics have three ways of coming to be: intentional production for diverse applications, generation during the manufacturing of polymers, or via the fragmentation of larger plastics.[75-77] Nanoplastics-related terms co-occur with topics like toxicity[78, 79], antioxidants, and characterization techniques such as x-ray diffraction.[80-89] These associations are due mostly to concerns over the effects of nanoplastic waste in the environment. Co-occurrence with nanoparticles is also present due to some nanoplastics being identified as nanoparticles[90-92], but publications also discuss other associated nanoparticles (for example silver and TiO_2), regarding their removal alongside nanoplastics[80], their combined toxic effects[84], identification of nanoplastics in nanoparticle mixtures[93], their use to enhance sensors to quantify nanoplastics[94], and for other reasons.

MXenes are a class of inorganic 2-D materials that have been the subject of growing research interest since they were first reported in 2011.[95] Prominent applications of MXenes currently are in electrocatalysis,[96-98] photocatalysis,[99, 100] and batteries.[101, 102] They are well suited for use in these areas due to their high surface area, electrical conductivity, and high degree of versatility through altering their surface functionality and/or combining them with other nanoscale materials. Antimicrobial applications represent an especially fast growing area of use for the specific MXene $Ti_3C_2T_x$.[103, 104] MXenes are also frequently combined with other nanoscale materials, such as carbon nanotubes, to fully leverage their unique properties.

A more complete set of applications and materials that frequently co-occur in documents with MXenes are shown in Figure 5.

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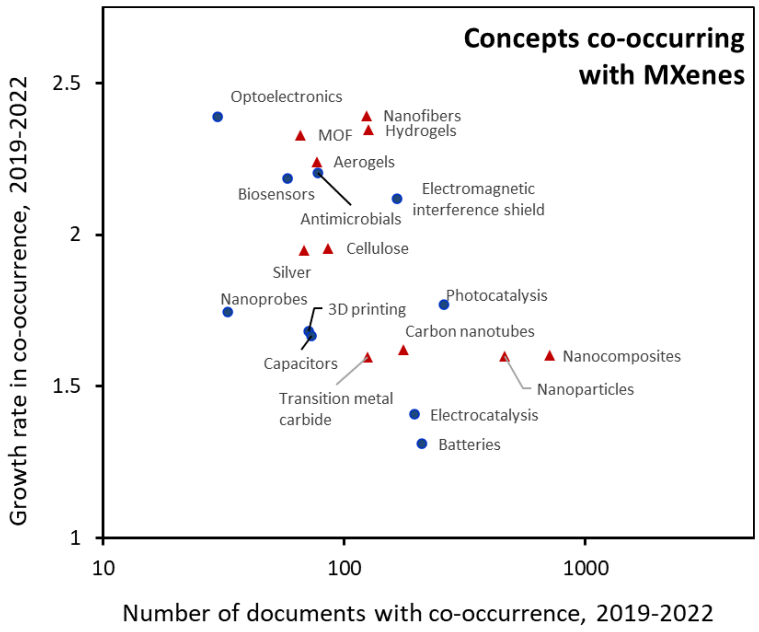

Figure 5: average 2019-2022 growth rate versus number of publications over that time period for terms co-occurring with MXenes.

Covalent organic frameworks (COFs) are 2D or 3D porous polymeric networks made of one or more covalently bonded monomers. COFs can be designed to be stable and insoluble under a variety of conditions. Furthermore, the chemical or catalytic properties and pore size of COFs can be customized by choosing the appropriate monomer(s).[105, 106] The pore sizes of COFs are in the micro as well as mesoporous range and are usually less than 10 nm. COFs are interesting for heterogeneous catalysis, which was usually dominated by inorganic materials, as they bridge the gap with homogeneous catalysis due to their level of customizability, which has historically only been possible only in homogeneous catalysis. COFs can act as catalysts in various ways, such as by using functional groups in their covalently bonded networks, as photocatalysts due to their semiconducting properties through π-π interactions,[107] catalyst nanoparticles[108] or enzymes anchored on the skeleton of COFs, using active sites on the walls of the pores,[109] or shape selective catalysis depending on the pore dimensions. Highly active single atom catalysts are obtained by anchoring them using coordination bonds to the heteroatoms in the COFs to achieve high catalytic activity.[110]

Zinc indium sulfide, also called indium zinc sulfide, is a ternary metal chalcogenide with a layered structure. It is a semiconductor with a bandgap of 2.2 eV which has attracted interest recently for photocatalytic and photoelectrochemical applications.[111] According to data from the CAS Content Collection, nearly 93% of the publications related to nanostructured $ZnIn_2S_4$ reference photocatalytic or photoelectrochemical applications, which include water splitting,[112] carbon dioxide reduction,[113] and removal[114] or degradation[115] of pollutants in aqueous media. The major advantages of $ZnIn_2S_4$ include its bandgap, which is suitable for sunlight absorption, band positions aligned to carry out the water splitting reactions / carbon dioxide reduction, non-toxic nature of its constituent elements, relatively moderate cost of its constituent elements, and its stability under photocatalytic water splitting conditions.[111] However, the widespread

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application of $ZnIn_2S_4$ is hindered by the high recombination of the photogenerated charge carriers and its limited absorption in the visible region only up to 563 nm.[116, 117] According to the CAS Content Collection data, the most favored nanostructure for $ZnIn_2S_4$ is nanosheet due to its layered structure. The other nanostructures in which $ZnIn_2S_4$ is reported include the following in the descending order of their number of publications: nanocomposites, nanoparticles, microspheres, nanorods, and quantum dots.

Notably, two naturally-derived materials appear in Figure 3. The first is lignin, a complex organic polymer found in plant cell walls, which is essential for providing structural support and rigidity. Its abundance and biodegradability make it an attractive material for nanoscience-related applications. For example, lignin nanoparticles can serve as drug delivery carriers by encapsulating pharmaceutical ingredients, and can be functionalized with various targeting ligands to enhance specificity and efficacy in drug delivery.[118, 119] Lignin nanoparticles can be incorporated into polymer matrices to create nanocomposites which can be used in packaging and automotive applications, and can also be used for environmental remediation applications including soil remediation, wastewater treatment and sustainable agriculture.[120, 121] Lignin can be processed into nanofibers which can be used in developing filtration systems and tissue culture scaffolds due to high mechanical strength, high surface area and biocompatibility.[122 123] Lignin can also be used to develop nanomaterials which can be used in energy storage applications and catalysis.[120, 121, 124, 125]

The second naturally derived material is biochar, which is made through the pyrolysis of biomass. Its most prominent application is in the removal of pollutants from water, including heavy metals[126] and organics.[127] The adsorptive capacity of biochar can be enhanced by modifying it with metals or other chemical functionality. This approach can also be used to impart it with the ability to oxidize organic contaminants using Fenton-like processes.[128]

Extracellular vesicles, which represent a route of intercellular communication and are involved in essential physiological processes have emerged as powerful tools in various fields including drug delivery, diagnostics, and biotechnology.[129] However, their limited targeting ability, insufficient production yield, and low drug encapsulating capability have hampered their clinical development. Therefore, engineering of multifunctional hybrid nanovesicles mimicking natural extracellular vesicles but with favorable adaptability and flexibility has become a key challenge in expanding their application.[130-132] Such nanovesicles are nano-sized vesicles composed of lipid bilayers and/or other materials. They have garnered significant interest due to their unique properties and ability to encapsulate and deliver therapeutic agents, biomolecules, and imaging agents, thus offering opportunities for targeted drug delivery, diagnostics, and therapeutic interventions. Nanovesicles can be composed of lipids, polymers, proteins, or a combination of these materials.[133-137] They can be loaded with imaging contrast agents or fluorescent dyes for non-invasive imaging of tissues and cells *in vivo*. Nanovesicles derived from stem cells or other cell types hold promise for tissue regeneration and repair by delivering bioactive molecules and promoting cellular signaling pathways.[138-140]

Connections between concepts

To understand connections between concepts in the mind map, we have performed an NLP-based analysis which counts the number of co-occurrences of individual concepts in the same sentences of journal abstracts. This allows us to quantify the degree of connection between any two concepts shown in the mind maps in Figures 2 and 3.

The plots in Figure 6 show the average number of documents published between 2019 and 2022 where pairs of terms co-occur in the same sentence (x axis), and the average growth rate of documents with

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those co-occurrences over the same time period (y axis). For clarity, combinations are separated into two figures, showing co-occurrence of concepts within the same maps (i.e. terms which both appear in the application map, or that both appear in the materials map), and co-occurrence of terms in different maps. The general trend observed in this data is that there is a wide range of growth rates for the combinations with relatively low publication frequency (less than 20-30 documents per year), with a long tail extending to high publication numbers but relatively low growth rates.

The most interesting pairs on the graphs, represented by labeled data points, fall into two categories. The first are pairs that have a relatively high growth rate compared to other concept pairs with a similar number of total documents, which represent emerging connections between concepts. The second includes pairs with a fairly high number of documents but a low growth rate, which can be described as well-established or more mature combinations.

There are a number of observations that can be made based on the data shown in Figure 6(A). For example, ZnO and Ag, which both co-occur in the same sentence as nanoparticle terms in over 2000 documents between 2019-2022, appear to be very well-established nanoparticle materials. In contrast, the combination of MXenes with nanofibers and nanoparticles represents a faster growing area of research, but with fewer overall publications. Within these combinations, publications where MXenes are combined with nanoparticles are more frequently studied compared to their combination with nanofibers, which is growing more quickly but with fewer overall publications.

In Figure 6(B), we see that the combination of vaccines and lipid-based materials appears prominently, with an exceptionally high growth rate given the total number of references for this combination, which can be attributed to the large number of publications related to COVID-19 vaccines published in 2021 and 2022. Other biomedical applications (anticancer-nanoemulsions, vaccines-nanoparticles, and antimicrobial nanomaterials) also appear prominently in this analysis, along with energy conversion, catalysis, and EMI shielding combinations.

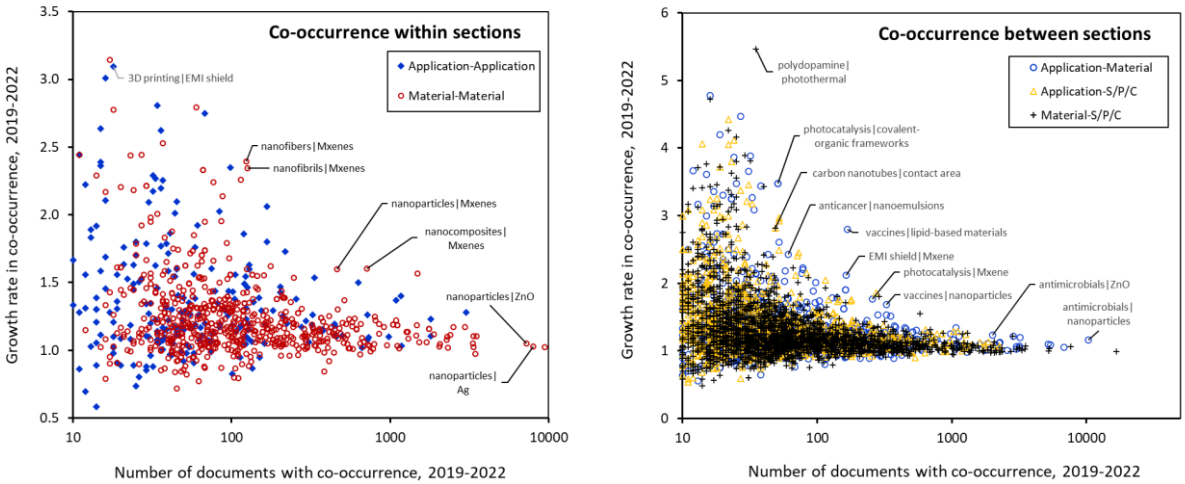

Figure 6: average year-over-year growth rate versus absolute number of publications from 2019-2022 for concepts co-occurring in the same sentence in journal abstracts for concepts (A) in the same mind map and (B) in different mind maps. S/P/C refers to synthesis, properties, and characterization concepts.

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Applications of Nanoscale Materials in Drug Delivery Systems

Introduction

The development and use of nanotechnology has grown substantially in the past decades. In the last decades, nanotechnologies have gained an impressive momentum. The application of nanotechnology inventions or products has revolutionized many aspects of everyday life including various medical applications and specifically the drug delivery systems (DDS), maximizing the therapeutic efficacy of the contained drugs by means of bioavailability enhancement or minimization of adverse effects.

Overall, drug delivery has been a complex challenge, often impeded by the limited solubility, stability, and bioavailability of many therapeutic agents. These constraints have motivated a widespread quest to find more efficient ways to deliver drugs to their intended targets. Among the transformative advancements in drug delivery technologies, nano-sized DDS have emerged as a formidable force in the world of pharmaceutical science and practice offering a dynamic range of solutions that transcend traditional pharmaceutical boundaries.

Typically, nano-sized objects contain a small number of atoms or molecules, a significant part of which is located on their surface. Therefore, while the characteristics of the macrosystems are determined by their bulk properties, for nanosystems the surface effects are dominant. Unlike macrosystems, the properties of which generally do not depend on their size, the properties of the nano-sized systems are essentially dependent on their size. As a result, nanoscale particles exhibit unique structural, chemical, mechanical, magnetic, electrical, and biological properties, which are often of significant value in their applications as DDS. Prominent characteristics of the nanosized DDS are their high surface area/volume ratio, their chemical and geometric tunability, as well as their capability to interact with biomolecules in order to facilitate uptake across the cell membrane. The large surface area relates to high affinity for drugs and small molecules such as ligands or antibodies to bind and adsorb, facilitating targeting and controlled release.

Due to the advantage of their size, nanoscale systems have been demonstrated to be efficient drug delivery systems and may be useful for encapsulating drugs, enabling more precise targeting with a controlled release. Their use may address some of the most pressing challenges in drug delivery, such as solubilizing poorly water-soluble drugs, protecting labile drugs from degradation, and delivering drugs selectively to disease sites. Nanosized structures stay in the blood circulation for a prolonged time, allowing the sustained release of incorporated drugs. Thus, they cause fewer plasma fluctuations with reduced adverse effects. [141] Being nanosized, these structures penetrate tissue, facilitate easy uptake of the drug by cells, enable an efficient drug delivery, and ensure activity at the targeted location. The uptake of nanostructures by cells is much higher than that of large particles. [142, 143] Hence, they directly interact to treat diseased cells with improved efficiency and reduced side effects. Modifying or functionalizing nanoparticles to deliver drugs through the blood-brain barrier for targeting brain tumors has been one superb outcome of medical nanotechnology. [144] Furthermore, due to their size, shape and functionality, nanoparticle systems are crucial components of DNA delivery vectors. [144, 145] Furthermore, due to their size, shape and functionality, nanoparticle systems are crucial components of DNA delivery vectors. [145] They can penetrate deep into tissues and are absorbed by the cells efficiently. [146] Moreover, nanoparticles have widened the scope of pharmacokinetics for insoluble drugs.

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Advantages of nano-sized DDS

The rationale behind employing nanosized drug delivery systems lies in the numerous advantages they offer compared to traditional drug delivery methods, which contribute to improved therapeutic outcomes, reduced side effects, and enhanced patient compliance. These advantages can be summarized as follows:

– Nanosized carriers can be engineered to target specific cells, tissues, or organs. This **targeted delivery** minimizes the exposure of healthy tissues to the drug, concentrating its effects at the intended site of action. [16, 147]

– Many drugs, especially those with poor water solubility, can have limited bioavailability. Nanosized drug delivery systems can improve drug solubility, leading to **enhanced bioavailability** and, consequently, improved therapeutic efficacy. [16, 148] Thus, nanotechnology may help with drug repurposing: drugs whose development might have been abandoned due to poor bioavailability, but which otherwise show satisfactory activity against intended targets, can be repurposed with the help of nanotechnology. [149, 150]

– Nanocarriers can extend the time a drug circulates in the bloodstream. This **prolonged circulation time** contributes to a sustained release of the drug, reducing the frequency of administration and improving patient compliance. [151, 152]

– Nanocarriers can **protect drugs** from degradation, metabolism, or elimination before reaching the target site. This protection enhances the stability of drugs and ensures a higher concentration reaches the intended location. [151, 153, 154]

– By selectively delivering drugs to the target site, nanosized drug delivery systems can minimize exposure to healthy tissues, reducing the potential for **toxicity** and lessening the occurrence of **side effects** commonly associated with systemic drug administration. [16, 147]

– Nanosized drug delivery systems allow for the simultaneous delivery of multiple drugs. This is particularly beneficial for **combination therapy**, where different drugs with complementary mechanisms of action can be delivered together for a synergistic therapeutic effect. [155, 156]

– Nanosized carriers can **overcome biological barriers**, such as the blood-brain barrier, allowing drugs to reach and act on specific locations that are otherwise difficult to access. [157, 158]

– Nanocarriers provide **flexibility in loading** a variety of drugs, including small molecules, proteins, nucleic acids, and imaging agents. This versatility makes them suitable for a wide range of therapeutic applications. [151, 159]

– The size and surface properties of nanocarriers can be tailored to **optimize pharmacokinetics**, leading to improved drug distribution, absorption, and elimination. [148, 154]

– Nanosized drug delivery systems can be designed for **personalized medicine** approaches, where treatments are tailored to individual patients based on diagnostic information. This customization can lead to more effective and targeted therapies.[160, 161]

– Some nanosized carriers can be designed to **combine diagnostic and therapeutic functions**, allowing for simultaneous imaging and treatment. This integration can provide real-time information about treatment efficacy. [162, 163]

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– The reduced side effects, less frequent dosing, and improved efficacy associated with nanosized drug delivery systems contribute to enhanced **patient compliance** with prescribed treatment regimens. [164, 165]

Landscape of the nano-sized drug delivery systems research

In recent years, sizeable methodological progress and a wealth of knowledge have promoted the advancement of research on nano-sized DDS, enhancing our understanding of their structure and efficiency. This is reflected in the consistent growth in the number of related scientific publications (journal articles and patents) in the last two decades (Figure 7A).

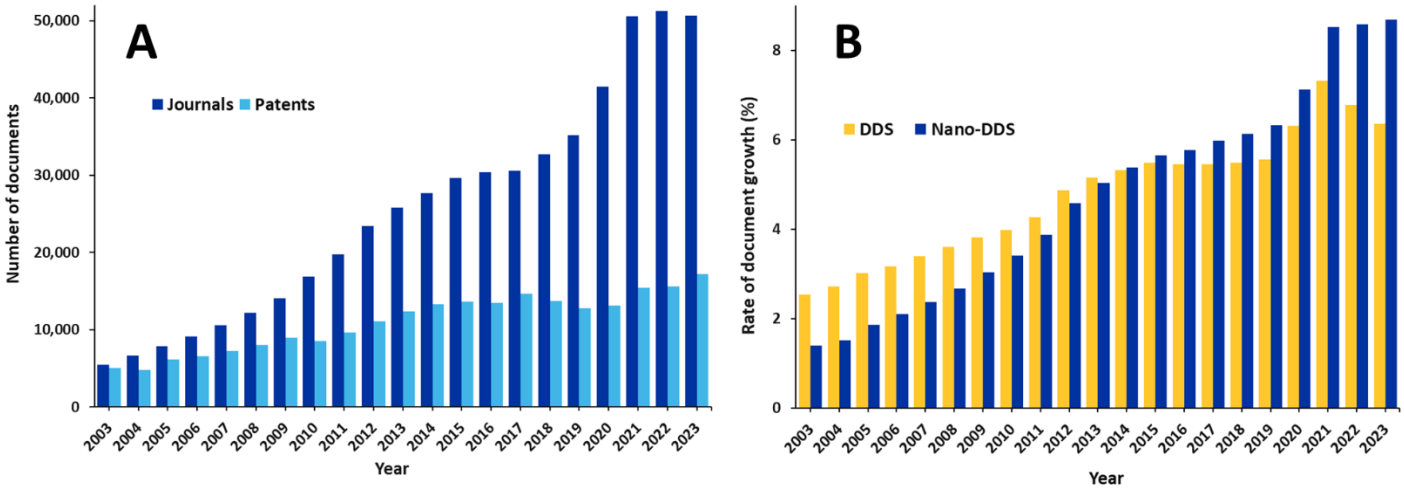

Figure 7. (A) Yearly growth of the number of documents (journal articles and patents) related to nanosized DDS in the CAS Content Collection; (B) Nano-DDS vs. overall DDS-related documents yearly growth.

In Figure 7B, the yearly growth rate of the number of publications in the CAS Content Collection related to nano-sized DDS are compared to those generally related to DDS. While in the years 2003-2013 the nano-DDS exhibit slower rate, during the last decade the number of publications related to nano-DDS has grown at similar or greater rates than the number of publications for DDS as a whole, with a notable increase in the last three years. The recognition of the potential advantages of nano-DDS over traditional DDS has likely driven increased interest in and publication rates for nano-DDS.

Currently, there are over 600,000 scientific publications (mainly journal articles and patents) in the CAS Content Collection related to nano-DDS. Journal article and patent publication counts have increased steadily over the last decades, with journal articles increasing by over 30% in the last three years (Figure 7A). Growth in the number of patents is slower when compared to journal publications and this is indicative of the field being in the phase of scientific knowledge accumulation often preceding subsequent transition into patentable and more commercial applications.

China, the United States, India, South Korea, and Japan, are the leaders with respect to the number of published journal articles and patents related to nano-DDS research, with China emerging as an eminent leader (Figure 8).

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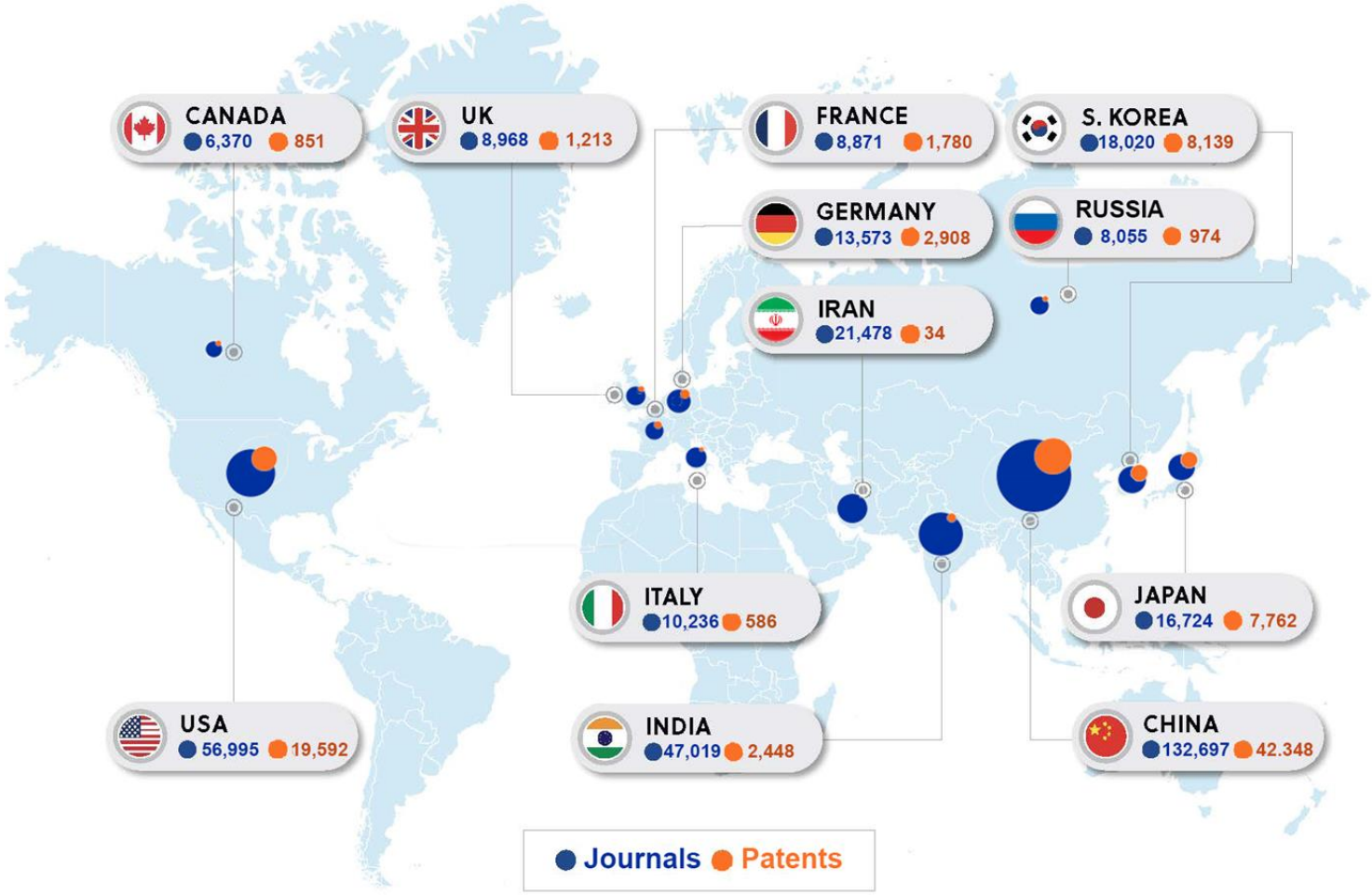

Figure 8. Leading countries/regions with respect to the numbers of nano-DDS-related journal articles (blue) and patents (orange). Data includes publications (journals and patents) from the CAS Content Collection for the period 2003-2023

The scientific journals *ACS Applied Materials & Interfaces, RSC Advances, Colloids & Surfaces, ACS Nano,* and *Nanoscale* have published the highest number of articles related to nano-DDS (Figure 9B), while *ACS Nano* and *Journal of the American Chemical Society (JACS)* lead in terms of number of citations (Figure 9C). When the citations per article, an indicator of the impact of journal publications, are considered, *JACS, Biomaterials*, and *ACS Nano* emerge at the top (Figure 9A).

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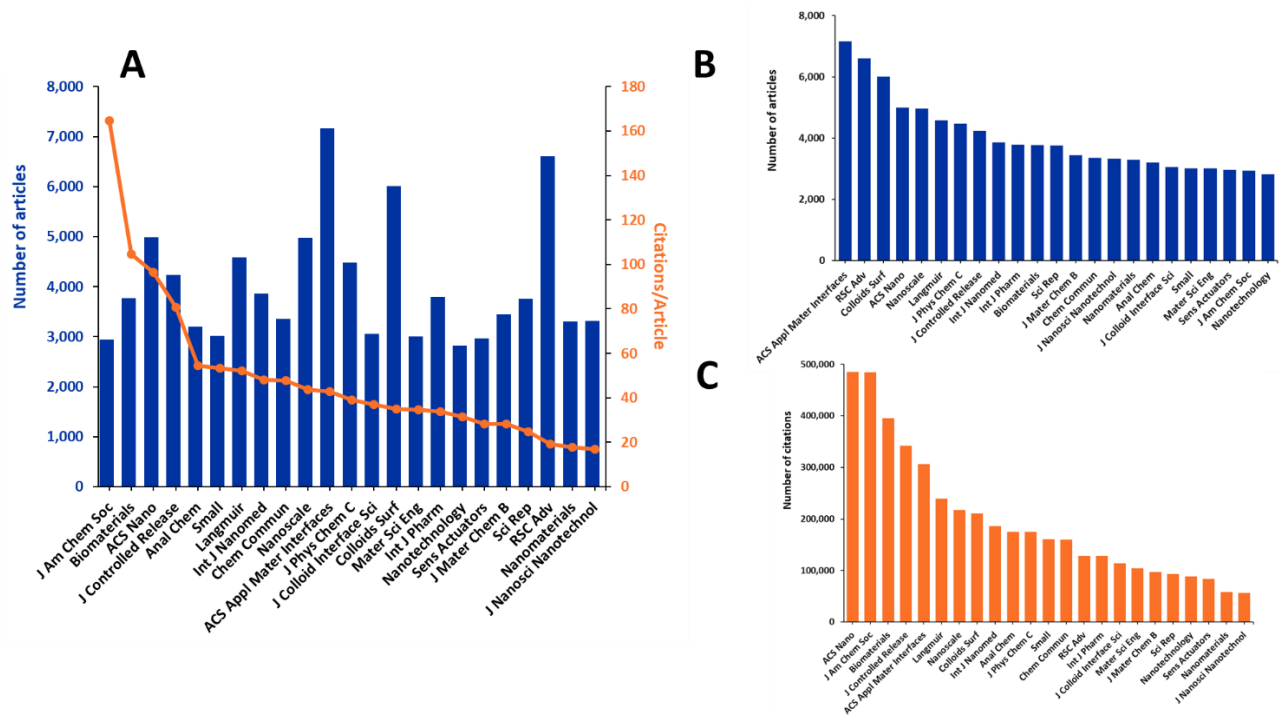

Figure 9. (A) Leading scientific journals with respect to the number of published nano-DDS-related articles (blue bars) and the average number of citations per article (orange line). This figure was made by first selecting the top 100 journals in terms of nano-DDS publications, then ranking them based on average citations per article. The top 23 journals based on this ranking are shown. Insets: Classification of the top scientific journals with respect to the number of published nano-DDS-related articles (B), and number of citations (C).

Ranking research institutions first by the volume of journal publications (Figure 10A) followed by the average number of citations per publication (Figure 10B) allows the identification of leading academic organizations actively participating in the area of nano-DDS research. The Chinese Academy of Sciences, a group of 124 individual research institutions,[166] is a distinct leader with respect to the number of published nano-DDS-related journal articles (>6,000). The field is largely dominated by Chinese universities and academic organizations (accounting for ~80% of the top 20 organizations) when only the volume of journal publications is considered (Figure 10A). The average number of citations per publication is considered as an indicator of the scientific impact of a given publication. By this measure, the leading organizations show a much more diverse spread across different countries or regions (Figure 10B), with most of them having - a relatively low number of publications which are highly cited. Three universities from the USA (Northwestern University, Stanford University, and the Massachusetts Institute of Technology), although ranking relatively low in terms of the actual number of journal publications, have the highest number of citations per publication (>100) indicating the high scientific impact of those publications (Figure 10B). Indeed, the International Institute of Nanotechnology [167] at Northwestern University (USA) is known for performing high impact nano-DDS-related research (see, e.g., [168-172]).Indeed, the International Institute of Nanotechnology [167] at Northwestern University (USA) is known for performing high impact nano-DDS-related research (see, e.g., [168-172]). One such highly cited article (1,025 citations according to SciFinder[n]) from that organization titled “Surface Engineered Polymersomes for Enhanced Modulation of Dendritic Cells During Cardiovascular Immunotherapy” describes polymeric nanocarriers decorated with an optimized surface density of a lipid construct, to demonstrate the therapeutic augmentation and dosage lowering capability of cell-targeted nanotherapy in the treatment

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of cardiovascular disease. An article titled "PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs" authored by researchers from Stanford University has received over 3,000 citations. [173] Another highly cited article: "Knocking down barriers: advances in siRNA delivery" (> 2,400 citations) authored by scientists at the Massachusetts Institute of Technology highlights novel synthetic materials for the encapsulation and intracellular delivery of siRNA. [174]

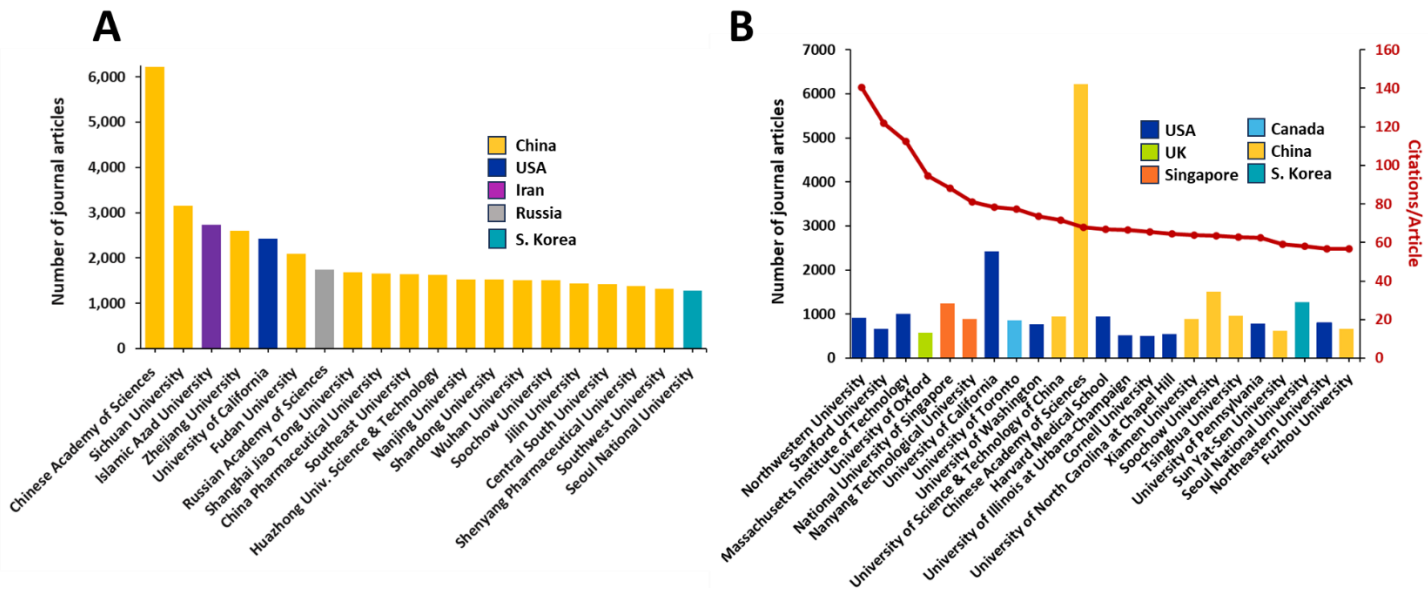

Figure 10. Leading academic research organizations with respect to the number of published nano-DDS-related articles (bars) (A), and the number of citations per article (red line) (B). The bars have been colored to represent different countries or regions as indicated by the legend. In (B), organizations were selected from the top 100 in terms of number of publications in the nano-DDS area.

The University of California is the distinct leader with respect to the number of patents by academic organizations (Figure 11A). Among commercial organizations, F. Hoffmann-La Roche (Switzerland), Procter & Gamble (USA), and Novartis (Switzerland) are the companies with the highest number of nano-DDS-related patents (Figure 11B). Recent patents of F. Hoffmann-La Roche appear to be focused on cancer immunotherapy and hepatitis B therapy utilizing nucleic acid nanocarriers such as lipid vesicles[175] and hyaluronic acid conjugates,[176, 177] as well as highly porous polymer[178] and nanopore-based[179] diagnostic methods. Novartis, a Swiss pharmaceutical company, has filed patents in recent years that related to treatment of cancer, liver and infectious disease utilizing nanocarriers such as micelles, liposomes and emulsions,[180] mesoporous silica nanoparticles,[181] and nanostructured amorphous materials.[182] Patents of Procter & Gamble and L'Oreal relate mainly to nanodelivery in cosmetics, a burgeoning application for nano-DDS.

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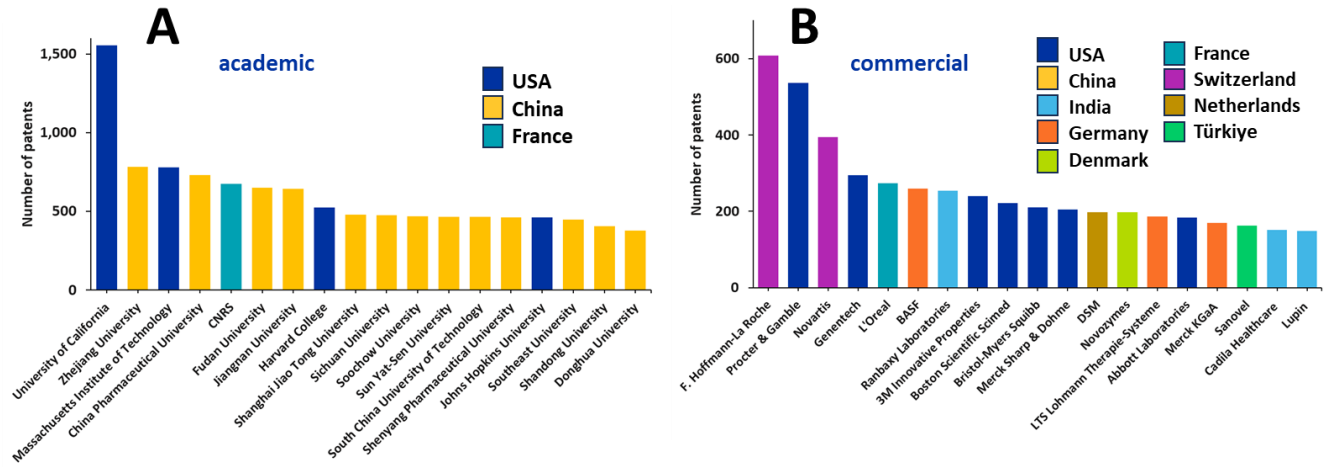

Figure 11. Top academic (A) and commercial (B) organizations with respect to the number of nano-DDS-related patents.

Key nano-DDS forms, materials, and applications

Since its dawn, nanotechnology has become a focus and a vital part of pharmaceutical science and has found numerous remarkable applications in drug delivery. For example, the potential of liposomes as drug delivery systems was recognized almost immediately after their discovery in the 1960s.[183-187] The use of the term "nanoparticle" in the context of drug delivery dates as far back as 1978.[188] Continued interest resulting in extensive research and development has led to wide variety of nano-sized DDS forms. Analysis of >600,000 documents allowed identification of the nano-sized DDS forms, a few representative examples of which are shown in Figure 12A, and their trends, both in terms of growth in publications (Figure 12B) as well as distribution of certain nano-sized DDS across subcategories (Figure 12C).

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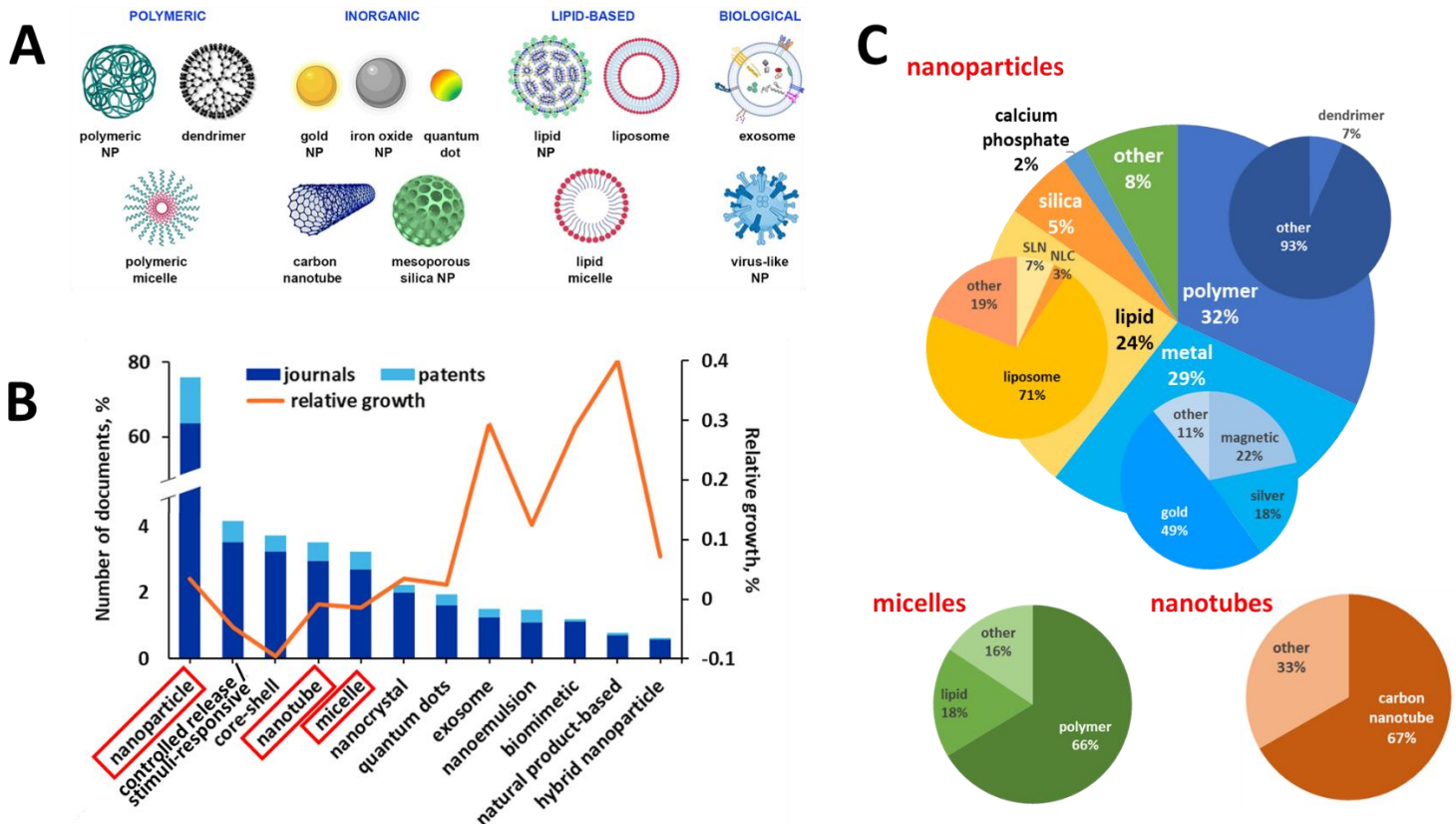

Figure 12. (A) Schematic representation of various types of nano-DDS (some individual icons sourced from www.biorender.com); (B) Percentage of documents (journal articles and patents, blue bars) and relative growth (orange line; calculated as the increase in the number of documents in the last three year normalized over the total number of documents for the given nano-DDS type) related to various nano-DDS types; the red rectangles indicate the DDS represented on the right; (C) Distribution of documents related to nanoparticles (with the lipid, polymeric, and metal nanoparticles subcategories shares), micelles (with polymer and lipid shares), and nanotube (with carbon nanotube share) DDS.

Nanoparticles

Nanoparticles (NPs) are submicron-sized colloidal particles with uniquely tunable properties, selectively designed for specific applications. Nanoparticulate DDS are intended to maximize drug efficacy and minimize cytotoxicity. A particularly important design feature of nanoparticles NPs for drug delivery is their surface functionalization accomplished by bioconjugation or passive adsorption of molecules onto the nanoparticle surface. Better efficacy and lower toxicity are often achieved by functionalizing nanoparticle surfaces with ligands that improve drug binding, suppress immune response, and/or afford targeting/controlled release.

The composition of the nanoparticle is chosen with respect to the target environment and/or anticipated effect. For example, biodegradable nanoparticles can be designed to degrade upon delivery, reducing their bioaccumulation and toxicity.[189] Metal NPs have optical properties that allow for less invasive imaging techniques.[189, 190] Metal NPs have optical properties that allow for less invasive imaging techniques.[190] The photothermal response of nanoparticles to optical stimulation can be exploited in tumor therapy.[191]

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Polymeric NPs are currently the most popular class of nanoparticles in drug delivery accounting for 32% of documents in the nano-sized DDS dataset in the CAS Content Collection (Figure 12C). They are beneficial for drug delivery because they can be modulated with adequate physical properties, encapsulants, and surface ligands; they can be also tailored to co-deliver multiple therapeutic agents.[192] Various stimuli-responsive (e.g., enzyme-, pH- and redox-responsive) polymers, including natural and synthetic polymers, have been utilized as smart nanocarriers for drug delivery. Redox-responsive polymeric nanohydrogels exhibiting tissue-like mechanical properties and high porosity have been extensively studied and shown to be effective in protecting payloads including protein drugs, gene therapeutics, and small-molecule drugs in blood circulation, as part of a strategy for controlled release.[193] The most commonly used natural polymers – polysaccharides – include cellulose and its esters, chitosan, alginic acid / sodium alginate, hyaluronic acid, dextran, xanthan gum, while polyethylene glycol (PEG) and its copolymers such as poloxamines, poloxamers, also polystyrene, poly(ethylene terephthalate), poly(methyl methacrylate), polyvinyl pyrrolidone, polyacrylamide, polyvinyl alcohol, and polysorbates, as well as the biodegradable polylactic acid, polycaprolactone, and poly(lactic-co-glycolic acid) are preferred synthetic polymers.[192]

Lipid NPs [194] are widely used nanocarriers (Figure 12C), contributing to 24% of publications in the nanoparticle DDS subset. Lipid-based nanoparticles have been applied in drug delivery since the discovery of liposomes, which are spherical vesicles with lipid bilayers surrounding an aqueous core, in the 1960s. Subsequently they exhibited several significant advancements: (i) with the introduction of PEGylation,[195] which increased their circulation half-lives further improving their efficiency [196]; (ii) with the discovery of the cationic/ionizable liposomes able to deliver anionic nucleic acids [194, 197] are widely used nanocarriers (Figure 12C), contributing to 24% of publications in the nanoparticle DDS subset. Lipid-based nanoparticles have been applied in drug delivery since the discovery of liposomes, which are spherical vesicles with lipid bilayers surrounding an aqueous core, in the 1960s. Subsequently they exhibited several significant advancements: (i) with the introduction of PEGylation,[195] which increased their circulation half-lives further improving their efficiency [196]; (ii) with the discovery of the cationic/ionizable liposomes able to deliver anionic nucleic acids [197], as well as (iii) with the development of the solid lipid nanoparticles (SLN), consisting of solid lipids, and the nanostructured lipid carriers (NLC), combining solid and liquid lipids, offering enhanced drug-loading capacity and flexibility, higher stability, and largely improved scalability.[198, 199] A strong advantage of lipid nanoparticles drug carriers is the fact that most of their components are physiological lipids and excipients which are generally recognized as safe (GRAS). [200] They are superior to other nanosized drug delivery systems in minimizing systemic toxicity while maintaining adequate solubility[201] and constitute a common type of regulatory approved nanomedicines.[202] Lipid-based nanoparticles can successfully deliver small molecules, as well as protein and nucleic acid therapies *in vivo* to achieve remarkable activity. Their elegance lies in their ability to overcome some of the most pressing challenges in drug delivery – improving the solubility of poorly water-soluble drugs, protecting labile compounds from degradation, and precisely targeting disease sites within the body. [187, 198, 199, 203-211] A strong advantage of lipid nanoparticles drug carriers is the fact that most of their components are physiological lipids and excipients which are generally recognized as safe (GRAS). [200] They are superior to other nanosized drug delivery systems in minimizing systemic toxicity while maintaining adequate solubility[201] and constitute a common type of regulatory approved nanomedicines.[202] Lipid-based nanoparticles can successfully deliver small molecules, as well as protein and nucleic acid therapies *in vivo* to achieve remarkable activity. Their elegance lies in their ability to overcome some of the most pressing challenges in drug delivery – improving the solubility of poorly water-soluble drugs, protecting labile compounds from degradation, and precisely targeting disease sites within the body. [187, 203-211] Lipid NPs have a wide range of applications, including cancer therapy (reducing systemic toxicity and enabling targeted delivery), infectious disease treatment (improving drug stability and selective delivery to infected

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tissues), vaccine delivery (enhancing immune responses), and gene therapy (safe and efficient gene transfection). [194, 212] They are employed also in the treatment of neurological disorders (overcoming blood-brain barrier challenges), ophthalmic conditions (enhancing drug retention in the eye), cardiovascular therapies (improving drug solubility and controlled release), and more.

Inorganic nanoparticles provide an appropriate framework in which multiple modules can be combined to give multifunctional capabilities. Inorganic materials such as metals (gold, silver, iron, and others), silica, calcium phosphate, and others have been used to prepare nanoparticles for various drug delivery and imaging applications (Figure 12A). Metallic NP formulations are particularly advantageous because of their potential for dense surface functionalization and capability for optical or thermal based therapeutic and diagnostic methods.[213] Gold nanoparticles, for example, have been fabricated into various forms including nanospheres, nanorods, nanostars, nanoshells and nanocages. [214, 215] Inorganic nanoparticles have unique physical, electrical, magnetic and optical properties. Gold nanoparticles have oscillating free electrons at their surface imparting them with photothermal properties. [216] They are also easily functionalized, providing them with additional beneficial delivery capacities. [214] Iron oxide nanoparticles are another kind of metal nanoparticles which make up the majority of US FDA-approved inorganic nanomedicines. [217] Magnetic nanoparticles comprising magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) exhibit superparamagnetic properties at certain nanosizes and have been successfully used in imaging, drug delivery, and thermosensitive medications. [213, 218] Gold nanoparticles, for example, have been fabricated into various forms including nanospheres, nanorods, nanostars, nanoshells and nanocages. [214, 215] Inorganic nanoparticles have unique physical, electrical, magnetic and optical properties. Gold nanoparticles have oscillating free electrons at their surface imparting them with photothermal properties. [216] They are also easily functionalized, providing them with additional beneficial delivery capacities. [214] Iron oxide nanoparticles are another kind of metal nanoparticles which make up the majority of US FDA-approved inorganic nanomedicines. [217] Magnetic nanoparticles comprising magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) exhibit superparamagnetic properties at certain nanosizes and have been successfully used in imaging, drug delivery, and thermosensitive medications. [218] Other commonly used inorganic nanoparticles include mesoporous silica nanoparticles, which have been successfully applied for gene and drug delivery. [219, 220]

– **Magnetic iron oxide nanoparticles.** Iron oxide nanoparticles can generate heat when exposed to an alternating magnetic field, a property that has been utilized to induce cell death and stimulate an immune response in hyperthermia-based cancer treatment. [221] Iron oxide nanoparticles can also be used as contrast agents for magnetic resonance imaging, allowing for non-invasive tracking of immune cell migration and infiltration into tumor sites. In order to enhance their cellular uptake and effectiveness, these nanoparticles can be modified with a specific coating, conjugated to drugs, proteins, enzymes, antibodies, or nucleotides, and can be directed to an organ, tissue, or tumor sites using an external magnetic field. They can be also used in the development of dual-purpose probes for the *in vivo* transfection of siRNA.[222]

– **Silver nanoparticles.** Silver nanoparticles known for their antibacterial activity, are also known to enhance the anti-tumor effects of anticancer drugs in combination therapies, allowing use of lower doses to reduce cytotoxic effects and increase efficacy.[223] They can thus operate as direct anti-cancer agents, as well as delivery platforms of various cytotoxic drugs or enhance the anti-cancer performance of combinational partners upon chemo- or radiotherapy.[224]**Silver nanoparticles.** Silver nanoparticles known for their antibacterial activity, are also known to enhance the anti-tumor effects of anticancer drugs in combination therapies, allowing use of lower doses to reduce cytotoxic effects and increase efficacy.[223] They can thus operate as direct anti-cancer agents, as well as delivery platforms of various cytotoxic drugs or enhance the anti-cancer performance of combinational partners upon chemo- or radiotherapy.[224] Silver

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nanoparticles can exhibit a plasmon resonance effect and generate heat when exposed to specific wavelengths of incident light.[225] This property can be harnessed for photothermal therapy, where the localized heat generated by the nanoparticles can selectively damage cancer cells and stimulates immune response.

– **Gold nanoparticles.** Possessing multifunctional therapeutic modalities, gold nanoparticles can be used as targeted delivery systems for vaccines, nucleic acids, and immune antibodies, as theranostic agents, and as tools in photothermal cancer therapy. They have been successfully applied also in medical imaging, such as radiotherapy, magnetic resonance angiography, and photoacoustic imaging. Gold nanostructures including nanoparticles, nanorods, nanocages, etc., are easily synthesizable in diverse shapes and sizes through various chemical, physical, or biological methods, which empowers their manageability, since even minor modifications of their size and shape can produce significant alterations in their functional properties including biodistribution, metabolism, cytotoxicity, and immunogenicity.[226, 227] Similar to silver nanoparticles, gold nanoparticles can be utilized in photothermal therapy via localized surface plasmon resonance.[228 226, 227] Similar to silver nanoparticles, gold nanoparticles can be utilized in photothermal therapy via localized surface plasmon resonance.[228]

– **Silica nanoparticles.** Mesoporous silica exhibits high porosity, appropriate biocompatibility, and facile surface functionalization. Silica nanoparticles can be engineered to various shapes, sizes, and surface properties, making them versatile tools for targeted drug delivery, imaging, and immunomodulation.[229] After the introduction of a sub-micrometer mesoporous silica termed MCM-41[230] and its successful application as a nanocarrier,[231] it has been regarded as a promising drug delivery system. [229] After the introduction of a sub-micrometer mesoporous silica termed MCM-41[230] and its successful application as a nanocarrier,[231] it has been regarded as a promising drug delivery system. Moreover, mesoporous silica exhibits self-adjuvant property, significantly enhancing anticancer immunity without additional immunomodulators.[232] Mesoporous silica has emerged as a prospective nanocarrier for cancer vaccines as well,[232] alleviating antitumor effect through dual loading of antigen and adjuvant on a single platform.[229]

Nanocrystals

Certain drugs are highly insoluble, not only in aqueous solvents, but also in lipids or oils due to their strong crystalline lattice energy. They are frequently formulated as nanocrystals, since amorphization or the reduction in particle size through nanonization can overcome or improve solubility issues. Such nanocrystalline drug technology involves the reduction in the bulk size of the drug particles down to the nanosize range, thus altering their physicochemical properties, including enhancing drug bioavailability.[233] Nanocrystals are carrier-free drug nanoparticles surrounded by stabilizers such as polymers or surfactants, and suspended in aqueous medium. [234] Among the polymeric stabilizers, the most widely used are poloxamers (e.g., Pluronic F68, Pluronic F127), polyvinyl alcohol, polyvinylpyrrolidone, and cellulose derivatives (hydroxypropyl methylcellulose, hydroxypropyl cellulose). Among surfactants, Tween 80, sodium lauryl sulfate, and others, have been widely used. [235, 236] Due to high drug loading, nanocrystals exhibit effective therapeutic concentration to produce desirable pharmacological action. In addition to therapy, nanocrystal technology can be applied also in diagnostics. [237-239] Examples of nanocrystalline drugs on the market include Rapamune® (Wyeth), an mTOR inhibitor immunosuppressant especially useful in preventing transplant rejection; Emend® (Merck), preventing nausea and vomiting caused by certain anti-cancer chemotherapy medicines; Tricor® (Abbott) and Triglide® (Sciele Pharma), both lowering cholesterol and triglyceride levels in blood; and Megace ES® (Par Pharmaceutical), used to increase appetite and prevent weight loss in patients with AIDS.[233]

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Nanoemulsions

Emulsions are liquid–liquid dispersions with one liquid phase dispersed in the other liquid phase as small droplets with the droplets being nano-sized in the case of nanoemulsions. Surfactants play a critical role in producing and stabilizing nanoemulsions by residing at the interface between the two immiscible phases. [240] Nanoemulsions can be easily produced at large scale using industrial methods including high-pressure homogenization and ultrasonication. Because of their small size and easily dispersible components with different hydrophobicity (e.g. hydrophobic drugs in the dispersed oil phase and hydrophilic proteins in the continuous aqueous phase), they are considered promising drug delivery vehicles to deliver hydrophobic drugs, and have been used as adjuvants for vaccines, demonstrating their clinical significance. [240-242]

Nanotubes

Carbon nanotubes are successful drug and gene delivery platforms which can be functionalized with a variety of biomolecules, including antibodies, proteins, or nucleic acids allowing for specific payload targeting particular tissues, organs, or cells. Carbon nanotubes are easily internalized by cells through passive and endocytosis-independent mechanisms, delivering drugs to the cytoplasm or nucleus. Nanotubes keep a perpendicular position with respect to the cell membrane during uptake, perforating and diffusing through the lipid bilayer to move into the cytoplasm. [243] Carbon nanotubes are large molecules, consisting of a repeating pattern of hexagonally arranged hybridized carbon atoms, wrapped into a cylinder of approximately 2.5–100 nm in diameter. Carbon nanotubes can be single- or multi-walled depending on the number of layered carbon sheets in their structure. [244]

Carbon nanotubes have been used as carriers of anticancer drugs such as docetaxel, doxorubicin, methotrexate, paclitaxel, and gemcitabine, anti-inflammatory drugs, osteogenic dexamethasone, steroids, and others. The unique optical properties of carbon nanotubes are the reason for their use in phototherapy. [245] The effortless surface functionalization of carbon nanotubes has motivated their use in gene delivery, as delivery vectors for plasmid DNA (pDNA), micro-RNA (miRNA), and small interfering RNA (siRNA). Despite great promise, carbon nanotubes possess a few disadvantages such as poor aqueous solubility and high cost as well as sustained and substantial concerns regarding their biodegradability with efforts being made to minimize these drawbacks.[246] There are persistent concerns about the lack of biodegradability of carbon nanotubes.[247]

Micelles

Micelles are colloidal systems formed by self-assembly of amphiphilic molecules in aqueous media at concentrations above their critical micelle concentration. They comprise a hydrophobic core and a hydrophilic shell. The most widely used amphiphiles are lipids or polymers thus the resultant micelles are either lipid micelles, polymeric micelles or lipid-polymeric hybrid micelles. Polymeric micelles are made of amphiphilic block copolymers that self-assemble to form a core-shell structure in the aqueous solution. The hydrophobic core can be loaded with hydrophobic drugs such as camptothecin, docetaxel, paclitaxel, while the hydrophilic shell makes the whole system soluble in water and stabilizes the core. [16] The most commonly used polymers for micelle formation are amphiphilic di-block copolymers such as polystyrene-PEG, and triblock copolymers such as poloxamers, with graft and ionic copolymers (e.g. poly(ethylene glycol)-poly(ε-caprolactone)-g-polyethyleneimine) used in some circumstances. [248-252] The hydrophilic part

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is most often composed of PEG, but other polymers such as poly(vinyl pyrrolidone), poly (acryloylmorpholine), or poly(trimethylene carbonate) have been also exploited; the hydrophobic segment can be made up of poly(propylene oxide), polyesters such as poly(ε-caprolactone) or homopolymers and co-polymers of glycolic and lactic acids.

While liposomes have a lipid bilayer structure encapsulating an aqueous moiety, lipid micelles consist of a monolayer with the lipophilic chains forming the inner core and the hydrophilic heads exposed toward the aqueous environment. The nanoscale dimensions and the hydrophilic shell protect them from elimination by the reticuloendothelial system, thereby increasing their circulation time and ability to deliver drugs to the targets. [253] Hybrid micelles prepared from lipid-polymer conjugates comprising water-soluble polymers, such as polyethylene glycol (PEG) or polyvinyl pyrrolidone (PVP), conjugated with phospholipids or long-chain fatty acids have been used to deliver various poorly soluble anticancer agents. [254] For example, micelles formed by conjugates of phosphatidylethanolamines (PE) with PEGs of various molecular weights , e.g., PEG750 –PE, PEG2000–PE, and PEG5000–PE, have been reported to accumulate efficiently in tumors. [255]

Natural product-based nano-DDS

The class of natural product-based nano-DDS is the fastest growing nano-DDS class in the CAS Content Collection (Figure 12B).

Chitosan exhibits mucoadhesive properties and has been used to operate at the tight epithelial junctions. Chitosan-based nanomaterials are widely used for sustained drug release systems for various types of epithelia, including intestinal, nasal, buccal, ocular and pulmonary.[256-260] Alginate is another biopolymer (polysaccharide) frequently used in drug delivery. Alginate is terminally substituted with carboxylate groups, rendering it anionic and imparting stronger mucoadhesion than for neutral or cationic mucoadhesive polymers.[261, 262] Xanthan gum is a high MW polyanionic heteropolysaccharide with good bioadhesive properties, produced by *Xanthomonas campestris*. It is widely used as a pharmaceutical excipient since it is considered non-toxic and non-irritating. [263] Cellulose and its derivatives are extensively used in drug delivery systems mainly for modification of the solubility and gelation of drugs, resulting in the control of their release profile. [256-260, 263, 264] Cellulose and its derivatives are extensively used in drug delivery systems mainly for modification of the solubility and gelation of drugs, resulting in the control of their release profile. [256-260, 264]

The combined use of nanotechnology along with the extreme variety of bioactive natural compounds is attractive, and has been growing very rapidly in recent decades. [16] Natural products have been used as medicines since ancient times. Nowadays, about 35% of the pharmaceutical compounds are either from natural products or their derivatives and analogs, mainly including plants (25%), microorganisms (13%) and animal (3%) sources.[265] Natural compounds have been widely studied in curing diseases owing to their various activities, such as inducing tumor-suppressing autophagy and antimicrobial properties. For example, autophagy has been exhibited by curcumin and caffeine,[266] and antimicrobial effects have been shown by cinnamaldehyde, carvacrol, curcumin and eugenol.[267, 268]For example, autophagy has been exhibited by curcumin and caffeine,[266] and antimicrobial effects have been shown by cinnamaldehyde, carvacrol, curcumin and eugenol.[267, 268] Application of nanotechnologies gave rise to substantial enhancement of their properties, such as bioavailability, targeting and controlled release. Thus, thymoquinone, a bioactive compound in *Nigella sativa*, exhibited a sixfold increase in bioavailability after encapsulation in a lipid nanocarrier in comparison to free thymoquinone.[269] It also improved its pharmacokinetic characteristics thus accomplishing better therapeutic effects.

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Quantum dots

Quantum dots are nanometer-sized crystalline semiconductor particles with unique fluorescence properties, commonly made of materials such as lead sulfide, lead selenide, cadmium selenide, cadmium sulfide, cadmium telluride, indium arsenide, and indium phosphide. They can also take the form of core-shell structures incorporating two semiconductor materials. They are used primarily in imaging applications and *in vivo* diagnostics.[270, 271] Due to their magnetic, radioactive or plasmonic properties, these inorganic nanoparticles are uniquely qualified for applications such as diagnostics, imaging and photo-thermal therapies. Most have good biocompatibility and stability, and fill niche applications that require properties unattainable by organic materials. However, they are limited in their clinical application by low solubility and toxicity concerns, especially in formulations using heavy metals.[218, 272]

Core-shell nanoparticles

Core-shell nanoparticles are nanostructures in which the core acts as a reservoir for drugs, including small molecules, proteins, nucleic acid therapeutics (DNA, siRNA, or oligonucleotides), or molecular imaging probes, while the shell protects the cargo from the environment.[273-275] This distinct architecture offers advantages such as tunable physicochemical properties, improved biocompatibility and permeability, target-specific drug delivery, as well as multidrug delivery. For example, polymer/liposome composite systems with a core/shell structure have been designed, with a lipid vesicle core utilized as delivery systems for small molecules and proteins; nanoparticles with reverse geometry, having polymeric cores, have been also engineered.[273, 276, 277]

Biomimetics

Development of nanoparticles with intrinsic characteristics similar to circulatory cells such as leukocytes and platelets for use as biomimetic DDS has been intended to solve the issues of conventional DDS. Specifically, synthetic biomimetic nanoparticles coated with cellular membranes have been engineered and shown able to cross the endothelial layer of the inflamed vessels and permeate into tumor tissue mimicking the properties of leukocytes, making it possible to securely deliver drugs to diseased sites.[278] Thus, biomimetic DDS, developed by directly utilizing or mimicking the biological structures and processes, provide promising approaches for overcoming biological barriers and specifically blood-brain barrier for brain drug delivery.[279, 280]

Exosomes

Superior innate stability, low immunogenicity, biocompatibility, and excellent capacity for membrane penetration allow exosomes to be valuable natural nanocarriers for efficient drug delivery.[281] As important mediators of intercellular communications, exosomes are increasingly gaining interest in the context of cancer immunotherapy.[282, 283] Exosomes, either tumor-derived, comprising tumor-associated antigens, or derived from dendritic cells presenting antigens, can trigger immune activation and therefore they can be used in developing anti-cancer vaccines.[284] Moreover, tumor-derived exosomes hold information from primary cells, thus they can activate CD8 T-cells, which offer unique therapeutic approaches for developing cancer vaccines.[284-286] Moreover, tumor-derived exosomes hold information from primary cells, thus they can activate CD8 T-cells, which offer unique therapeutic approaches for developing cancer vaccines.[285, 286] Exosomes participate in the formation of the cancer immunosuppressive microenvironment, thus tumor exosome production control might be an effective

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treatment strategy. Exosomes also play a key role in the PD-1/PD-L1 immune checkpoint inhibitor treatment.

Major material classes, top substances, annual trends

Proteins are the largest class of substances related to nano drug delivery – both as drugs and as drug carriers (Figure 13A). Natural biomolecules, such as proteins, are commonly used in pharmaceutical nanoformulations because of their safety. Protein nanocarriers offer significant advantages, such as biocompatibility, biodegradability, environmental sustainability, cost efficiency and availability at larger scales. Furthermore, the preparation procedures and the encapsulation process can be carried out under milder conditions not involving toxic chemicals or organic solvents. Protein nanocarriers can be prepared using various proteins, such as albumin, gelatins, collagens, keratins, silk fibroin, elastin, lipoprotein, and ferritin proteins. [287, 288] Plant proteins such as maize zeins, soy protein and wheat gliadin are also frequently explored for various drug-delivery applications. [287]

The number of protein drugs has significantly increased since the introduction of the first recombinant protein therapeutic, which was human insulin. [289, 290] Protein therapeutics have several advantages over small-molecule drugs such as higher specificity, lower immunogenicity, and faster clinical development and approval. The anticoagulant heparin, the antibiotics vancomycin and bleomycin along with the antibodies trastuzumab, bevacizumab, cetuximab, pembrolizumab, rituximab, adalimumab, tocilizumab, alemtuzumab, and ranibizumab are the most widely represented protein/peptide drugs in the CAS Content Collection (Figure 13B).

Nucleic acid medicines, including DNA and RNA (miRNA, siRNA, mRNA) have recently shown themselves useful in treating a variety of diseases. [291] However, while nucleic acid therapeutics can expand the range of treatable diseases, their wide-ranging use is limited by multiple delivery challenges. [292] First of all, nucleic acids need to cross multiple biological membranes, cellular and intracellular, escape from endosomes, and in some cases enter the nucleus. Second, nucleic acids encounter various enzymes upon their delivery to the target cells, which may degrade them or trigger immune response. [293, 294] Third, nonspecific biodistribution to non-target cells and tissues can lead to low efficacy. [295] In addition, nucleic acids exhibit a strong negative charge, preventing their permeation across the cellular membranes. Thus, delivery vectors for transporting these therapeutics to the desired location are needed. [296] Beyond the physical barrier of the cellular membrane, there are multiple systemic and intracellular challenges which motivate the need for effective delivery vehicles. [297] Nucleic acids are subject to endo- and exonucleases that degrade them. Numerous strategies for the encapsulation or stabilization of nucleic acids have been developed in order to achieve intracellular delivery. Common carriers for nucleic acid remedies include cationic polymers, cationic lipids, and cationic peptides. [295]

Polymeric nanocarriers are one of the most widely used nano-DDS (Figure 13C). [298] Polyethylene glycol, its copolymers with polypropylene glycol (poloxamers), polyvinylpyrrolidone, and polystyrene are among the most common nanocarrier constituents (Figure 13B). Natural polymers such as chitosan, dextrin, polysaccharides, hyaluronic acid, poly(glycolic acid), poly(lactic acid) and their copolymers, have also been widely used for polymeric drug delivery systems. Synthetic polymers such as poly(ethylenimine)s, dendritic polymers, biodegradable and bio-absorbable polymers have been also discussed for polymeric drug delivery. Cationic polymers form complexes with nucleic acids by means of electrostatic interaction and create a net positive charge of the nanocarriers, which facilitates cell attachment, internalization, and endosomal escape. [299] The structures of cationic polymers are diverse, including linear polymers such as chitosan and linear poly(ethyleneimine), branched polymers such as branched poly(ethyleneimine), circle-like polymers such as cyclodextrin, crosslinked poly(amino acids), and dendrimers. [295]

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Lipid nanoparticles, one of the widely applied drug nanocarriers, include various lipid constituents, with their composition determined by the intended morphology and application. Along with the most common constituents, phospholipids and cholesterol, frequent components of the lipid nanoparticles include cationic ionizable lipids and PEG-lipid conjugates (PEG-lipids), as well as various other components. [187] Cholesterol is the lipid component used in the largest number of nano-DDS-related documents in the CAS Content Collection (Figure 13C). Phospholipids such as phosphatidylcholines, phosphatidylethanolamines, phosphatidylglycerols, and phosphatidylserines are the most widely used lipid classes. Preferred phospholipid species with respect to their hydrocarbon chains include saturated dimyristoyl-, dipalmitoyl-, and distearoyl- chains, as well as unsaturated dioleoyl- chains. [187] Phospholipids from natural sources, such as soya phospholipids and egg phosphatidylcholines, have also been used often in lipid nanoparticle formulations. Since the discovery that PEG-lipid conjugates can significantly increase the circulatory half-lives in the sterically stabilized "stealth" liposomes, PEG-lipids have been also widely used in pharmaceutical lipid nanoparticle formulations.

Cationic lipid nanoparticles, comprising stable complexes between synthetic cationic lipids and anionic nucleic acids, represent the most widely used nonviral delivery system for nucleic acid drugs. Cationic lipids are the most commonly used carriers for nucleic acid delivery. A large number of cationic (ionizable) lipid amphiphiles have been designed, synthesized and tested as nucleic acid carriers since the introduction of N-[1-(2,3-dioleoyloxy)propel]-N,N,N-trimethylammonium (DOTMA). [300] Commonly used cationic lipids for nucleic acid delivery include various amine derivatives such as DOGS and DC-Chol, quaternary ammonium compounds such as DOTMA, DOTAP, DORIE, and DMRIE, cationic phosphatidylcholines such as EDOPC and EDMPC, combinations of amines such as DOSPA and GAP-DLRIE, and amidinium salts such as Vectamidine. [300-306] Commonly used cationic lipids for nucleic acid delivery include various amine derivatives such as DOGS and DC-Chol, quaternary ammonium compounds such as DOTMA, DOTAP, DORIE, and DMRIE, cationic phosphatidylcholines such as EDOPC and EDMPC, combinations of amines such as DOSPA and GAP-DLRIE, and amidinium salts such as Vectamidine. [300-306] Of particular note are the cationic lipids used in the recent mRNA COVID-19 vaccines, ALC-0315 and SM-102. [307-309]

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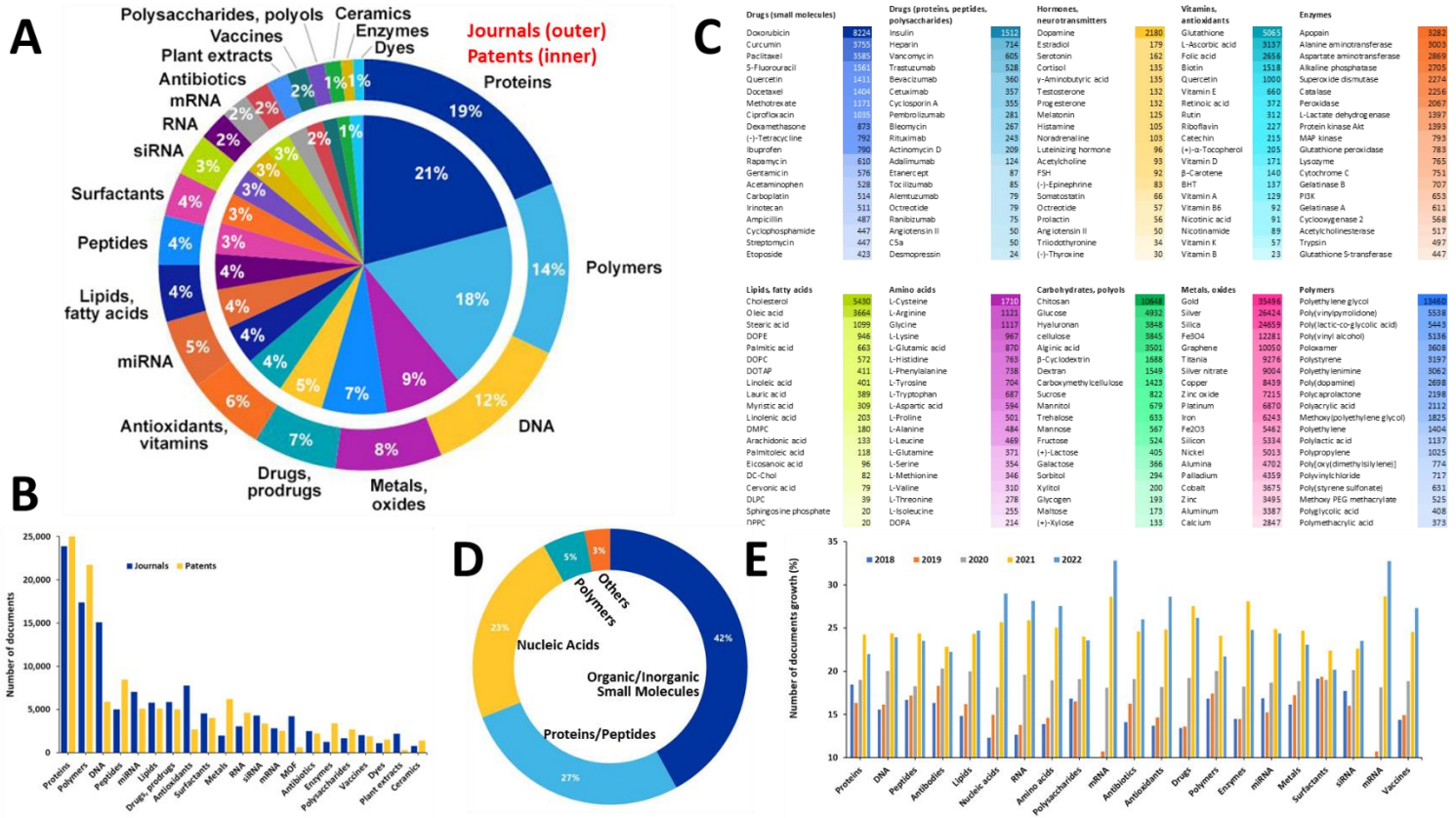

Figure 13. (A) Major substance classes related to nano-DDS as presented in the CAS Content Collection in the period 2003-2022; (B) Distribution between journal articles (blue) and patents (yellow) for major substance classes; (C) Representative top substances of the major classes related to the nano-DDS; (D) Substance type distribution for the nano-DDS; (E) Publication growth rate of the major substance classes related to the nano-DDS for the 5-year period 2018-2022.

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Table 1. Exemplary approved and globally marketed nanotechnology-based drug formulations [16, 154, 217, 288, 310-315]

Nano-DDS type	Formulation name	Active ingredient(s)	Company	Indication(s)
Lipid-based nanomedicine				
Liposome	DaunoXome [316]	Daunorubicin citrate	Galen	HIV-associated Kaposi's sarcoma
Liposome	Myocet [317]	Doxorubicin citrate, anthracycline cytotoxic agent	Teva Pharmaceutical Industries	Metastatic breast cancer
Liposome	Visudyne [318]	Verteporfin	QLT PhotoTherapeutics	Severe eye conditions: macular degeneration, decreased vision, ocular histoplasmosis, pathologic myopia
Liposome	DepoDur [319]	Morphine sulfate	Endo Pharmaceuticals	Postoperative analgesia
Liposome	Mepact [320]	Mifamurtide	Takeda France SAS	High grade non-metastatic osteosarcoma and myosarcoma
Liposome	Lipodox [321]	Doxorubicin hydrochloride	Sun Pharmaceutical Industries (SPIL)	Kaposi's sarcoma, ovarian cancer, multiple myeloma
Liposome	Lipusu [322]	Paclitaxel	Luye Pharma	Lung squamous cell carcinoma
Liposome	Vyxeos [323]	Daunorubicin and Cytarabine	Jazz Pharmaceuticals	Acute myeloid leukemia
Unilamellar liposome	AmBisome [324]	Amphotericin B	NeXstar Pharmaceuticals	Fungal infections; Aspergillosis, candidiasis, cryptococcosis infections
PEGylated liposome	Doxil [325, 326]	Doxorubicin hydrochloride	Johnson & Johnson	Ovarian cancer, HIV-associated Kaposi's sarcoma, multiple myeloma
PEGylated liposome	Caelyx [327]	Doxorubicin hydrochloride	Janssen Pharmaceutica	Breast cancer, ovarian cancer, AIDS-related Kaposi's sarcoma

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PEGylated liposome	Onivyde [328]	Irinotecan	Merrimack Pharmaceuticals	Metastatic pancreatic cancer
PEGylated cationic lipid nanoparticle	mRNA-1273 vaccine [329]	mRNA vaccine	Moderna	COVID-19 infection vaccine
PEGylated cationic lipid nanoparticle	Onpattro [330]	Patisiran sodium	Alnylam Pharmaceuticals	Polyneuropathy of hereditary transthyretin-mediated amyloidosis
PEGylated cationic lipid nanoparticle	BNT162b2 vaccine [329]	mRNA vaccine	Pfizer Pharmaceuticals	COVID-19 infection vaccine
Pulmonary surfactant	Curosurf [331]	Pulmonary surfactant	Chiesi Farmaceutici	Respiratory Distress Syndrome (RDS)
Nanoemulsion	Diprivan [332]	Propofol	AstraZeneca	Anesthetic agent for sedation of patient under critical carer
Lipid suspension, DMPC & DMPG	Abelcet [333]	Amphotericin B	Liposome Co.	Aspergillosis, invasive fungal infections
Micelle	Apealea [334]	Paclitaxel	Oasmia Pharmaceutical	Ovarian cancer, peritoneal cancer, fallopian tube cancer
Polymer-based nanomedicine				
PEGylated protein	Adagen [335]	Adenosine deaminase	Enzon Pharmaceuticals	Adenosine deaminase-severe combined immunodeficiency disorder
PEGylated protein	Oncaspar [336]	L-asparaginase	Enzon Pharmaceuticals	Acute lymphoblastic leukemia
PEGylated protein	PEGintron [337]	PEGylated interferon α-2B	Merck & Co	Hepatitis
PEGylated protein	Neulasta [338]	Filgrastim	Amgen	Neutropenia
PEGylated protein	Pegasys [339]	PEGylated interferon α-2A	Genentech	Hepatitis B and Hepatitis C
PEGylated protein	Somavert [340]	Recombinant HGH receptor antagonist	Pfizer	Acromegaly
PEGylated protein	Mircera [341]	Epoetin beta	Vifor pharma	Renal anemia

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PEGylated protein	Cimiza [342]	Certolizumab pegol	UCB	Rheumatoid arthritis, Crohn's disease, psoriatic arthritis, ankylosing spondylitis
PEGylated protein	Krystexxa [343]	Pegloticase	Savient Pharmaceuticals	Severe and treatment-refractory chronic gout
PEGylated protein	Plegridy [344]	Peginterferon β-1a	Biogene	Relapsing remitting multiple sclerosis
PEGylated protein	Adynovate [345]	Recombinant antihemophilic factor	Baxalta US	Hemophilia A
GlycoPEGylated protein	Rebinyn [346]	Recombinant coagulation factor IX	Novo Nordisk	Hemophilia B
Nanoemulsion	Restasis [347]	Cyclosporine	Allergan	Chronic dry eye
Nanoemulsion	Estrasorb [348]	Estradiol hemihydrate	Novavax	Moderate to severe vasomotor symptoms in postmenopausal women
PEGylated aptamer	Macugen [349]	Pegaptanib sodium	Pfizer	Wet age-related macular degeneration
Polymeric micelle	Genexol-PM [350]	Paclitaxel	Lupi	Breast cancer
Polymeric (PLGA) microspheres	Zilretta [351]	Triamcinolone acetonide	Flexion Therapeutics	Knee osteoarthritis
Nanocrystals				
Nanocrystal	Avinza [352]	Morphine	King Pharma	Chronic pain
Nanocrystal	Ritalin LA [353]	Methylphenidate hydrochloride	Novartis	Attention deficit hyperactivity disorder in children
Nanocrystal	Zanaflex [354]	Tizanidine hydrochloride	Acorda	Muscle relaxant
Nanocrystal	Emend [355]	Aprepitant	Merck & Co	Antiemetic
Nanocrystal	Tricor [356]	Fenofibric aid	Abott Laboratories	Antihyperlipidemic

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Nanocrystal	NanOss [357]	Hydroxyapatite	RTI Surgical	Bone substitute
Nanocrystal	Megace ES [358]	Megestrol acetate	Par Pharmaceuticals	Anorexia, cachexia and AIDS-related weight loss
Nanocrystal	IVEmend [359]	Fosaprepitant dimeglumine	Merck & Co	Antiemetic
Nanocrystal	Focalin XR [360]	Dexmethylphenidate hydrochloride	Novartis	Attention deficit hyperactivity disorder in children
Nanocrystal	Invega [361]	Paliperidone palmitate	Janssen Pharmaceuticals	Schizophrenia
Nanocrystal	Ryanodex [362]	Dantrolene sodium	Eagle Pharmaceuticals	Malignant hypothermia
Nanocrystal	Ostim [363]	Hydroxyapatite	Heraeus Kulzer	Bone substitute
Nanocrystal	EquivaBone [364]	Hydroxyapatite	Zimmer Biomet	Bone substitute
Nanocrystal	Vitoss [365]	Calcium phosphate	Stryker	Bone substitute
Nanocrystal	Rapamune [366]	Sirolimus	Wyeth Pharmaceuticals	Immunosuppressant
Inorganic nanoparticles				
Iron nanoparticle	DexFerrum [367]	Iron dextran	American Regent	Iron deficiency in chronic kidney disease
Iron nanoparticle	Venofer [368]	Iron sucrose	Luitpold Pharmaceuticals	Iron deficiency in chronic kidney disease
Iron nanoparticle	Ferrlecit [369]	Sodium ferric gluconate	Sanofi	Iron deficiency anemia
Iron nanoparticle	INFed [370]	Iron dextran	Allergan	Iron deficiency anemia
Hafnium oxide nanoparticle	Hensify [371]	Hafnium oxide	Nanobiotix	Locally advanced squamous cell carcinoma
Iron oxide nanoparticle	Combidex [372]	Iron oxide	AMAG Pharmaceuticals	Magnetic resonance lymphography

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Superparamagnetic iron oxide nanoparticle	Resovist [373]	Iron oxide	Bayer Schering Pharma	MRI imaging of liver lesions
Gadolinium nanoparticle	Primovist [374]	Gadoxetate	Bayer Schering Pharma	MRI imaging of liver lesions
Superparamagnetic iron oxide nanoparticle	Endorem [375]	Iron oxide	Guerbet	MRI imaging of liver lesions
Core-shell carbon-dot doped silica nanoparticle	C-Dots [376]	Cy5 fluorophore	Elucida Oncology	PET-optical dual-modality imaging
Protein based nanoparticles				
Engineered fusion protein nanoparticle	Ontak [377]	Denileukin diftitox	Eisai Co.	Leukemia, T cell lymphoma
Albumin nanoparticle	Abraxane [378, 379]	Paclitaxel	Eli Lilly	Metastatic breast cancer

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Targeted diseases and their correlation to DDS

Development of nanotechnology in nanomedicine is taking place at a rapid pace. The application of nanomaterials ranges from nanosilver for antibacterial use to early diagnosis and treatments of numerous severe diseases such as cancer, immune-related diseases, genetic disorders, infections, inflammations and many others (Figure 14A). During the last decades, a tremendous amount of research has reported diagnostic and therapeutic applications of nanotechnology, some of which have already been approved or have reached advanced clinical trials.

Cancer is a major global health threat, causing millions of fatalities yearly. [380] Nano-DDS can be engineered to selectively accumulate in tumor tissues, allowing for more precise cancer treatment. Specific targeting of cancer cells is an essential characteristic of nano-carriers for drug delivery, as it offers a way to attack tumors with large doses of drugs thus augmenting therapeutic efficacy while protecting normal cells from cytotoxicity and avoiding the harmful side effects that often accompany chemotherapy to the detriment of patients. Passive targeting of nano-DDS is mainly accomplished by the enhanced permeability and retention (EPR) phenomenon, which exploits the enhanced vascular permeability and weakened lymphatic drainage of cancer cells and enables nanocarriers to target cancer cells passively. Active targeting is attained by the interaction between ligands and cellular receptors. Specific receptors on cancer cells include transferrin receptors, folate receptors, glycoproteins (e.g., lectin), and epidermal growth factor receptor (EGFR).[224] The earliest nanoformulation, approved by FDA in 1995, is the anticancer liposomal formulation Doxil, designed to improve the pharmacokinetics and biodistribution of the anthracycline drug doxorubicin.[326] Multiple other nano-based pharmaceuticals have received approval and have been successfully used since then for cancer treatment. [381, 382] [326] Multiple other nano-based pharmaceuticals have received approval and have been successfully used since then for cancer treatment. [381, 382]

Another complementary, nanotechnology-based approach for the treatment of cancer is therapeutic hyperthermia, a technique in which the body temperature is locally raised above the normal level.[383, 384] The response of cancer cells to radiation and chemotherapy can be augmented by increasing the tumor temperature.[383] Nanoparticles are applied in inducing localized heating within tumors. Hyperthermia can be induced either by laser radiation or an applied magnetic field. Magnetic nanoparticles can be used as heating mediators. [385] The unique optical properties of noble metal nanoparticles have been used for inventive light-based treatment approaches for cancer treatment. Thus, the combination of noble metal (Au, Ag) and magnetic iron oxide nanoparticles is reported to augment the effectiveness of hyperthermia. [383, 384, 386] [383, 384] The response of cancer cells to radiation and chemotherapy can be augmented by increasing the tumor temperature.[383] Nanoparticles are applied in inducing localized heating within tumors. Hyperthermia can be induced either by laser radiation or an applied magnetic field. Magnetic nanoparticles can be used as heating mediators. [385] The unique optical properties of noble metal nanoparticles have been used for inventive light-based treatment approaches for cancer treatment. Thus, the combination of noble metal (Au, Ag) and magnetic iron oxide nanoparticles is reported to augment the effectiveness of hyperthermia. [383, 384, 386]

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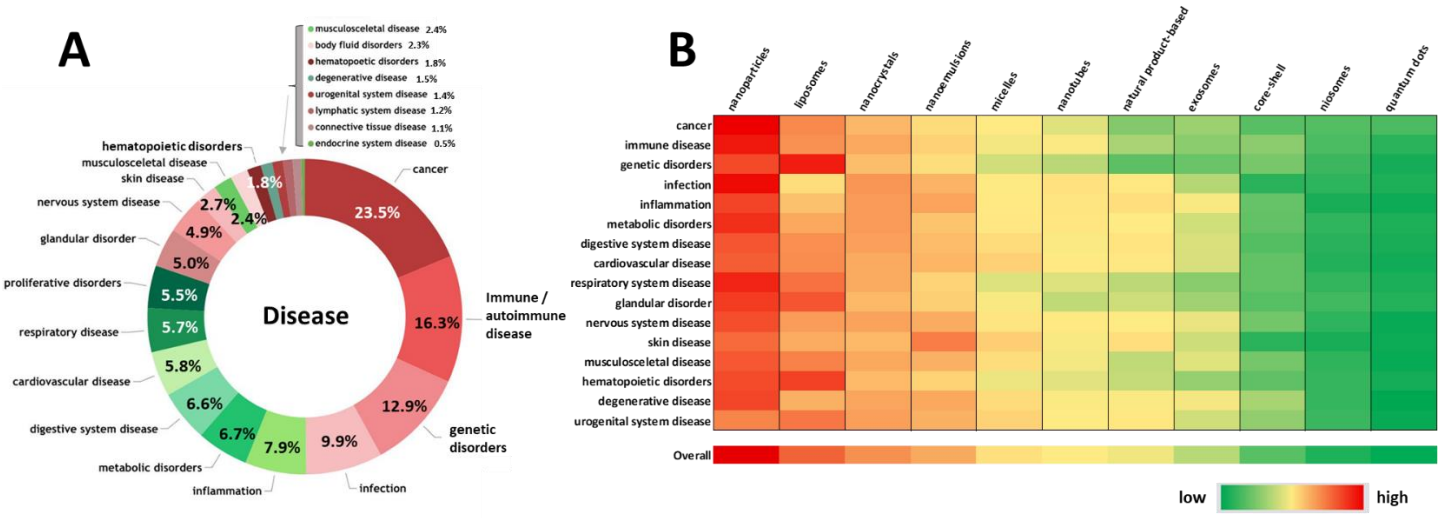

Figure 14. (A) Distribution of nano-DDS-related publications in the CAS Content Collection with respect to the treated diseases; (B) Heat map of the relationship between various types of nano-DDS and the diseases they have been applied to.

Numerous diseases have their sources at the **genetic** level. The human genome project and the advances in molecular genetics and high throughput technologies have revealed the genetic basis of many pathologies and identified new therapeutic approaches. Gene-based therapies must cross multiple biological barriers in order to reach their site of action. Because of their negative charge, nucleic acids cannot cross the cellular membrane, which is also negatively charged. Therefore, delivery vehicles that allow gene medicines to reach their site of action avoiding degradation, crossing cellular membranes, and escaping the endosomes, is needed. [387] Nanomaterials are presently being developed for the delivery of genetic material, as non-viral vectors for gene therapy use. A number of nanostructures including lipid, polymeric, and various inorganic nanocarriers can incorporate certain genetic materials, such as plasmid DNA, mRNA, and siRNA. One of the most significant applications for nano-base gene delivery is the use of nanoparticles in genetic-based vaccines. [388, 389]

Infectious diseases are a dominant driver for the global disease burden. High mortality rates are associated with lower respiratory infections, diarrhea, tuberculosis, human immunodeficiency virus (HIV) infection, and malaria. [390] Nanotechnology-based approaches have been the focus of intensive research efforts to improve the therapeutic index of anti-infective drugs and simplify their use. The introduction and advancement in medical nanotechnology can develop a more straightforward treatment regimen with lower dose frequency. Long-acting injectable nanoparticles comprising antiretroviral drugs are a novel treatment method for reducing the frequency of doses for HIV patients and represents the most clinically advanced nanotechnology treatment for this virus. Nanotechnology like this also has the potential to be used as a preventative measure, which could benefit a large population who are at a higher risk for HIV. The targeting potential of nanotechnology is a significant advantage, helpful in overcoming challenges associated with the treatment of these diseases, including low on-target bioavailability and low patient adherence due to drug-related toxicities and extended therapeutic regimens. [391] It would be significantly beneficial for malaria, usually treated with chemotherapy drugs that have adverse side effects including toxicity, missed doses, and the development of resistance. Furthermore, nanocarriers can be applied for formulating vaccines, which represent a major defense in combat against infectious diseases [391, 392]

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Antibiotic drug resistance has been identified as a global concern by the World Health Organization since 2014 [393, 394] and is still regarded as a primary health concern. [395] A major contributing factor to the rise of multidrug resistance (MDR) is the rampant misuse of antibiotics both in humans and animals (as part of the food industry). [314, 396]**Antibiotic drug resistance** has been identified as a global concern by the World Health Organization since 2014 [393, 394] and is still regarded as a primary health concern. [395] A major contributing factor to the rise of multidrug resistance (MDR) is the rampant misuse of antibiotics both in humans and animals (as part of the food industry). [314, 396] This, along with the slow pace of development of novel antibiotics, has further intensified the MDR crisis. In this context, the exploration of other avenues such as use of nano-DDS to combat MDR has become a vital need. Furthermore, repurposing known classes of antibiotics into nano-based DDS have been found to overcome resistance mechanisms and can potentially help reduce the burden of MDR. [397, 398]

The present treatments for **autoimmune diseases** involve administration of broad-spectrum, nonspecific, anti-inflammatory, or immunosuppressive drugs, which reduce the proliferation of inflammatory cells and inhibit the immune reactions. Such treatment can alleviate clinical symptoms but is unable to address the underlying cause and therefore incapable of curing the disease. Moreover, extensive use of immunosuppressants reduce the body's normal immune response, increasing susceptibility to other diseases. [399, 400] The application of nanocarrier-based drug delivery systems in treatment of autoimmune diseases such as rheumatoid arthritis, multiple sclerosis, and lupus can increase the efficiency of inducing antigen-specific tolerance *in vivo*. [400] Nanocarriers have significant potential as tolerance delivery vehicles with certain benefits to autoimmune disease, allergy, and transplantation rejection immunotherapy. Nanocarrier-mediated delivery-induced tolerance *in vivo* is a promising approach in autoimmune disease or transplantation. The capability of nanoparticles to deliver antigens and immunomodulators, primarily targeting antigen-presenting cells and lymphocytes, can increase the potential to induce specific tolerance.

Inflammation, a common feature of numerous diseases, is a basic immune response that facilitates survival and sustains tissue homeostasis. In some conditions, the inflammatory process becomes harmful, contributing to the pathogenesis of a disease. Targeting inflammation by using nanomedicines, either through the detection of molecules overexpressed onto the surface of activated macrophages or endothelial cells, or via enhanced blood vessel permeability, provides a promising solution for the treatment of inflammatory diseases. [401] Various types of nanocarriers have been developed or are still in development for the management of inflammation, including liposomes, polymer nanoparticles, micelles, dendrimers, or hydrogel-based formulations, which can target passively, through the leaky vasculature, or actively the main triggers of inflammation, including macrophages, endothelial cells, membrane receptors on inflammatory cells, anti-inflammatory genes and cytokines. [401]

The various types of nano-DDS and the diseases they co-occur with in the CAS Content Collection are depicted in Figure 14B as a heat map. In most diseases, nanoparticles are the most frequently used nano-DDS.

For genetic disorders, liposomes are the preferred delivery systems. Indeed, after the invention of cationic lipids in 1987 [300], cationic liposomes have been widely applied for gene delivery. [301, 402]For genetic disorders, liposomes are the preferred delivery systems. Indeed, after the invention of cationic lipids in 1987 [300], cationic liposomes have been widely applied for gene delivery. [301, 402] Complexation with positively charged lipids stabilizes nucleic acids and enhances their resistance to nuclease degradation, allowing them to be delivered to their desired target cells.

Liposomes are the preferred nano-DDS for treating hematopoietic disorders as well (Figure 14B). Introduced in the 1990s, PEGylated liposomal doxorubicin has been approved as an antitumor agent in the US and other countries and is widely used in patients with multiple myeloma. [403] Another liposome-

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encapsulated formulation delivers a synergistic 5:1 drug ratio of cytarabine and daunorubicin for treating acute myelogenous leukemia. [404] It was recently reported that surface-modified liposomes can present a promising approach to deliver liposomal drugs into bone marrow via specific bone marrow phagocytosis. [405] This bone marrow delivery formulation can be a successful nanocarrier for therapy of hematopoietic malignancies such as myelocytic leukemia and multiple myeloma.

One of the larger uses of liposomal DDS is for treating urogenital diseases. (Figure 14B). It was recently reported that intravesical instillation of liposome-encapsulated botulinum toxin A can be a successful treatment opportunity for functional bladder disorders such as overactive bladder, interstitial cystitis/bladder pain syndrome, and bladder oversensitivity.[406] Liposomal tacrolimus instillations have been reported to be promising for the treatment of hemorrhagic cystitis.[406, 407] Liposomal tacrolimus instillations have been reported to be promising for the treatment of hemorrhagic cystitis.[407] Liposomal amphotericin B has been found effective in the treatment of urinary tract infections caused by *Candida albicans*. [406, 408] Liposomal tacrolimus instillation have been reported to be a promising treatment for hemorrhagic cystitis. [409]

Topical delivery of active pharmacological ingredients is a challenge because of the mechanical barrier created by the skin. Nanoemulsions have emerged as a promising nano-DDS system in the field of dermatology, for the encapsulation of active substances and for their controlled release. Indeed, decreasing particle size in nanoemulsions increased the contact surface area, resulting in increased drug efficacy and generally exhibiting superior performance in safety, permeability, and bioavailability. [410] Polymeric micelles are another successful topical nanocarriers. They have been reported to enhance the deposition of drugs in targeted sites of the skin in dermatological diseases such as psoriasis and acne. [411]

Exosomes secreted by cells involved in inflammation exhibit high inflammatory affinity and targeting, hence they can successfully deliver cargo to inflammatory cells and can achieve superior anti-inflammatory effect. [412] Exosomes derived from mesenchymal stem cells, astrocytes and dendritic cells with immunomodulatory functions are widely applied as delivery vehicles to transport cargo to inflammatory sites for enhanced anti-inflammatory efficiency. [412-414] Successful application of exosomes has been also reported in a variety of conditions, including neurodegenerative diseases [415], cardiovascular [416], and cerebrovascular diseases [417], and others. [412, 418] Exosomes derived from mesenchymal stem cells, astrocytes and dendritic cells with immunomodulatory functions are widely applied as delivery vehicles to transport cargo to inflammatory sites for enhanced anti-inflammatory efficiency. [412-414] Successful application of exosomes has been also reported in a variety of conditions, including neurodegenerative diseases [415], cardiovascular [416], and cerebrovascular diseases [417], and others. [412, 418]

Delivery routes and their correlation with DDS types

Nanomedicines can be administered through various routes, depending on the specific characteristics of the nanomaterials and the targeted disease (Figure 15). The choice of administration route is influenced by factors such as the desired therapeutic effect, the site of action, and the physical and chemical properties of the nanomedicine.

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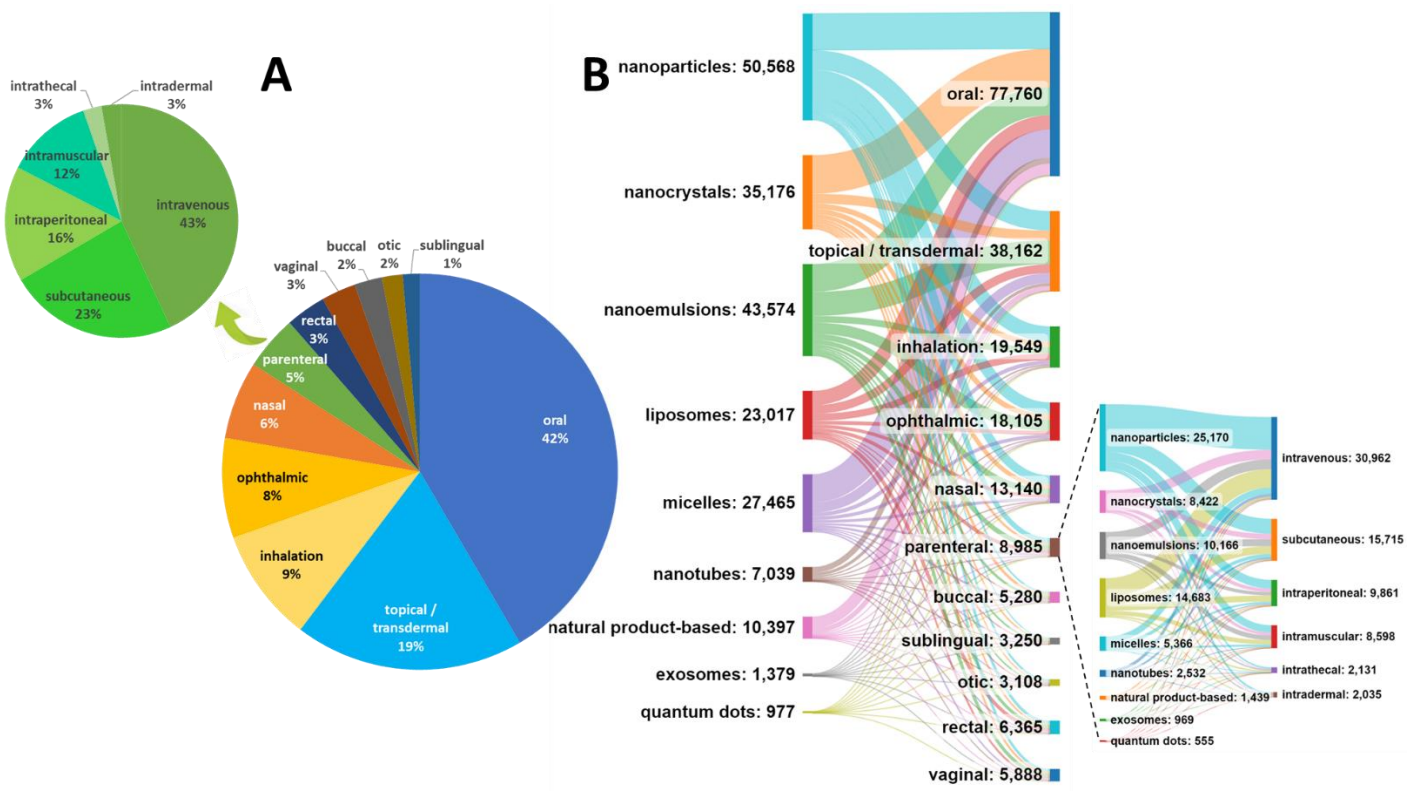

Figure 15. (A) Distribution of documents in the CAS Content Collection related to various administration routes of the nano-DDS; (B) Sankey diagram of the correlations between the types of nano-DDS and their administration routes.

Nanoparticles can be incorporated into **oral** formulations such as tablets, capsules, or liquid suspensions. The oral route is a preferred method of drug administration owing largely to its facility, convenience, and highest degree of patient compliance, however effective drug delivery with minimum off-target side effects is often challenging. [419] Nanoparticles can protect drugs from degradation in the digestive system and enhance their absorption. Formulation into nanoparticles can enhance drug stability in the harsh gastrointestinal tract environment, improving the likelihood for successful targeting, increasing drug solubility and bioavailability, and affording sustained release within the gastrointestinal tract.

Nanoparticles can be delivered directly into the bloodstream through **intravenous injection**. This route is commonly used for systemic delivery of nanomedicines to target specific organs or tissues throughout the body. Injection of nanomedicines into muscle tissue (**intramuscular**) or just beneath the skin (**subcutaneous**) allows for sustained release and gradual absorption. This route is often used for sustained delivery of drugs or vaccines. Injection of nanomedicines directly into the peritoneal cavity (**intraperitoneal**) or the tumor site (**intratumoral**) can be used for localized treatments. This route is often employed in cancer therapy to deliver drugs directly to the tumor. Injection of nanomedicines into the cerebrospinal fluid (**intrathecal**) or directly into the brain tissue (**intracerebral**) can be used for treating neurological disorders. This route allows for bypassing the blood-brain barrier to deliver therapeutic agents to the central nervous system. Injection of nanomedicines into the skin (**intradermal**) or delivery through the skin (**transdermal**) is employed for localized treatments or sustained drug release. Transdermal patches containing nanoparticles can facilitate controlled drug delivery over an extended period.

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Nanoparticles can be administered directly into the vitreous humor of the eye (**intravitreal)** for the treatment of ocular diseases. This route is used to target specific tissues within the eye while minimizing systemic exposure. Nanoparticles can be engineered for **inhalation**, allowing for targeted delivery to the respiratory system. This route is useful for treating lung diseases and achieving rapid absorption of drugs into the bloodstream through the lungs. Nanoparticles can be formulated for **nasal** delivery, providing a non-invasive route for systemic or local drug delivery. This route is particularly advantageous for drugs that may be degraded in the digestive system.

The selection of a specific delivery route depends on the therapeutic goals, the nature of the drug, and the characteristics of the targeted disease or condition. Each route comes with its own set of considerations, advantages and disadvantages (Table 2), and ongoing research aims to optimize drug delivery for improved efficacy and patient outcomes.

Table 2. Advantages and disadvantages of the administration routes of nano-DDS [420-426]

Administration route	**Advantages**	**Disadvantages**
Intravenous (i.v.)	Provides direct access to the bloodstream, ensuring a rapid onset of action. Avoidance of first-pass metabolism results in high bioavailability. Precise dosing due to direct delivery into the systemic circulation.	Invasive method which requires a skilled healthcare professional. Potential for infection at the injection site. May cause undesirable immune reaction
Oral	Non-invasive. Convenient and promotes better patient compliance. Cost effective.	Subject to first-pass metabolism, reducing bioavailability. Absorption can be inconsistent due to factors such as gastrointestinal pH and enzymatic activity.
Transdermal	Non-invasive. Allows for sustained and controlled release over an extended period. Prevents deterioration of drug due to gastrointestinal interaction	Limited permeability. May cause enzymatic deterioration.
Inhalation	Direct pulmonary delivery. Quick absorption, due to the large surface area of the lungs.	Ensuring optimal particle size for deep lung penetration can be challenging. May cause irritation in the respiratory tract.
Intramuscular (i.m.) / Subcutaneous (s.c.)	Allows for controlled release, especially with sustained-release formulations. Bypasses first-pass metabolism to some extent, enhancing bioavailability.	Requires a healthcare professional for administration. May cause local reactions at the injection site.
Intraperitoneal (i.p.)	The peritoneal cavity provides a large surface area for drug absorption. Bypasses first-pass metabolism, leading to increased bioavailability.	Requires a skilled healthcare professional for administration. Potential for infection at the injection site.
Intranasal	Non-Invasive. Rapid absorption due to the rich blood supply in the nasal mucosa.	Restricted to small drug volumes due to nasal cavity constraints. Absorption may vary among individuals. Intolerance in nasal mucosa.

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	Prevents interaction with gastrointestinal tract.	
Intrathecal / Intraventricular	Direct drug delivery to the cerebrospinal fluid (CSF) for CNS disorders. Bypasses the blood-brain barrier, enhancing drug access to the CNS.	Invasive, involves injection into the spinal canal or brain ventricles, requiring expertise. Carries a risk of infection and potential neurological complications.
Rectal	Bypasses first-pass metabolism, improving bioavailability. Absence of enzymes helps in avoiding enzymatic degradation. Administered rectally, offering a non-invasive alternative.	Absorption may be variable and dependent on rectal conditions. Patient acceptance may be lower due to the nature of administration route.
Ocular	Allows for targeted drug delivery to the eyes for ocular conditions. Minimizes systemic exposure, reducing potential side effects.	Limited volume capacity in the eye for drug administration. Some formulations may cause eye irritation .
Vaginal	Targeted delivery for gynecological conditions, minimizing systemic exposure. Bypasses first-pass metabolism for improved bioavailability.	Absorption may vary among individuals. May cause local irritation in the vaginal mucosa.

Application – therapy, diagnostic, imaging, cosmetics, nutraceuticals, agriculture

Drug delivery systems have found diverse applications beyond the traditional medical field including drug/vaccine/gene delivery and diagnostic/imaging, extending into areas such as food and dietary supplements, cosmetics, agriculture, and others.

In the field of food and dietary supplements, nanoparticles and microencapsulation technologies are applied to protect sensitive nutrients, such as vitamins and omega-3 fatty acids, from degradation, ensuring their stability and bioavailability. Encapsulation can also be used to mask undesirable tastes or aromas, protecting sensitive flavors or adding controlled-release properties to enhance the sensory experience of food and dietary supplements. Microencapsulation helps protect probiotics from harsh stomach conditions, ensuring their survival and efficacy in the digestive system. [427-433]

Drug delivery systems in cosmetics involve the encapsulation of active ingredients in nanocarriers like liposomes or nanoparticles. This ensures controlled release, targeted delivery, and enhanced penetration of substances into the skin for improved efficacy. Nanocarriers can deliver anti-aging compounds, such as retinoids or peptides, in a controlled manner, minimizing irritation and maximizing their impact on skin health. Nanoparticles can be used to deliver sun-blocking agents, improving the stability and distribution of sunscreens on the skin. [434-440]

In agriculture, nanoparticles and microencapsulation are utilized for the controlled release of fertilizers, pesticides, and growth regulators. This promotes precision farming, reduces environmental impact, and enhances crop yield. Controlled-release systems in agriculture involves encapsulating fertilizers in polymer coatings, allowing for a gradual and sustained release of nutrients to crops. Nanocarriers can be used for the targeted delivery of biopesticides, minimizing the environmental impact of pest control. [441-445]

Figure 16A shows the percentage of documents – journal articles and patents – related to the various application fields, and Figure 16B presents the relative annual growth of those documents. As anticipated,

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the medical applications including drug/vaccine/gene delivery and diagnostic/imaging dominate, comprising in combination 91% of journal articles and 82% of patents.

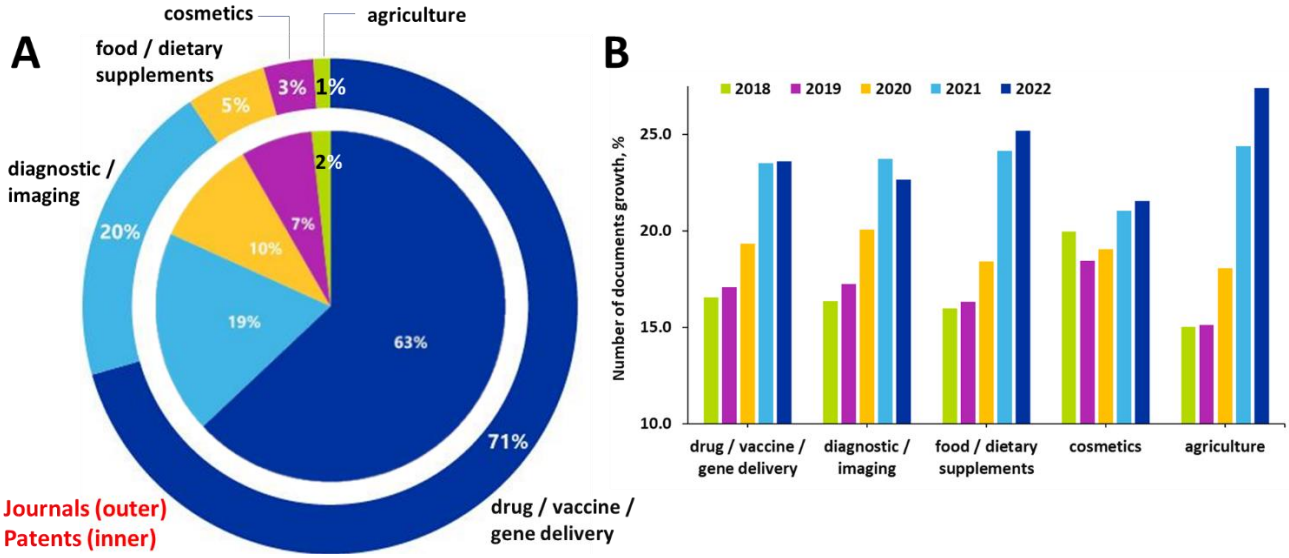

Figure 16. Applications of the nano-DDS as reflected in the CAS Content Collection: (A) Percentage of nano-DDS related documents: journals (outer circle) and patents (inner circle) in the period 2003-2022; (B) Yearly growth of the relative percentage of documents related to various nano-DDS applications for the 5-year period 2018-2022.

Notable patents

Table 3 below summarizes exemplary notable patents related to nano-DDS. These examples were selected to represent the range of discussed materials and applications, also based on especially innovative uses of nanomaterials in DDS.

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Table 3. Notable patent application publications in the field of nano-DDS in recent years

Patent Number	Publication Year	Patent Assignee	Title	Details
WO2023237788	2023	Cellvie (Switzerland)	Mitochondria as a targeted delivery platform	A mitochondrion comprising payloads including nucleic acids, polypeptides, drugs or a combination thereof, electrostatically attached to the outer membrane of the mitochondrion, to provide a drug delivery platform of notable efficiency.
WO2020061367	2020	ModernaTX (USA)	Compounds and compositions for intracellular delivery of therapeutic agents	Preparation of novel lipids and their nanoparticle compositions useful in delivery of therapeutic and/or prophylactics such as RNA, with improved endosomal escape and sustained efficiency and safety.
WO2023144127	2023	AGS Therapeutics (France)	Extracellular vesicles from microalgae, their biodistribution upon administration, and uses	Drug delivery systems containing extracellular vesicles from microalgae loaded with bioactive cargo, administered by a variety of routes, with applications as therapeutics, including as vaccines, as anti-cancer therapeutics, as therapeutics for psychiatric diseases.
US20120040397	2012	Cornell University (USA)	Photo-crosslinked nucleic acid hydrogels	Methods and compositions for producing hydrogel nucleic acid structures using photo-crosslinking, and using these hydrogels for cell-free protein production, and for encapsulating and delivering compounds.
WO2013086373	2013	Alnylam Pharmaceuticals (USA)	Lipids for the delivery of nucleic acids	Novel cationic lipids that can be used in combination with other lipid components such as cholesterol and PEG-lipids to form lipid nanoparticles with oligonucleotides, to facilitate the cellular uptake and endosomal escape, and to knockdown target mRNA.

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WO2021077066; WO2021077067	2021	University of Pennsylvania (USA)	Lipid nanoparticles and formulations thereof for CAR mRNA delivery	Lipid nanoparticles for delivery of mRNAs encoding CAR, nucleic acid, and/or therapeutic agents to selected target cells.
WO2011076807	2011	Novartis (Switzerland)	Preparation of cationic and stealth lipids and compositions for drug delivery	Compositions comprising cationic lipids, stealth lipids and helper lipids, and optimization protocols for delivery of therapeutically effective amounts of active agents to liver, tumors, and/or other cells or tissues.
WO2021030776	2021	Codiak Biosciences (USA)	Extracellular vesicle-antisense oligonucleotide constructs targeting STAT6 and use for treating disease	Exosomes, comprising an antisense oligonucleotide with a contiguous nucleotide sequence complementary to a nucleic acid sequence within a STAT6 transcript, as well as methods for producing the exosomes and using them to treat and/or prevent diseases.
US20060040286	2006	Nanosphere (USA)	Utilizing reporter oligonucleotides as bio-bar-codes for detection of target analytes and diagnostic uses	Screening methods and kits for detecting the presence or absence of one or more target analytes, e.g., proteins, such as antibodies, nucleic acids, or other compounds in a sample. In particular, reporter oligonucleotides are used as biochem. bar-codes for detecting multiple protein structures in a solution.
WO2018227012	2018	Massachusetts Institute of Technology (USA)	Polymer-lipid materials for delivery of nucleic acids	Nanoparticles comprising a conjugated polyethyleneimine polymer (conjugated lipomer), and a lipid-PEG conjugate, useful for the delivery of active agents, for the treatment of disease.
WO2022159855	2022	Johns Hopkins University (USA)	Photo-crosslinked bioreducible polymeric nanoparticles for enhanced RNA delivery	Photo-crosslinked bioreducible nanoparticles for stable siRNA encapsulation in high serum conditions, shielded surface charge, efficient intracellular trafficking, and triggered cytosolic RNA release, allowing robust siRNA-mediated knockdown in cancer cells and systemic siRNA delivery to tumors in lungs.

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WO2021119402	2021	Harvard College (USA)	Compositions and methods for light-directed biomolecular barcoding	Compositions and methods for nucleic acid barcoding that can be used to linearly, combinatorially, or spatially barcode a plurality of targets in a sample, as well as a device for use in a barcoding method comprising a light source and a sample holder.
WO2023092040	2023	Northwestern University (USA)	Spherical nucleic acids for cgas-sting and stat3 pathway modulation for the immunotherapeutic treatment of cancer	Spherical nucleic acids: nanostructures comprising a nanoparticle core and a shell of oligonucleotides attached to the external surface of the nanoparticle core, the oligonucleotide shell comprising a double-stranded or single-stranded stem loop DNA oligonucleotide activating cyclic GMP-AMP synthase.
WO2012110636	2012	Instituto Nacional de Investigacion y Tecnologia Agraria y Alimentaria (Spain)	Carrier peptides for cell delivery	Delivery of mols. into cells, using peptides binding proteins from the cell microtubule motor complex, preferably dynein-binding peptides, as carrier/ delivery peptides; or functionalized structures, as nanoparticles, linked to said peptides, for use in diagnosis, therapy and pharmacol.
WO2005116226	2005	Midatech; Consejo Superior de Investigaciones Cientificas (Spain)	Magnetic nanoparticles comprising metals and semiconductor atoms conjugated to siRNA or microRNA for diagnosis and therapy of diseases	Magnetic nanoparticles having a core comprising metals and semiconductor atoms conjugated to siRNA or microRNA for diagnosis and therapy of diseases, for targeted transcriptional gene silencing, for targeted mRNA degradation, for imaging mRNA, as a tool in functional genomics

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Outlook, challenges, and perspectives

The application of nanotechnology in biomedical sciences, in healthcare as a whole, and specifically in drug delivery, is considered an emerging area of nanotechnology, playing a significant role in the field of medicine and pharmaceutics, mainly due to its potential to overcome the major limitations and problems related to conventional drug delivery systems . The outlook for nano-DDS is promising, with ongoing research addressing challenges and paving the way for innovative and impactful therapeutic solutions. The major perspectives and expectations for nano-DDS can be summarized as follows:

- Personalized treatment paradigm: Nano-DDS contribute to the growth of precision medicine by enabling targeted and personalized therapies. They offer the potential to shift towards more patient-centric treatment approaches.
- Therapeutic innovation: They facilitate the delivery of a wide range of therapeutic agents, including small molecules, biologics, and nucleic acids.
- Multifunctional platforms: Nano-DDS enable integration of multifunctional nanoparticles that combine therapeutic and diagnostic capabilities for theranostic applications.
- Disease-specific approaches: Nano carriers can be tailored for specific diseases, improving drug delivery efficiency and reducing side effects.
- Combination therapies: They provide opportunities for combining multiple drugs in a single nanocarrier for enhanced synergistic effects.
- Overcoming biological barriers: Ongoing research focuses on designing nanoparticles to overcome biological barriers, such as the blood-brain barrier.
- Remote-controlled delivery: Advancements are made in remote-controlled or stimuli-responsive nano systems for on-demand drug release.
- Drug repurposing opportunities: Nanocarriers provide opportunities for repurposing existing drugs by improving their delivery and efficacy.
- Global health impact: Addressing challenges can lead to breakthroughs that impact global health, especially in the treatment of complex diseases.
- Advancing cancer treatment: Nano delivery systems continue to play a crucial role in advancing cancer treatment options, providing targeted and less toxic alternatives.
- Emerging applications: Nano-DDS can be utilized in new applications, such as in the delivery of gene-editing tools and RNA-based therapies.
- Regulatory adaptations: There are ongoing efforts to adapt regulatory frameworks to accommodate the unique characteristics of nano drug delivery systems.

Along with the benefits, nano-DDS need to address certain challenges and roadblocks that impact their development, translation to clinical use, and widespread application. These include:

- Biocompatibility and toxicity
- Clinical translation
- Scale-up challenges
- Biodistribution variability

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- Immunogenicity
- Long-term safety concerns
- Regulatory hurdle
- Standardization issues
- Complex manufacturing processes
- Interdisciplinary collaboration
- Cost considerations
- Inadequate understanding of pharmacokinetics
- Ethical concerns
- Market acceptance

Efforts are ongoing to overcome these challenges through continuous research, technological innovation, collaboration, and regulatory adaptation. As the field evolves, addressing these challenges will be crucial for realizing the full potential of nano-DDS in improving drug efficacy and patient outcomes.

Applications of Nanoscale Materials in Nanosensors

Sensors play a pivotal role in revolutionizing various practices and activities related to healthcare, manufacturing, monitoring, and various other everyday technologies. Nanosensors are devices designed at the nanoscale and can utilize various kinds of nanomaterials. These sophisticated devices operate at an intersection of nanotechnology, physics, and materials science. They can convert various kinds of physical, chemical, or environmental stimuli into measurable signals that can be interpreted, and the information can be used to monitor, understand, or modulate the target.[446] Usually, as the nanosensors come into contact with the target, they detect any physical, chemical, or biological variable which is later transduced to a measurable signal depending on the type of nanomaterials used, later the signal is amplified and refined by filtering excess noise.[447] The information generated is translated into a readable output depending on the type of nanosensor. Typically, nanosensors employ different transduction mechanisms to convert one form of energy including electric, optic, thermal, or mechanical – to another form of energy.[448, 449] Incorporating nanomaterials such as nanoparticles, nanowires, nanotubes, or quantum dots enhances the specificity and sensitivity of sensors, enabling precise measurement.[449-452] Moreover, nanomaterials provide a high surface area to volume ratio, thereby amplifying the interactions between sensor and target. In addition, they offer a cost advantage due to their miniature size.

The most commonly used nanosensors are temperature, proximity, motion, pressure, light, gas, sound, and humidity sensors among others. Biological nanosensors are a specialized subcategory of nanosensors that effectively combine biological components with nanoscale materials to detect biological processes, biomolecules such as nucleic acids, proteins, antibodies, enzymes, biomarkers, entities such as pathogens, etc. Biological nanosensors are used in medical diagnostics, bioassays, and for monitoring drug delivery and disease progression.[453-455] The major challenge in developing nanosensors is the requirement of precision that could potentially lead to reproducibility issues and controlling the signal-to-noise ratio.

In this section, we have presented our findings from a comprehensive analysis of more than 250,000 publications pertaining to the field of nanosensors from the CAS Content Collection spanning across two

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decades (2003-2023). Our analysis was centered around identifying key publication and substance data trends, as well as emerging materials in the field including their applications.

Journal and Patent publication trends

The number of journal publications related to nanosensors shows a steady increase over the last 20 years (Figure 17), doubling between 2013 and 2023. In contrast, the number of patent publications show a much more sedate pace of increase indicating a substantial gap between basic research and commercialization.

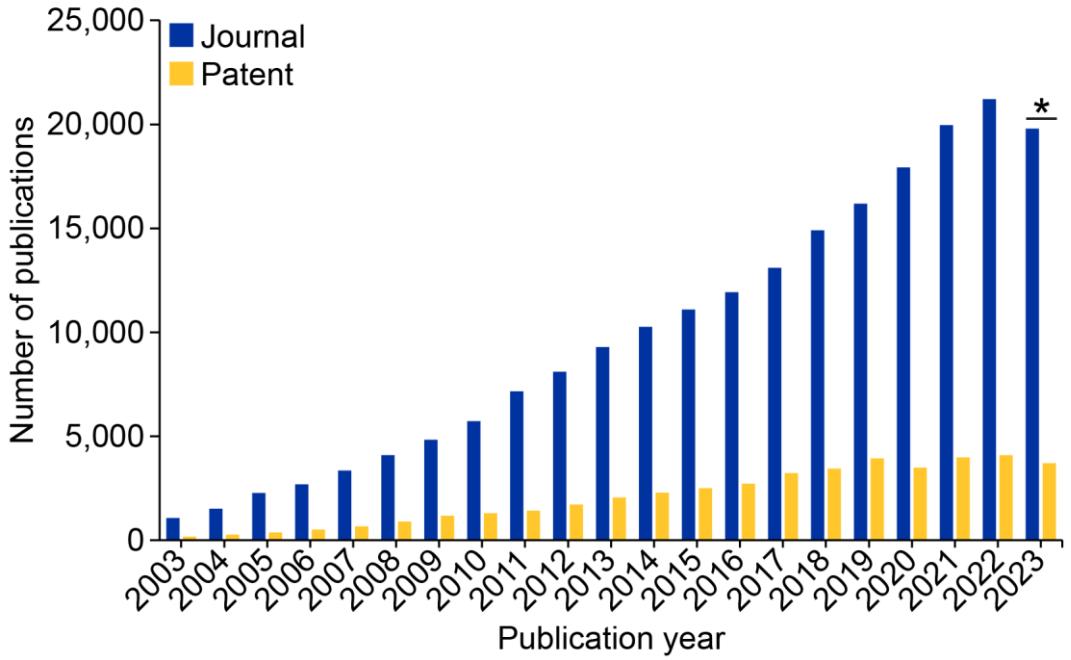

Figure 17. Publication trends for nanosensor related research over the last two decades. Data includes journal and patent publications from the CAS Content Collection for the period 2003-2023.

We identified leading scientific journals that are prolific both in terms of volume of publications as well as citations to those publications, a rough quantification of their influence (Figure 18). While journals such as Analytical Chemistry (Anal Chem) and Biosensors & Bioelectronics (Biosens Bioelectron) appear to lead in terms of absolute number of publications, others such as Journal of the American Chemical Society (J Am Chem Soc) and Angewandte Chemie (Angew Chem) lead in terms of average number of citations per publication (Figure 18). While ACS Nano appears to be somewhere in the middle of the pack in terms of number of journal publications, the average number of citations is nearly double those of Biosensors & Bioelectronics. A few examples of recent journal articles from ACS Nano that are highly cited include the use of nanosensors for rapid detection of SARS-CoV-2[456-458] as well as wearable[459] including epidermal sensors.[456-458, 460, 461] as well as wearable[459] including epidermal sensors.[460, 461]

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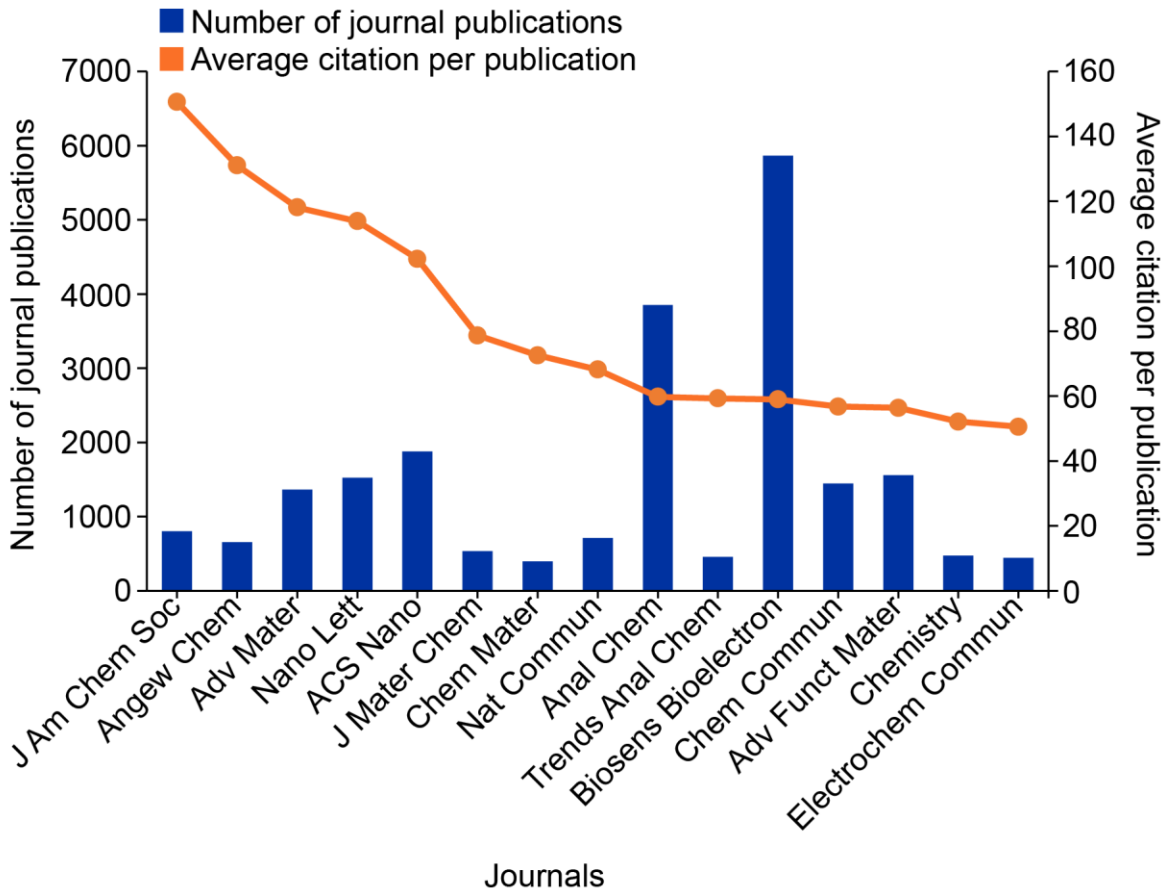

Figure 18. Leading scientific journals in the field of nanosensors based on data from the CAS Content Collection for the period 2003-2023. Blue bars represent number of journal publications while the orange line represents average number of citations per publication. This figure was made by first selecting the top 100 journals in terms of nano-DDS publications, then ranking them based on average citations per article. The top 15 journals based on this ranking are shown.

A similar methodology was utilized to identify leading research organizations actively involved in research in the field of nanosensors (Figure 19). The top 15 research organizations are mostly dominated by research organizations in the United States (USA) (7 out of 15) and China (CHN) (5 out of 15). Singapore (SGP), Germany (DEU), and South Korea (KOR) contributed one research organization each to the top 15 (Figure 19). Academic institutions from China tend to dominate in terms research publication output with the Chinese Academy of Sciences having nearly 5X the number of journal publications as compared to the University of California, the most prolific research organization from USA. Research organizations from USA appear to lead more in terms of average number of citations indicative of the quality and influence of research output from these organizations with Northwestern University, Georgia Institute of Technology, Stanford University and Massachusetts Institute of technology being the leaders overall (Figure 19). Examples of highly cited journal articles originating from these research organizations revolve around the use of nanosensors in wearable electronics,[462] agriculture,[463] and detection and/or monitoring of neurotransmitters[464] among other applications.

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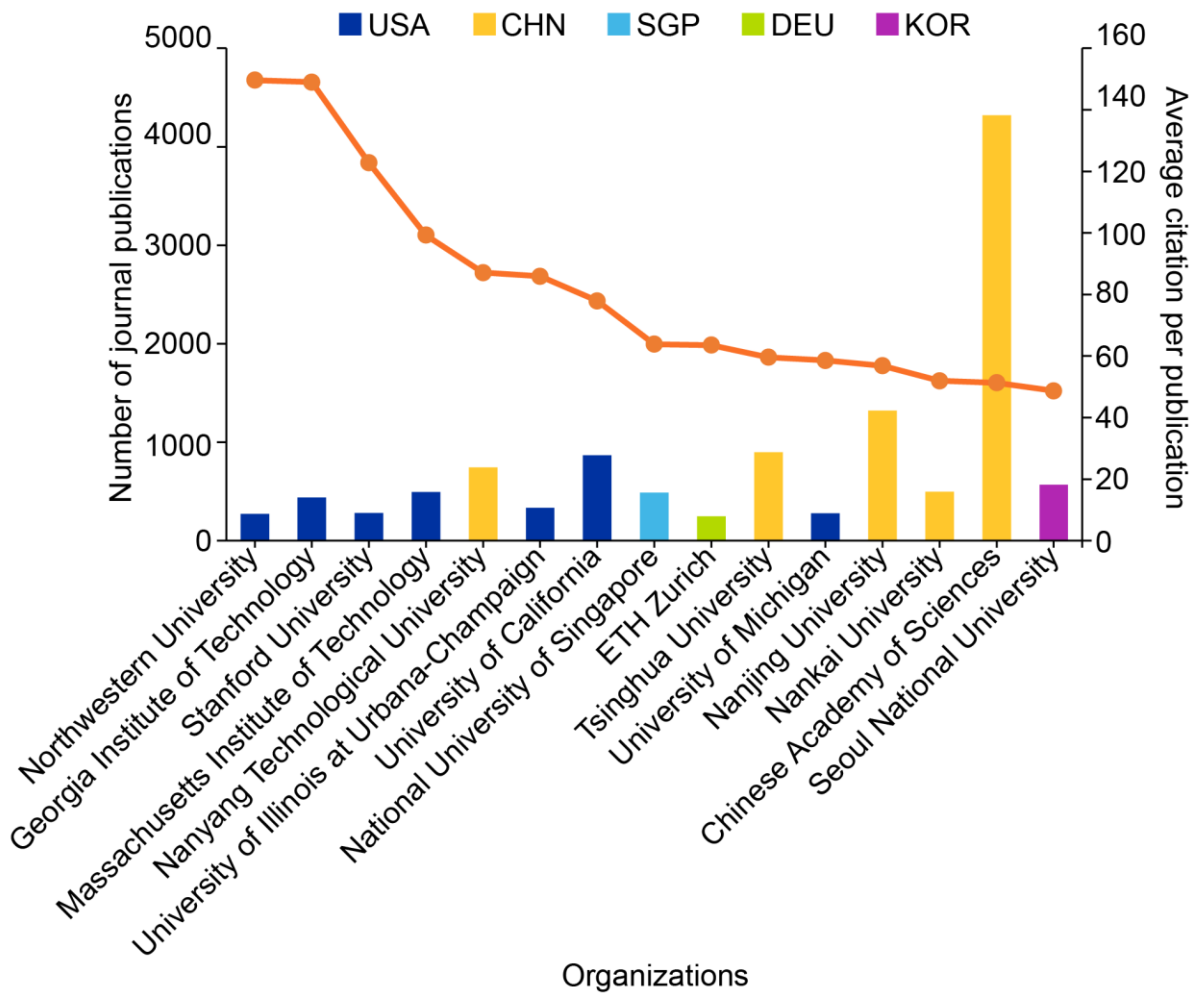

Figure 19. Leading research organizations in the field of nanosensors based on journal publication data from the CAS Content Collection for the period 2003-2023. Colored bars represent number of journal publications while the orange line represents average number of citations per publication. This figure was made by first selecting the top 100 research organizations in terms of total publications in the nanosensor area, then ranking them by average number of citations per publication. Bars have been color coded by country/region with standard three letter codes used to represent them (USA: United States of America, CHN: China, SGP: Singapore, DEU: Germany, KOR: South Korea).

To identify leading organizations/institutions/companies in terms of patent applications we first separated patent assignees into commercial and non-commercial categories. Geographical distribution of the leading commercial patent assignees was diverse with commercial entities from 7 different countries – South Korea (KOR), USA, Japan (JPN), Germany (DEU), Finland (FIN), China (CHN) and the Netherlands (NLD) (Figure 20A). On the other hand, leading non-commercial patent assignees were composed overwhelmingly of organizations from China with only 2 out 15 leading assignees originating from South Korea (KOR) (Figure 20B). A majority of commercial patent assignees were associated with the computing and electronics industry (Samsung Electronics, IBM, Hewlett-Packard, Nokia Technologies, Kabushiki Kaisha Toshiba, Intel, General Electrics, Fujitsu, BOE Technology Group, Koninklijke Philips Electronics) and to a smaller extent other industry types such as imaging (Fujifilm), engineering/consumer products (Robert Bosch), healthcare (3M Innovative Properties) and chemicals (Toray Industries). Patents by the

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multinational company Samsung Electronics involve image sensors,[465, 466] and their application in electronic devices as well as examples of acoustic sensors,[467] strain sensors,[468] and sensors for biometric inputs.[469] The Japanese multinational conglomerate, Fujifilm, appears to have patents related primarily to image sensors[470-472], healthcare (3M Innovative Properties) and chemicals (Toray Industries). Patents by the multinational company Samsung Electronics involve image sensors,[465, 466] and their application in electronic devices as well as examples of acoustic sensors,[467] strain sensors,[468] and sensors for biometric inputs.[469] The Japanese multinational conglomerate, Fujifilm, appears to have patents related primarily to image sensors[470-472] perhaps unsurprising considering their involvement in photography and electronics. 3M Innovative Properties company, an organization that is known to be involved in personal protective equipment and other medical products, in recent years has filed patents pertaining to sterilization sensors,[473-475] as well as sensors with potential use in wound dressings.[476] Finally, Toray Industries, the Japanese multinational company specializing in chemicals, has filed patents related to gas sensors[477, 478] as well as flexible wearable biomedical sensors that can be utilized in monitoring heart activity in last few years.[479, 473-475] as well as sensors with potential use in wound dressings.[476] Finally, Toray Industries, the Japanese multinational company specializing in chemicals, has filed patents related to gas sensors[477, 478] as well as flexible wearable biomedical sensors that can be utilized in monitoring heart activity in last few years.[479]

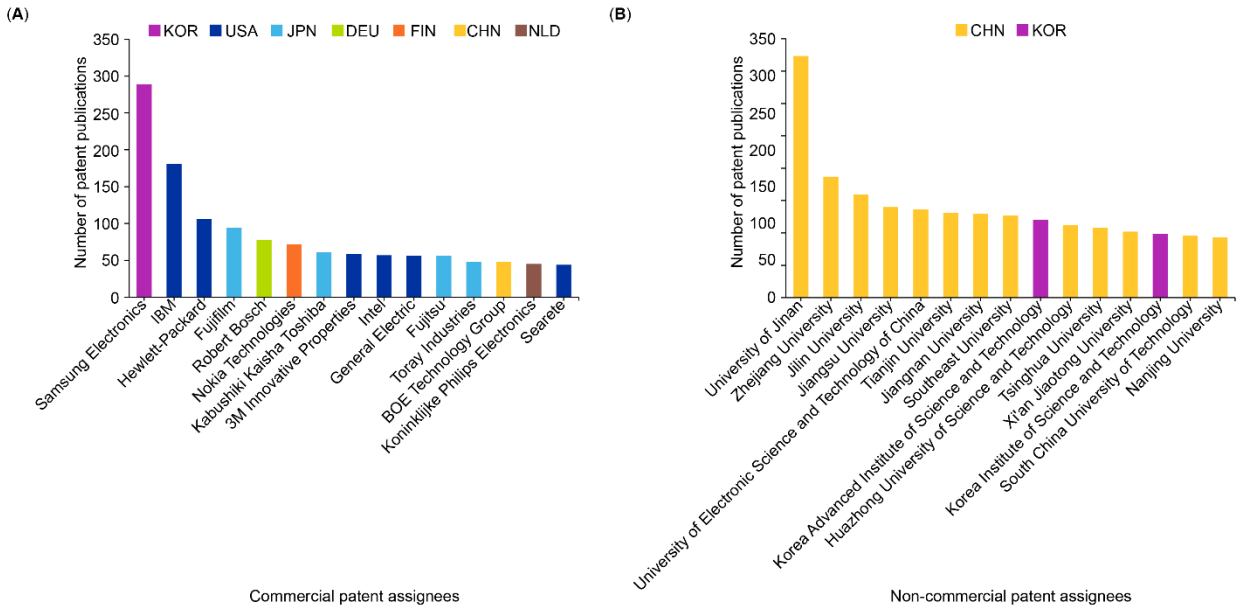

Figure 20. Leading patent assignees in the field of nanosensors in terms of numbers of patent publications between 2003-2023 based on data from the CAS Content Collection. Patent assignees have been categorized into (**A**) commercial and (**B**) non-commercial entities. Bars have been color coded by country/region with standard three letter codes used to represent them (KOR: South Korea, USA: United States of America, JPN: Japan, DEU: Germany, FIN: Finland, CHN: China, NLD: Netherlands).

In terms of non-commercial entities, University of Jinan, a public university located in the Shandong province of China appears to be a standout with twice as many patent applications as the second on the list, Zhejiang University (Figure 20B). Examples of patents by University of Jinan in recent years include those related to flexible wearable sensors,[480, 481] nanoprobes for cancer detection and imaging[482] and a fluorescent sensor to detect chemicals.[483] The only two non-commercial entities based outside of China are the Korean Universities - Korea Advanced Institute of Science & Technology (KAIST) and Korea

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Institute of Science & Technology (KIST). Examples of recent patents by KAIST involve gas sensors,[484, 485] a cerium oxide-based sensor that can be used to detect hydrogen peroxide[486] and a CNT based sensor for virus detection.[487] Similarly, patents filed by KIST cover a range of sensors including colorimetric sensors based on gold nanoparticles,[488] wearable sensors utilizing silver nanowire and SWCNT[489] and nitrogen dioxide gas sensors using SWCNTs decorated with carbon dots,[490] among many others.

Comprehensive analysis of substance data associated with nanosensors from our database (CAS Registry and CAS Content Collection) reveals steady increase in the number of individual substances used in nanosensor publications over the last two decades. This increase is more pronounced for journal publications than patent publications with a ~25% increase between 2020 and 2022. For patent publications, growth in associated substances appears to have been much more modest, remaining more or less constant since 2018 (Figure 21A). This plateau in patent publications is perhaps not surprising as patents might revolve around use of well-established materials in the context of newer applications. Overall, the number of substances associated with journal and patent publications are ~1.1 million and >400,000, respectively. Further breakdown across substance classes shows similar trends across journal and patent publications with substances classified as organic/inorganic small molecules dominating, followed by elements and polymers. Other substance classes that contribute to a smaller extent include

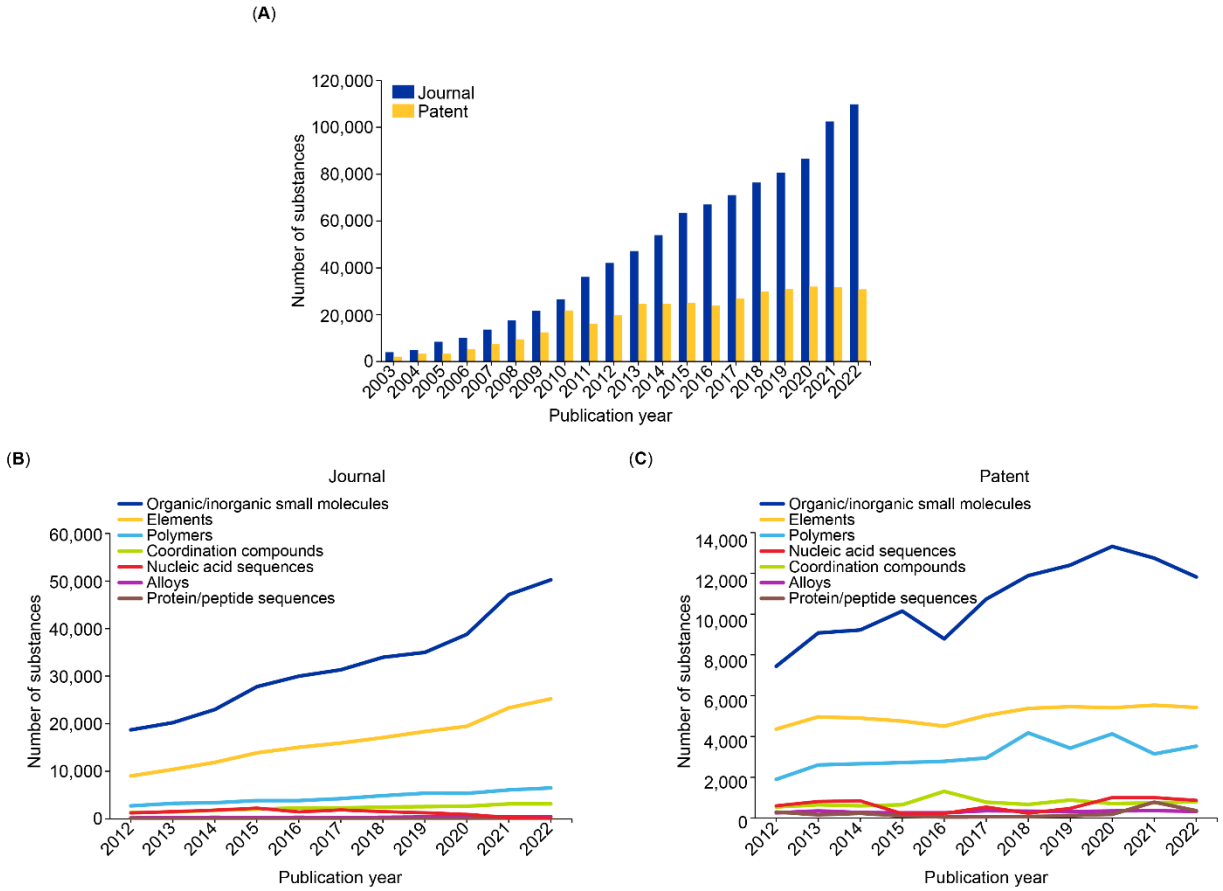

Figure 21. (**A**) Number of substances associated with journal and patent publications. Breakdown across various substance classes (organic/inorganic small molecules, elements, polymers, coordination compounds, nucleic acid sequences, alloys, and protein/peptide sequences) associated with (**B**) journal and (**C**) patent publications pertaining to nanosensors. Included are substance data from CAS Registry and CAS Content Collection associated with journal and patent publications for 2003-2023.

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coordination compounds, nucleic acid sequences, alloys, and protein/peptide sequences (Figures 21 and 22).

Highlighted in Figure 22 are the top individual substances associated with the different substance classes with an emphasis on the major contributors – organic/inorganic small molecules, elements, and polymers. It is important to note that the leading substances associated with nanosensor publications are representative of both materials potentially used to fabricate nanosensors as well as materials that are detected by nanosensors. The top substances associated across different classes show a high degree of overlap between journal and patent publications. A few exceptions include nickel, titanium, and palladium in the element subclass that show up in the top 10 for patent publications, but not for journal publications. Similarly, in the polymer subclass polytetrafluoroethylene (PTFE) occurs in the top 10 for patent publications only, while polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) occur in the top 10 for journal publications only. While our emphasis for the sake of discussion has been on the top 10 substances, it is important to note that some of these substances occur beyond top 10 for either journal and patent publications and in that sense there is a high degree of overlap. One potential reason for dissonance between leading substances in patent and journal publications could be because patent publications might be more focused on novelty in terms of sensor types and/or detection methods rather than material itself – for example, PTFE has been known since the late 1930s while PEDOT is much more recent (late 1980s).

Leveraging our access to extensive substance and bibliographic data, we identified emerging substances in each substance class highlighted in Figure 23. There exists a fair degree of commonality among identified emerging substances between journal and patent publications with this phenomenon being most highly pronounced for the polymer subclass (cellulose, poly(dimethylsiloxane), poly(dopamine), poly(vinylidene fluoride), poly(vinyl alcohol), poly(ethylene terephthalate), poly(poly(styrenesulfonic acid), poly(3,4-ethylenedioxythiophene), poly(vinylpyrrolidone), polyaziridine and polypyrrole), followed closely by the element subclass (sodium, potassium, fluorine, magnesium, calcium, sulfur, phosphorus, iron, zinc, and selenium). The organic/inorganic small molecule subclass shows the highest degree of divergence with only a few emerging substances common between journal and patent publications (3,3’,5,5’-tetramethylbenzidine, thiourea, molybdenum disulfide and glycerol).

The rare earth metal, ytterbium appears to be an emerging substance with respect to patent publications with a marked increase in relative growth increasing post 2008. In recent years, ytterbium appears to have been referred to in the context of fluorescent nanosensors[491] and colorimetric nanosensors[492] as $NaYF_4$ upconversion nanoparticles in patent publications. Another example from the element subclass that appears to be an emerging substance with respect to patent publications is graphene, showing exceptional increase in patent publications post 2010 with a plateau between 2017-2020 and a subsequent slight decrease. An interesting example of patent mentioning graphene did so in the context of semiconductor biosensors incorporated into face masks capable of analyzing exhaled breath to potentially detect biomarkers for cancer and viral infections.[493] Other examples include alcohol sensors[494] and carbon monoxide sensors.[495] The elements nitrogen, copper, chlorine, nickel and oxygen appear in the top 15 emerging substances with respect to journal publications (and not patents). Examples of these elements in the context of nanosensors appear to include both as materials used in the fabrication of nanosensors as well as substance detected using nanosensors. Examples of the former include nitrogenated holey graphene-based gas sensors used to detect flammable and toxic gases propane and butane,[496] Cu/Al electrodes in strain sensors[497] and $NiCo_2S_4$ nanosheets for sensing glucose and ascorbic acid.[498] Examples of latter include zinc oxide nanotube-based NO_2 gas sensors[499] and N-doped molybdenum oxide quantum dots-based fluorescence sensor for detection of Cu^{2+}.[500]

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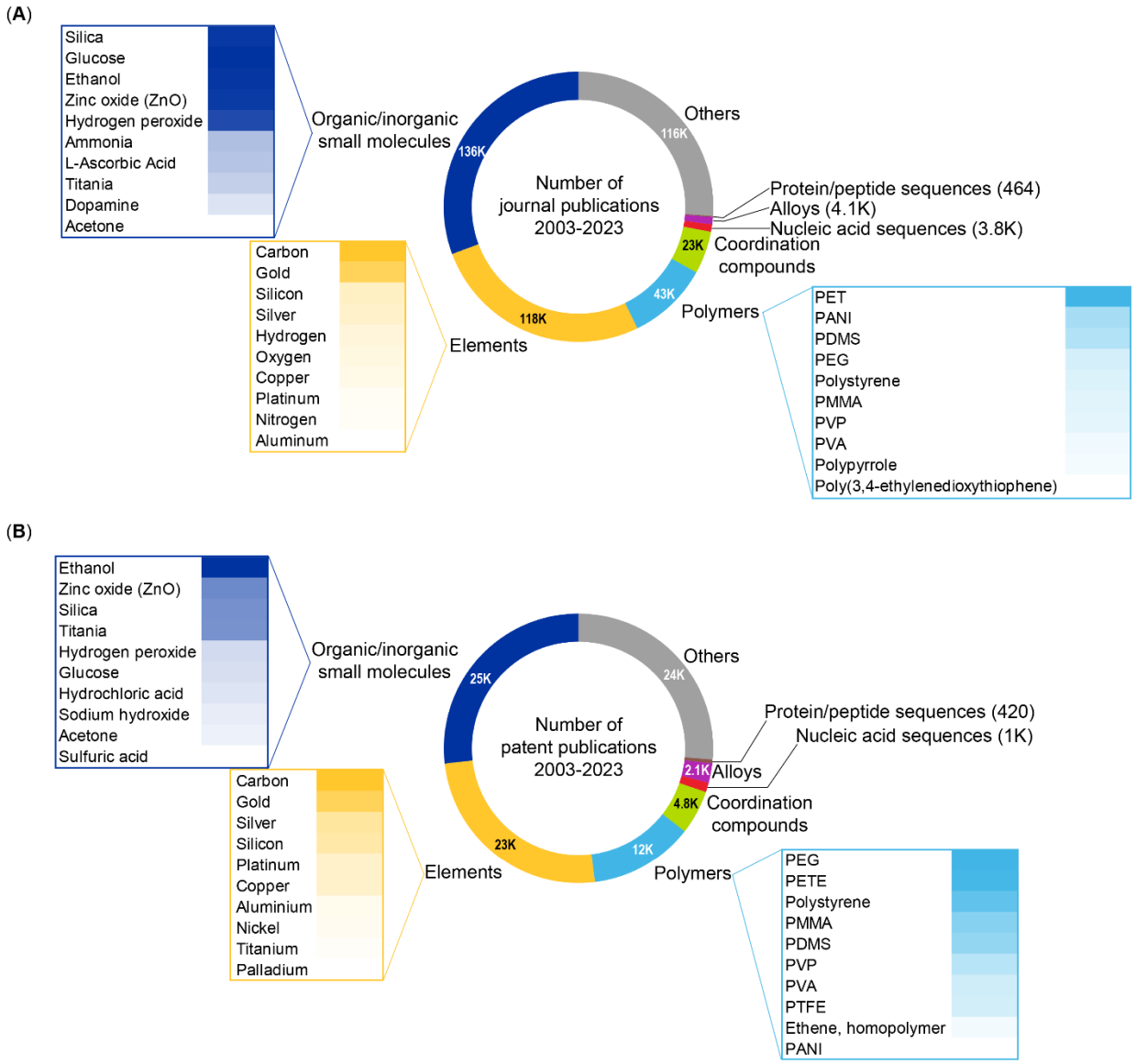

Figure 22. Leading substances in each individual substance class – organic/inorganic small molecules, elements and polymers associated with (**A**) journal and (**B**) patent publications shown as heat map tables with the intensity of the colors corresponding to number of publications associated with that substance. Included are substance and publication data from CAS Registry and CAS Content Collection associated with journal and patent publications for 2003-2023.

Among emerging polymers, synthetic polymers tend to outnumber natural polymers with cellulose and chitosan being the only natural polymers featured in the top 15 for both journal and patent publications (Figure 23). Examples include journal publications describing the use of cellulose in electrochemical,[501] flexible strain[502] and chemosensors[503] often as nanofibers and in combination with other materials (including synthetic polymers) used for applications such as health monitoring,[504] heavy metal detection[503] and in the food industry[505] amongst others. The use of chitosan has been explored in sensors across several biomedical applications including in wearable sensors for health monitoring[506, 507]

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including continuous monitoring of the neurotransmitter serotonin considered a biomarker for depression.[508] Often chitosan is used in conjunction with other materials in the fabrication of these sensors including synthetic polymers such as polyaziridne[509] Among emerging polymers, synthetic polymers tend to outnumber natural polymers with cellulose and chitosan being the only natural polymers featured in the top 15 for both journal and patent publications (Figure 23). Examples include journal publications describing the use of cellulose in electrochemical,[501] flexible strain[502] and chemosensors[503] often as nanofibers and in combination with other materials (including synthetic polymers) used for applications such as health monitoring,[504] heavy metal detection[503] and in the food industry[505] amongst others. The use of chitosan has been explored in sensors across several biomedical applications including in wearable sensors for health monitoring[506, 507] including continuous monitoring of the neurotransmitter serotonin considered a biomarker for depression.[508] Often chitosan is used in conjunction with other materials in the fabrication of these sensors including synthetic polymers such as polyaziridne[509] as well as metals[508] and metal oxides.[510] Patent publications show similar use/applicability of cellulose[511-513] and chitosan[514, 515] including metal organic framework (MOF)-multi-walled carbon nanotube (MWCNT)/chitosan composites for electrochemical detection of tryptophan enantiomers.[516]as well as metals[508] and metal oxides.[510] Patent publications show similar use/applicability of cellulose[511-513] and chitosan[514, 515] including metal organic framework (MOF)-multi-walled carbon nanotube (MWCNT)/chitosan composites for electrochemical detection of tryptophan enantiomers.[516]

Semiconducting polymers such as poly(dopamine) (PDA), PPy, polyaniline (PANI) and PEDOT; the fluoropolymer PTFE and poly(vinylidene fluoride) (PVDF); water soluble polymers such as poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP), polyethylene glycol (PEG) are some of the emerging synthetic polymers in the field of nanosensors based on our analysis. Other emerging synthetic polymers include poly(styrenesulfonic acid) and polyaziridine. PDA in particular exhibits a sharp growth in patent publications after 2012 (Figure 23B). A type of semiconducting polymer, PDA is composed of repeating units of dihydroxyindole, indoledione and dopamine[517] and is synthesized by subjecting dopamine to oxidation. Often fabricated as nanoparticles, [518-520] PDA is also frequently used as coating to modify surface properties of a wide variety of materials.[521 522] In the context of nanosensors, PDA coated carbon nanotubes were embedded in a PVA-PEG hydrogel matrix to fabricate flexible wearable sensors.[523] In another instance, PDA-Au nanoparticles were used to decorate stellate mesoporous silica in a bid to improve characteristics/properties such as stretchability, sensitivity, tensile strength, self-healing properties among others to enable design of [518-520] PDA is also frequently used as coating to modify surface properties of a wide variety of materials.[521 522] In the context of nanosensors, PDA coated carbon nanotubes were embedded in a PVA-PEG hydrogel matrix to fabricate flexible wearable sensors.[523] In another instance, PDA-Au nanoparticles were used to decorate stellate mesoporous silica in a bid to improve characteristics/properties such as stretchability, sensitivity, tensile strength, self-healing properties among others to enable design of wearable sensors.[524] Use of PDA reported in patent applications appears to be similar to those reported in journal publications including use of PDA-multi-walled carbon nanotubes in electrochemical sensors.[525]

Another well-known semi-conducting polymer, PEDOT, shows consistent and increasing growth in journal and patent publications since 2008 (Figure 23). The excellent conducting properties of PEDOT make it particularly well suited for use in nanosensors, examples of which include MXene/CNT/PEDOT composite-based respiratory sensor,[526] sensors composed of wood sponge decorated with SWCNT/PEDOT:PSS capable of detecting pulse and temperature[527] and MXene-PEDOT:PSS-PPy nanosheets used as wearable sensors for real-time monitoring of sweat in terms of sodium and creatinine levels.[527] PANI has been utilized to detect small molecules such as formaldehyde[528] in the form of PANI/Zn bismuthate nanocomposite decorated carbon electrodes; amoxicillin, a penicillin antibiotic, in water bodies as PANI-silver bromide composites[529]; as mesoporous silicon-PANI nanocomposite to detect levels

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of thiourea. Most often the small molecules detected are considered pollutants whose consumption adversely affects human beings. In addition, PANI-based sensors also find applicability in areas such as detection of pathogenic bacteria,[530] monitoring humidity[531] and colorimetric sensors for pH measurement.[532] Many PANI-based sensors are electrochemical sensors that utilize the excellent conducting properties of PANI.

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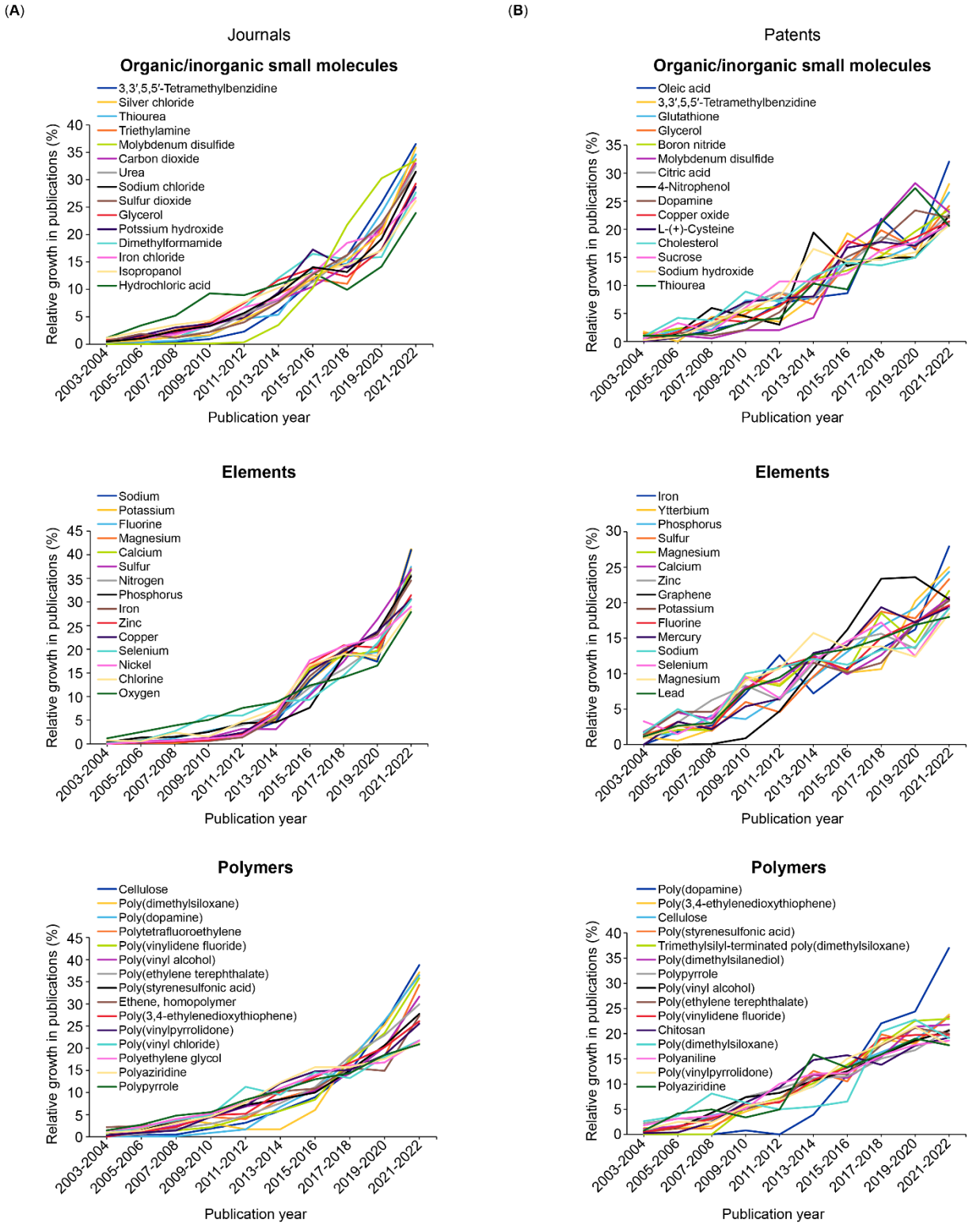

Figure 23. Relative growth in publications associated with emerging substances in each individual substance class – organic/inorganic small molecules, elements and polymers associated with (**A**) journal and (**B**) patent publications. Included are substance and publication data from CAS Registry and CAS Content Collection associated with journal and patent publications for 2003-2023.

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The organic/inorganic small molecule subclass of substances show the least/smallest overlap between emerging substances associated with journal and patent publications (3,3',5,5'-tetramethylbenzidine, thiourea, molybdenum disulfide and glycerol). Glycerol often appears in the context of a solvent used for synthesis of hydrogel sensors[533-535] as well as components of hydrogels[536] and in some instances as protectant against temperature induced changes.[537] Similarly, thiourea is often mentioned as part of synthesis of nanomaterials.[533-535, 538, 539] as well as components of hydrogels[536] and in some instances as protectant against temperature induced changes.[537] Similarly, thiourea is often mentioned as part of synthesis of nanomaterials.[538, 539] Another context in which thiourea often appears is in terms of development of nanosensors for its detection.[540-543] Molybdenum disulfide (MoS_2) nanoparticles appears to be often employed in a variety of different nanostructures including quantum dots,[544] nanoroses[545]/flower-like structures,[546, 547] and nanosheets[540-543, 548] Molybdenum disulfide (MoS_2) nanoparticles appears to be often employed in a variety of different nanostructures including quantum dots,[544] nanoroses[545]/flower-like structures,[546, 547] and nanosheets[548] for environmental applications including monitoring water quality[545] and detection of volatile organic compounds[547] as well as biomedical applications such as detection of biomolecules[544, 549, 550] and health monitoring[551] to name a few. MoS_2 is also often used as a modifier of CNTs[550, 552, 553] for environmental applications including monitoring water quality[545] and detection of volatile organic compounds[547] as well as biomedical applications such as detection of biomolecules[544, 549, 550] and health monitoring[551] to name a few. MoS_2 is also often used as a modifier of CNTs[550, 552, 553] often to enhance their conductivity. The wide applicability of MoS_2 can perhaps be attributed to its good electronic, optical, and chemical properties. The oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) resulting in a colored product is a well-known phenomenon with TMB which is exploited in colorimetric sensors along with a wide variety of other nano-based materials.[554, 555]

Salts such as silver chloride (AgCl), sodium chloride (NaCl), iron chloride ($FeCl_3$) and basic compounds such as triethylamine and potassium hydroxide (KOH) and the strong acid hydrochloric acid (HCl), are the other emerging small molecules more so in journal publications. Silver chloride (AgCl) is often used in reference electrodes[556-558] and as components of nanocomposites.[559] Nanosensors have been tested for their sensitivity in the presence of varying concentrations of sodium chloride (NaCl).[556-558, 560, 561] and as components of nanocomposites.[559] Nanosensors have been tested for their sensitivity in the presence of varying concentrations of sodium chloride (NaCl).[560, 561] Iron chloride ($FeCl_3$) appears in the context of synthesis and may be utilized in the synthesis of both ferric oxide nanoparticles[562, 563] and Fe-MOF nanocomposites.[564] Similarly, urea has also been used in the synthesis of nanocomposites.[562, 563, 565, 566] and Fe-MOF nanocomposites.[564] Similarly, urea has also been used in the synthesis of nanocomposites.[565, 566] Triethylamine can be used as a solvent in the synthesis of nano-based materials.[567, 568] Nanosensors have also been developed to detect presence and levels of triethylamine considered an environmental pollutant.[569, 570] Dimethylformamide (DMF)[571, 572] is also often used as solvent in synthesis. Potassium hydroxide (KOH) has been used to achieve activation of porous carbon nanosheets (PCN) for use as Pt-Ni@PCN nanocomposites in sensors for detecting environmental pollutants.[573] KOH has also been used in the synthesis of nanocomposites.[574, 575].[573] KOH has also been used in the synthesis of nanocomposites.[574, 575] Other small molecules associated with journal publications are toxic gases such as carbon dioxide[576, 577] and sulfur dioxide[578, 579] and isopropanol,[580-583] a volatile organic compound, detected using nanosensors.

As is often the case, most materials listed above are rarely if ever used alone. They are often used in conjunction with multiple other materials across different substance classes (polymers, elements, small molecules) for improved characteristics and properties enabling fabrication of sensors.

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Types of nanostructures

Figure 24 shows the fraction of journal and patent documents containing different types of nanostructures in in the CAS Content Collection, and the variation of their occurrences in journal and patent publications between 2018 and 2022. Nanoparticles are the most prevalent structure type in journal and patent documents, with similar prevalence in both journals and patents. The synthesis of nanoparticles is likely the best-known and most reproducible of the nanoscale synthetic methods and thus the most amenable to investigation. Their high surface area:mass ratios make them most available for reactivity and sensing and thus effective platforms for testing new sensing modalities. Quantum dots, while similar in shape and widely useful (as evidenced by the most recent Nobel Prize in Chemistry,[584] may be more limited to use in optical and electronic sensing because of their semiconducting nature, while the formation of stable nanocrystals is complex and (depending on crystal morphology) may reduce the desired effects.

Nanotubes are prevalent in sensors; the ready availability of carbon nanotubes, their tunability, and their electrical conductivity or semiconducting behavior make them useful in sensors. Significantly more patent documents used nanotube materials than journal documents, while for most other nanomaterials, similar fractions of journal and patent publications were published. The availability of nanotubes, particularly carbon nanotubes, likely makes them more accessible and thus potentially commercializable. In addition, because they have been known and produced for over 30 years, more methods likely exist for the manipulation and modification of nanotubes and there is likely to be more understanding of the limitations of modification and handling methods for nanotubes than for other morphologies.

Nanowires, nanorods and nanosheets have reduced dimensionality, making their components more accessible to external stimuli and thus more effective for sensing. Nanowires and nanorods may have particular utility for transduction of electrical and optical stimuli but may not be as suitable for other applications. Nanosheets such as graphene have also received significant attention and use but may be difficult to manufacture on larger scale and to integrate into electronic and optical sensors.

The rate of increase of journal publications for various nanoscale morphologies are similar, with the rate of publication increasing between 2018 and 2022 by approximately 8%. Nanocrystals, nanobelts, and nanopowders, however, show distinctly lower increases in journal publication rates, and the acceleration in journal publication for them is roughly 0%/year. The reduced rate of publication on these morphologies may be due to limited methods for their synthesis. The rate of patent publications for nanoplatelets and nanoplates has increased significantly more than patent publications discussing other morphologies between 2018 and 2022. While nanoplatelets and nanoplates make up a smaller fraction of overall publications, the development of methods to prepare nanoplates and nanoplatelets and the presence of commercial suppliers.[585] Graphene nanoplates and platelets, if they can be used, are likely to be more easily handled and used in applications such as batteries and in composites than larger nanosheets (which may not be sufficiently robust to be formed into battery components) and are more readily available.[586]

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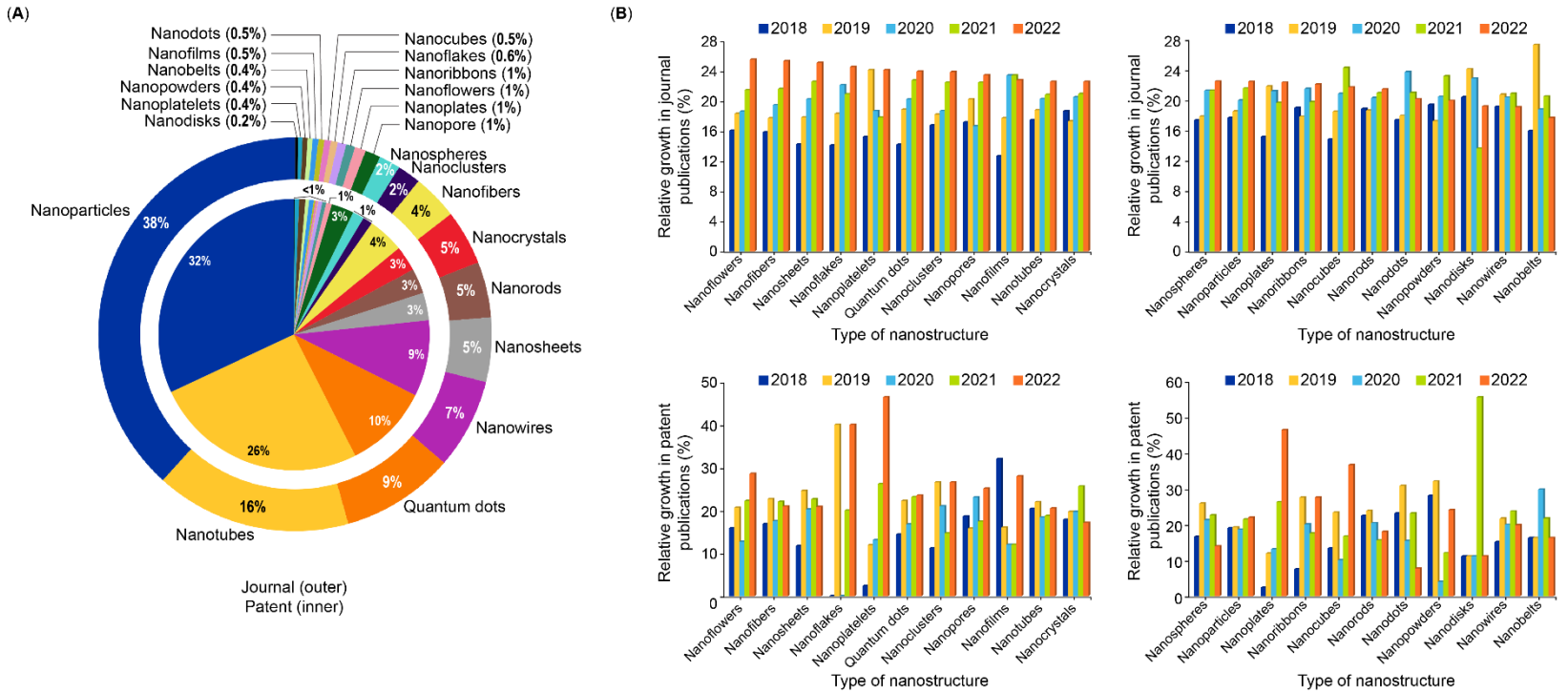

Figure 24. (**A**) Distribution of nanostructures in the field of nanosensors in journal (outer donut chart) and patent (inner pie chart) publications and (**B**) their relative growth in journal (left panel) and patent (right panel) publications over the last 5 years (2018-2022).

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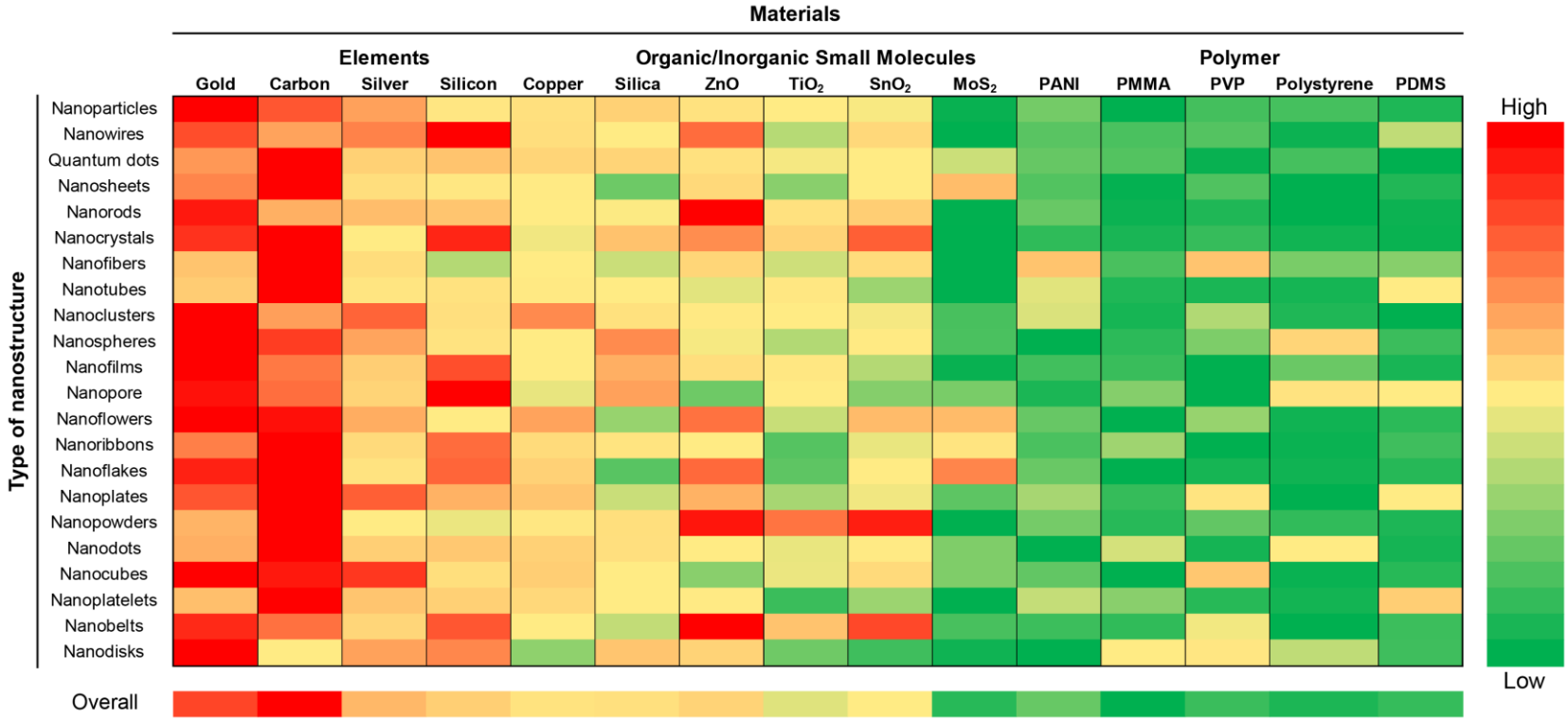

Figure 25. Heat map showing co-occurrences of specific types of nanostructure vs substances for journal publications. The substances shown here are the leading substances identified in each individual substance class (elements, organic/inorganic small molecules, polymer) shown in Figure 6A. Included are substance and publication data from CAS Registry and CAS Content Collection associated with journal publications for 2003-2023.

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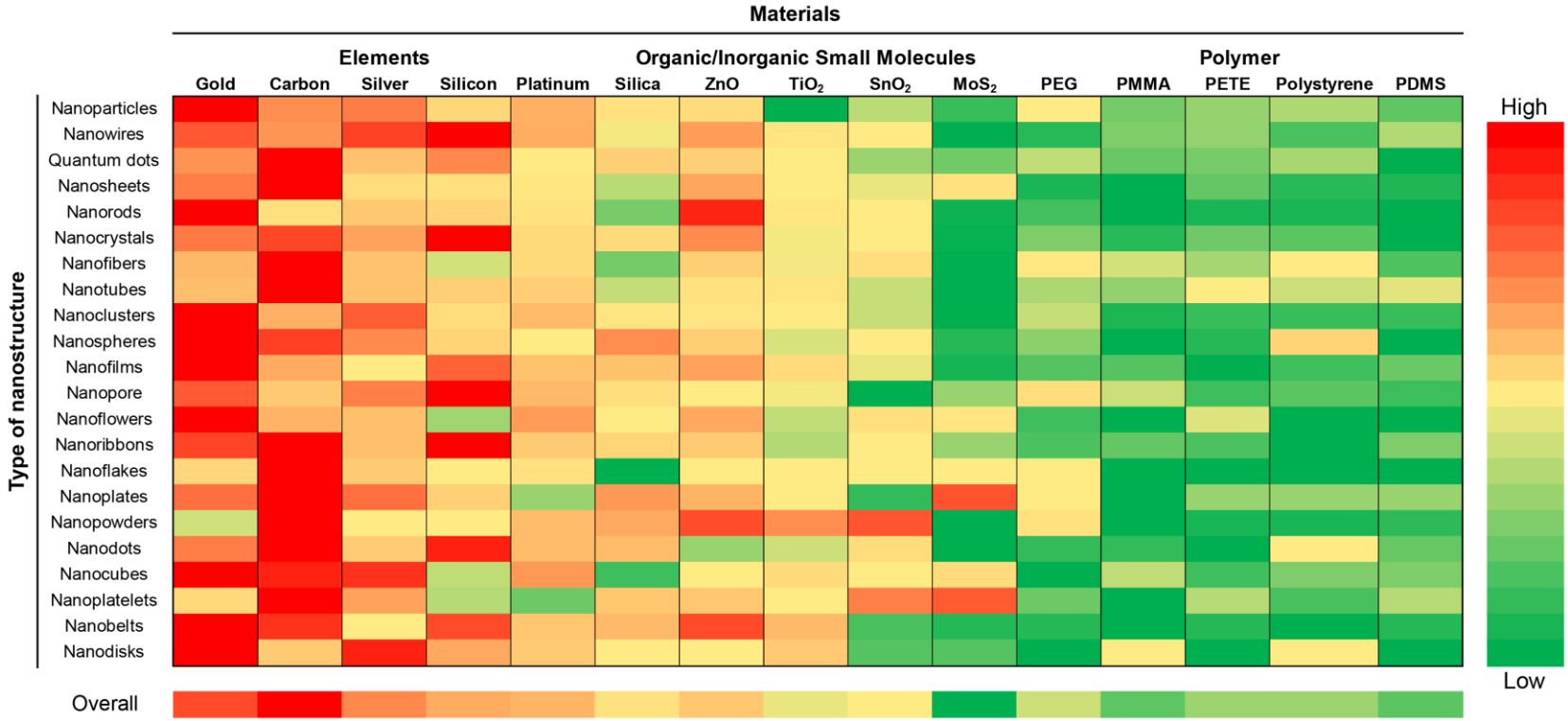

Figure 26. Heat map showing co-occurrences of specific types of nanostructure vs substances for patent publications. The substances shown here are the leading substances identified in each individual substance class (elements, organic/inorganic small molecules, polymer) shown in Figure 6B. Included are substance and publication data from CAS Registry and CAS Content Collection associated with patent publications for 2003-2023.

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Figures 25 and 26 provide heat maps illustrating the relative frequencies of nanostructure compositions and the most common morphologies seen for a given nanostructure composition in journal and patent publications between 2003 and 2023. In both journals and patents, elements were the most prevalent substances used in sensors, and the nanomorphologies used depended strongly on material. Of the elemental substances found in journals and patents, gold and carbon were the most reported materials in nanostructures. Carbon nanostructured materials have been an important example of nanostructured materials, and their discovery has been a significant impetus to the development of other nanomaterials. Carbon nanotubes are readily available and have both conducting and semiconducting forms; in addition, fullerenes are also available, with both C_{60} and C_{70} being useful in polymer-based solar cells as electron carriers.[587] The availability of methods to selectively prepare and separate specific morphologies of nanoscale carbon is likely to increase its use in sensors relative to other substances because of its ubiquity and low cost.

Gold, while expensive, is amenable to formation into nearly all of the common types of nanostructures, has known atomic structure, is conductive, and can absorb light; it is thus capable of responding to a variety of stimuli and is well-precedented and is a good material to build novel nanoscale sensing technologies. The ability to prepare a variety of nanostructures with carbon likely underlies their usage in sensors. In journals, silver nanostructures were reported frequently. Silver can form some of the same structures that gold can, has known atomic structures, is conductive, and is less expensive than gold, making it an attractive alternative to gold.[588] Because of its ubiquitous use in computers, methods to prepare nanostructures of silicon are well-known.

The more recent development of nanopore DNA sequencing using silicon likely improves the availability of silicon nanopores[589]; the mechanisms of identification of DNA bases and conversion to a perceptible signal by silicon nanopores may be applicable to the sensing of other analytes. The use of silicon in electronics also makes silicon useful in handling and transmitting signals from sensors.

The most common materials and morphologies observed in patent and journal documents are similar, except for the replacement of copper in journal documents with platinum in patent publications. Platinum is used as a catalyst in industry, can absorb and respond to gases, and is conductive. Despite its expense, the known properties, methods of handling, and gas response behavior of platinum may make it an effective material for sensors, particularly for gas and electrochemical sensors. While copper is prevalent in nanoclusters and nanoflowers, no single morphologies of nanoscale platinum predominate.

Copper and a variety of metal oxides have been used with similar frequencies; the oxides are most commonly used in sensors as nanopowders, although nanobelts and nanorods of zinc oxide are found relatively often in sensors. MoS_2 is used in a variety of morphologies in sensors[590]; it has been used as a lubricant additive in a variety of circumstances which may have led to the understanding and exploration of its nanoscale morphologies.

Finally, polymers have also been employed in a variety of morphologies but at lower frequencies than other materials in publications for sensors. The predominance of journal publications in general and for sensors may mean that the methods for polymer manipulation which are more common in industry may not be applicable to the use of polymers in nanomaterials; for example, the methods for manipulating polymers on larger scale may not be applicable to their manipulation at smaller scales. Nanofibers, however, show significant incorporation of polyaniline and polyvinyl pyrrolidinone. Polyaniline is used as a conducting polymer but is sensitive to oxidation and reduction; hence its use as a conducting component in wire-like materials for sensors on the nanoscale is reasonable, while the ability to change conductivity may make it useful in sensing or in transducing sensing outputs.

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Types of nanosensors

The publication distribution of sensor applications using nanostructures by types of stimulus and the rates of publication increase for various sensor types from 2018 to 2022 (Figure 27). For most stimuli, the fraction of journal publications and the fractions of patent publications are similar, implying similar proportions of exploratory and commercial interest. Chemical sensors (those designed to detect small molecules or elements primarily in nonbiological contexts) form the largest fraction of publications, followed by biological sensors (sensors functioning in biological systems detecting either small molecules, proteins, or subcellular or cellular entities), physical sensors (sensors detecting mechanical forces such as pressure or force), and electromagnetic sensors (sensors for detecting electrical or magnetic forces). Chemical stimuli are likely the easiest stimuli to model and thus for which to design detection methods. While quantum effects are useful on the nanoscale, the relative size of analytes and features for nanoscale sensors is large, making behavior at larger scales more predictive of sensor behavior. The size of biological analytes may be comparable to the feature sizes in sensors, making them less predictable, while methods for detecting and transducing forces on small scale may be more difficult to determine from behavior at macroscopic scales.

Of the particular uses for nanotechnological sensors, gas sensors make up the largest fraction, with similar prevalence of journal and patent publications. Detection of gases may allow detection of analytes while avoiding solvent or mass transfer effects existing in solution. Nanosensors may allow the detection of gases with lower spatial resolution or in biological systems. Nanoscale sensors may reduce the costs of gas sensing or increase its sensitivity and thus improve safety. For example, detection of H_2S,[591] CO,[592] and NO_2[593] using nanosensors has been a topic of interest. As for gas sensors, electrochemical sensors using nanomaterials may provide advantages because of feature size and fundamental mechanistic knowledge, while a variety of stimuli can be detected electrochemically.[594-596] For example, detection of H_2S,[591] CO,[592] and NO_2[593] using nanosensors has been a topic of interest. As for gas sensors, electrochemical sensors using nanomaterials may provide advantages because of feature size and fundamental mechanistic knowledge, while a variety of stimuli can be detected electrochemically.[594-596]

SPR-based sensors and immunosensors make up the largest fractions of sensors for biological applications. SPR can be used to detect a variety of binding events and to determine binding constants, making it useful in understanding and detecting biological events. The prevalence of gold in sensors is consistent with the use of gold surfaces for SPR; detection of plasmons in gold nanoparticles might improve sensitivity and allow use on smaller scales or to render them more convenient[597, 598] Immunosensors are important diagnostic tools; the ability to reduce their scale could either be used to reduce the cost of diagnostics, or to perform many tests at once, allowing testing of many cells and determining the behaviors of individual cells or to detect many immunomolecules (and perhaps disease states) at once. Temperature sensors have received significant interest in patents, though nearly as much interest in journal publication. Temperature nanosensors are useful in manufacturing because they allow temperature monitoring on smaller scales and thus may allow improvements in temperature control in industrial processes.[599] Glucose, pressure, and enzymic sensors are less explored on nanoscale. Glucose concentration and pressure are likely quantities relevant on macroscopic scales; the market for glucose sensing may also be mature and thus difficult to enter or to demonstrate superiority or reduced cost.

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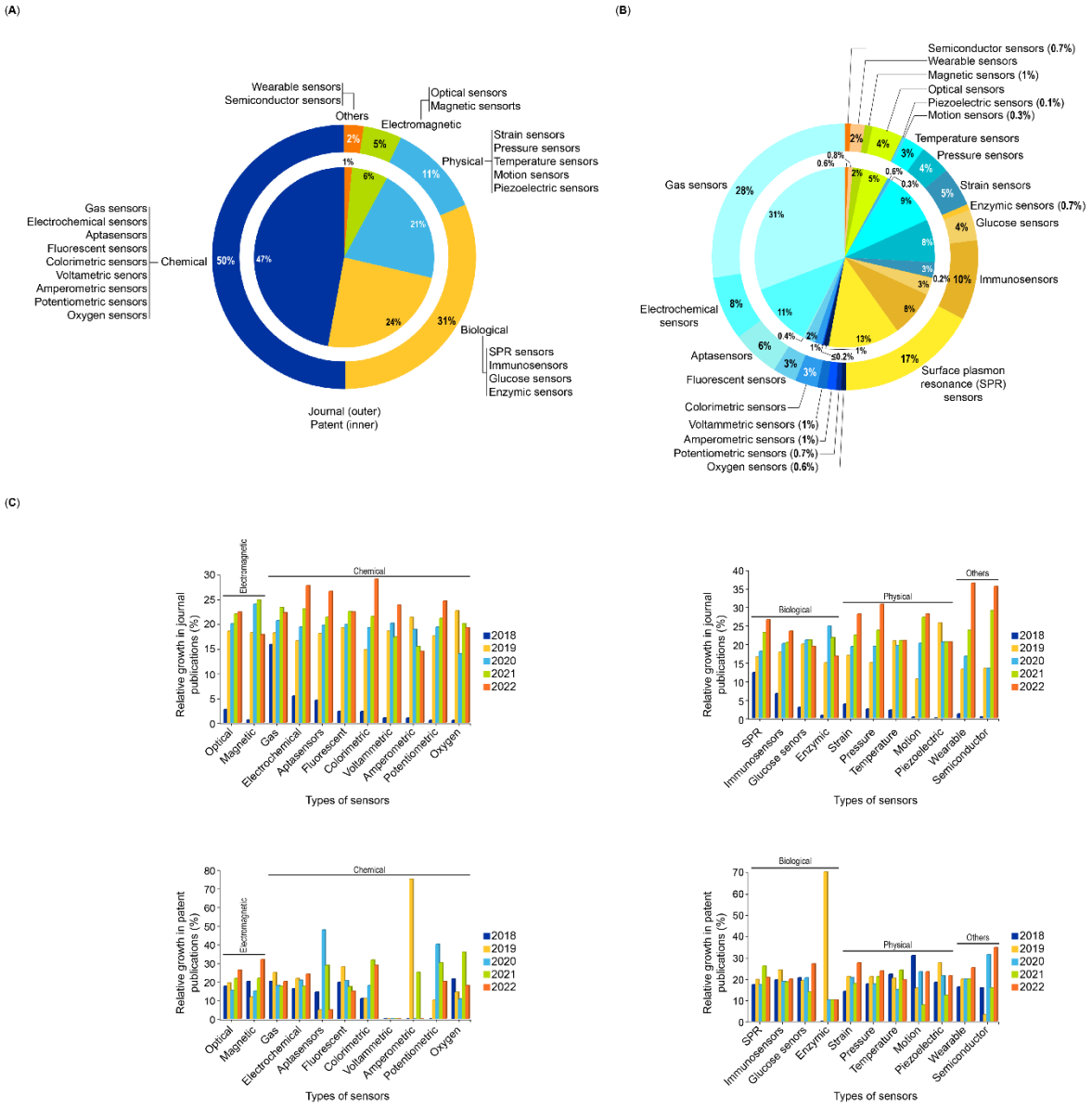

Figure 27. Distribution across (**A**) broader categories of nanosensors, (**B**) their breakdown into individual subtypes for the period 2003-2023 and (**C**) growth in publications (2018-2022). In (**A**) and (**B**), the outer donut chart represents journal publications while the inner pie chart represents patent publications. Data includes journal and patent publications from the CAS Content Collection for 2003-2023.

The growth rate of publication for journal and patent articles discussing nanosensors are similar, with relatively limited data for the increase in recent patent publication for chemical sensors, which is consistent with the trends observed on categorization of sensors by other characteristics. Within chemical sensors, the growth rate for colorimetric, electrochemical, and aptasensors was significantly larger than other types of sensors. Aptasensors also showed significant growth in patent publications in 2020 (potentially due to their utility in the detection of SARS-CoV-2 for diagnosis of COVID infection). Aptamers can be used to bind a wide range of analytes, and their development could provide a more general

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platform for sensor development. Colorimetric sensors are potentially useful because their output is visible and thus may not require further equipment for the detection of an analyte, making them more portable and potentially suitable for use where resources are limited. Wearable, strain, and semiconducting sensors showed relatively high acceleration in publication growth during the last five years, while pressure sensors showed growing interest in journal publications. Nanoscale strain sensors may be potentially useful for study of material behavior and for developing more durable or even self-healing materials. The recent interest in wearable sensors may be caused by the need to obtain health data remotely or without physical contact, and the commercial possibilities for such sensors. Finally, semiconducting sensors have shown increased rates in both patent and journal publications.

Applications

The many applications of nanosensors can be broadly categorized into biomedical, environmental, agriculture, and food industries. Biomedical applications can be further broken down into the use of nanosensors in cancer diagnosis and treatment, health monitoring using wearable sensors, detection of pathogens including bacterial species, detection of illicit drugs including opioids as well as blood glucose detection and biological imaging. Drug discovery is another major subset of biomedical applications and incorporates the use of nanosensors in high-throughput screening to identify viable lead compounds. In our document dataset, biomedical applications of nanosensors outweigh/contribute to a larger extent as compared to other applications (Figure 28A) accounting for nearly ~82% and ~80% of journal and patent publications. In the following paragraphs, we have described in detail a few of these applications.

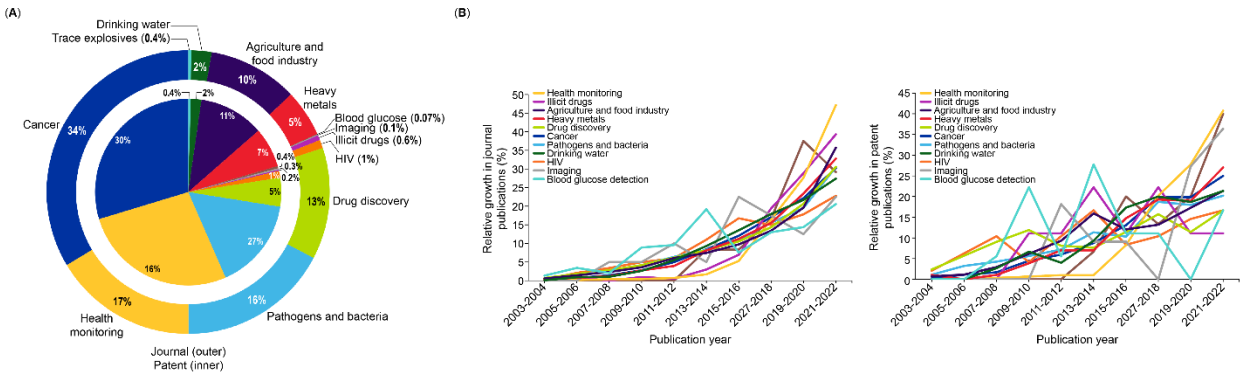

Figure 28. (**A**) Distribution of and (**B**) relative growth in publications (journals and patents) of various applications across which nanosensors appear to be utilized. Data includes journal and patent publications from the CAS Content Collection for the period 2003-2023.

Nanosensors in cancer: Nanosensors can be used in the detection, monitoring, and treatment of cancer. Due to their size and specificity, they can help in detecting specific biomarkers associated with cancer. For instance, a gold nanoparticle-based nanosensor array was developed to detect volatile organic compounds (VOCs) from exhaled breath of patients suffering from lung, breast, colorectal, and prostate cancers.[600] Nanosensors based on carbon nanotubes (CNTs) can be used to detect cancer-related biomolecules in trace amounts.[600-602] Nanosensors based on carbon nanotubes (CNTs) can be used to detect cancer-related biomolecules in trace amounts.[601, 602] Highly sensitive sensors developed using silicon nanowires, silver nanowires, etc. can be used to detect cancers. These nanosensors can detect subtle changes in electric conductivity upon their interaction with cancer biomarkers.[603, 604] magnetic nanoparticles (MNPs) such as superparamagnetic iron oxide nanoparticles (SPIONs) typically made from magnetite (Fe_3O_4) are used to develop magnetic nanosensors for cancer nanotheranostics.[605] For certain specific applications, magnetic

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nanoparticles are conjugated with immune components to develop immunomagnetic nanosensors that can be used for detecting and imaging cancer stem cells (CSCs). For instance, a study explained the detection of glioblastoma CSCs using an anti-CD133 monoclonal antibody (mAb) coupled to magnetic nanoparticles.[603, 604, 606] magnetic nanoparticles (MNPs) such as superparamagnetic iron oxide nanoparticles (SPIONs) typically made from magnetite (Fe_3O_4) are used to develop magnetic nanosensors for cancer nanotheranostics.[605] For certain specific applications, magnetic nanoparticles are conjugated with immune components to develop immunomagnetic nanosensors that can be used for detecting and imaging cancer stem cells (CSCs). For instance, a study explained the detection of glioblastoma CSCs using an anti-CD133 monoclonal antibody (mAb) coupled to magnetic nanoparticles.[606]

Nanosensors in pathogen and infectious diseases detection: These play a pivotal role in the detection of pathogens including bacteria, fungi, viruses, and protozoans with high sensitivity and selectivity owing to their miniature size and ease of portability. Interactions between the functionalized nanomaterials and pathogenic species can induce changes in the physical, chemical, and electrical properties of sensors. These altered signals can be measured and quantified for detecting/sensing pathogens. Carbon-based nanosensors,[607] metallic nanoparticles,[608] and metal-oxide-based nanoparticles[609] are used for bacterial detection and therapy. Certain metallic nanoparticle-based nanosensors, such as silver and gold experience localized changes in surface plasmon resonance (SPR).[610] Nanobiosensors are also being developed for fungi and viruses, especially for the COVID-19 virus.[611, 612] Specialized nanosensors are developed by coating nanomaterials with pathogen-specific recognition elements such as enzymes, aptamers, proteins, and peptides.[613] In certain cases, quantum dot nanosensors are engineered to bind with specific biomolecules resulting in changes in fluorescence, bioluminescence, chemiluminescence, and photoelectrochemical biosensors. These nanosensors are highly tunable and their emission signals can be controlled by altering their sizes.[614] In another example, graphene-based nanosensors utilize graphene's high surface area and excellent conductivity to detect pathogens for instance graphene field-effect transistors (GFETs) are used for ultrasensitive detection.[615] In addition, advancements in this field have led to the development of nanopore-based sensors for pathogen detection,[616] microfluidic nanosensors for high throughput pathogen detection,[617] and magnetic nanoparticles conjugated with aptamers or antibodies[618] for robust pathogen detection to name a few.

Nanosensors in health monitoring: Nanosensors can efficiently detect specific biomolecules such as proteins, DNA, RNA, or metabolites and their altered levels by precisely monitoring biomolecular processes, including antibody and antigen interactions, enzyme interactions, and cellular communication activities. Subtle changes in their levels could be indicative of health-related issues. Biosensors are used to detect biological markers, perform continuous monitoring of biological parameters, detect specific proteins, and detect nanomechanical changes in cells. Similarly, nanosensors can also be used to perform pH monitoring in bodily fluids such as sweat or urinal fluids which can aid in monitoring conditions such as acidosis and alkalosis which could be indicative of underlying health issues.[619, 620] In addition, engineered nanoparticles can also be used to develop imaging agents that can bind to specific targeting ligands to detect abnormalities at minute levels which can help in the early detection of diseases like cancers,[621] and cardiovascular disease.[622] For efficient management of diabetes, nanosensors can be injected into the skin or can be used as a wearable device for continuous glucose monitoring.[623, 624].[622] For efficient management of diabetes, nanosensors can be injected into the skin or can be used as a wearable device for continuous glucose monitoring.[623, 624] Nanosensors are also being developed that can perform metabolite detection from bodily fluids such as sweat, blood, urine, plasma, etc.[625, 626] Nanofabricated sensors can also be implanted in eyes to monitor intraocular pressure which can be important for managing conditions such as glaucoma.[627] Nansosensors can also detect minute levels of biotoxins such as anthrax and smallpox which could be utilized in security and military operations. Portable nanobiosensors are also being used to develop point-of-care diagnostics for faster and efficient detection,

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monitoring and/or managing health related conditions.[628] These examples indicate the usability of nanosensors in the field of health monitoring and healthcare.[625, 626] Nanofabricated sensors can also be implanted in eyes to monitor intraocular pressure which can be important for managing conditions such as glaucoma.[627] Nansosensors can also detect minute levels of biotoxins such as anthrax and smallpox which could be utilized in security and military operations. Portable nanobiosensors are also being used to develop point-of-care diagnostics for faster and efficient detection, monitoring and/or managing health related conditions.[628] These examples indicate the usability of nanosensors in the field of health monitoring and healthcare.

Other key applications of nanosensors appear to be related to environmental monitoring and the agriculture and food industry – these applications account for a sizeable fraction of publications (Figure 28A) and show a steady increase in publications perhaps more pronounced after 2014 (Figure 28B). Environmental monitoring consists of detecting levels of heavy metals[629-631] and monitoring of water quality.[632, 633] For an informative perspective on nanosensors for monitoring water quality please see Vikesland.[632-634] For an informative perspective on nanosensors for monitoring water quality please see Vikesland.[634] Agriculture and food industry related applications includes detection of contaminants (including pathogens) in food samples - example of commercially available nanosensors include RapidChek which has developed a line of sensors capable of rapidly detecting pathogens such as *Salmonella*, *E. Coli* and *Listeria*[635] in food samples.

Use of sensors in the agricultural sector[636] includes PANI-based[637] and CNT-based[638] strain sensors having the ability to perform real time monitoring of plant growth. Other applications of sensors in the agricultural sector involve detection of pesticides using carbon dot-based fluorescence sensors[639] and graphene dot-based electrochemical sensors[640] as well as monitoring soil quality in terms of moisture content[641] and bacterial flora.[642] Aflatoxins are toxic and carcinogenic compounds produced by fungal species *Aspergillus flavus* and *Aspergillus parasiticus* affecting a wide variety of crops such as corn, wheat and peanut among many others.[643] Aflatoxins are hepatotoxic and consumption can lead to a variety of symptoms such as nausea, vomiting, severe abdominal pain which possibility of acute liver injury in the case of large doses.[643, 644] Therefore, accurate, rapid and highly sensitive detection of aflatoxin levels in food samples is an important area of development for nanosensors[645, 646] including aptasensors.[647, 648] . Aflatoxins are toxic and carcinogenic compounds produced by fungal species *Aspergillus flavus* and *Aspergillus parasiticus* affecting a wide variety of crops such as corn, wheat and peanut among many others.[643] Aflatoxins are hepatotoxic and consumption can lead to a variety of symptoms such as nausea, vomiting, severe abdominal pain which possibility of acute liver injury in the case of large doses.[643, 644] Therefore, accurate, rapid and highly sensitive detection of aflatoxin levels in food samples is an important area of development for nanosensors[645, 646] including aptasensors.[647, 648]

Outlook, challenges, and perspectives

In conclusion, nanosensors have been explored in various categories due to their unparalleled sensitivity, selectivity, and miniature size. Therefore, they are used in various sectors such as medicine, diagnostics, healthcare, environmental, food and agriculture industries. As more research endeavors are made in this field, we can aim for more sophisticated nanosensors which utilize nanomaterials in novel ways, but the major challenges in this field are:

- Ensuring the stability of nanomaterial-based sensors in harsh environment.
- Integrating nanosensors into devices and instruments poses several challenges such as miniaturization and packaging, interfacing with electronics while minimizing noise and signal

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interference, designing power-efficient circuits, and efficient calibration and maintenance. In addition, sensors used for biomedical applications must be biocompatible and stable under biological conditions.

- Enhancing real-time monitoring capabilities of nanosensors for timely response against disease or sensing changes in environment.
- Balancing nanosensor cost vs the materials used for their fabrication to make them an economically viable option.
- Ensuring standardization of nanosensor devices for reproducible results.
- Making sure that ethical and safety concerns regarding the assembly, testing and disposal of nanosensors are addressed properly.
- Adhering to standardized guidelines regarding safety and use of nanosensors especially the issues related to data privacy and security while using nanosensors in biological systems.

Despite these challenges, the future of nanosensors appears promising and they have a potential to revolutionize various realms of science including healthcare and other industries.

Applications of Nanoscale Materials in Catalysts

Natural language processing (NLP) analysis of the dataset of around 3 million nanoscience documents from the CAS Content Collection showed that one of the major applications of nanomaterials is in the field of catalysis. Catalysts decrease the activation energy of a reaction by chemical and/or physical interaction with the reactants and / or intermediates without being consumed during the reaction. Catalysts present in the same phase as the reactants are known as homogeneous catalysis. On the contrary, heterogeneous catalysts are in a different phase than reactants. In most cases, heterogeneous catalysis involves solid-supported catalysts which function by interactions between the reactants or intermediates and the active sites on the catalyst. Nanoscience is most likely to improve the performance of heterogeneous catalysis because heterogeneous catalysis relies on structures larger than single molecules and depends on the structure, morphology, and size of the catalyst, features which nanoscience provides the opportunity to control.

In this section, using data from the CAS Content Collection, we provide data-based scientific insights and context from nanocatalysis documents. We have derived connections between substances, materials, nanostructure types, applications, and reactions involved in nanocatalysis, and their trends. These insights will help researchers to quickly understand this research area and develop strategies for their research problems. In addition, we provide a landscape view of nanocatalysts by providing yearly publication trends, the top publishers in various categories, and the average citations per publication trends in various categories.

Substance Data Trends

The CAS Content Collection has substances indexed for the various roles in which they are used in the study, and catalyst is one of the roles. Figure 29 lists the various categories of substances used as catalysts along with a heatmap of the top substances in a substance type. With a contribution of 34.9%, oxides are the most used category followed by noble metals, transition metals and non-metals with 22.5%,17.1% and 15.1% contributions, respectively. The other categories of substances in decreasing order of their share are metal sulfides, post transition metals, other metals, metal phosphides, metal hydroxides, metal carbides, metalloids, natural polymers, and enzymes. Titanium dioxide, zinc oxide and silicon dioxide are

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the most found metal oxides. Many of the other oxides in this category are transition metal oxides known for their catalytic properties. Metal oxide nanomaterials have applications such as photocatalysis,[649] energy,[650] electrocatalysis,[10] and environmental remediation.[651] The most common transition metals found in nanocatalysts are nickel, copper, cobalt, and iron. Transition metal catalysts have many applications, including electrochemical CO_2 reduction,[38] hydrogenation,[652] and electrochemical water splitting.[653] Platinum, palladium, gold, and silver are the most prevalent noble metals seen in nanocatalysis with applications in electrocatalysis, photocatalysis and organic synthesis.[654] Carbon and its allotropes graphene, and graphite dominate non-metal nanocatalysis. Carbon-based materials such as carbon black are widely used as support for electrocatalysts,[655-657] whereas graphene is applied as catalyst for pollutant removal,[658] electrocatalytic nitrogen reduction,[659] and photocatalytic CO_2 reduction.[660] Molybdenum disulfide and cadmium sulfide are the most prominent metal sulfides used in nanocatalysis. Cadmium sulfide is used as a photocatalyst,[661] while MoS_2 is used in applications such as sensors, bioimaging,[662] and electrocatalysts.[663] [655, 656] whereas graphene is applied as catalyst for pollutant removal,[658] electrocatalytic nitrogen reduction,[659] and photocatalytic CO_2 reduction.[660] Molybdenum disulfide and cadmium sulfide are the most prominent metal sulfides used in nanocatalysis. Cadmium sulfide is used as a photocatalyst,[661] while MoS_2 is used in applications such as sensors, bioimaging,[662] and electrocatalysts.[663]

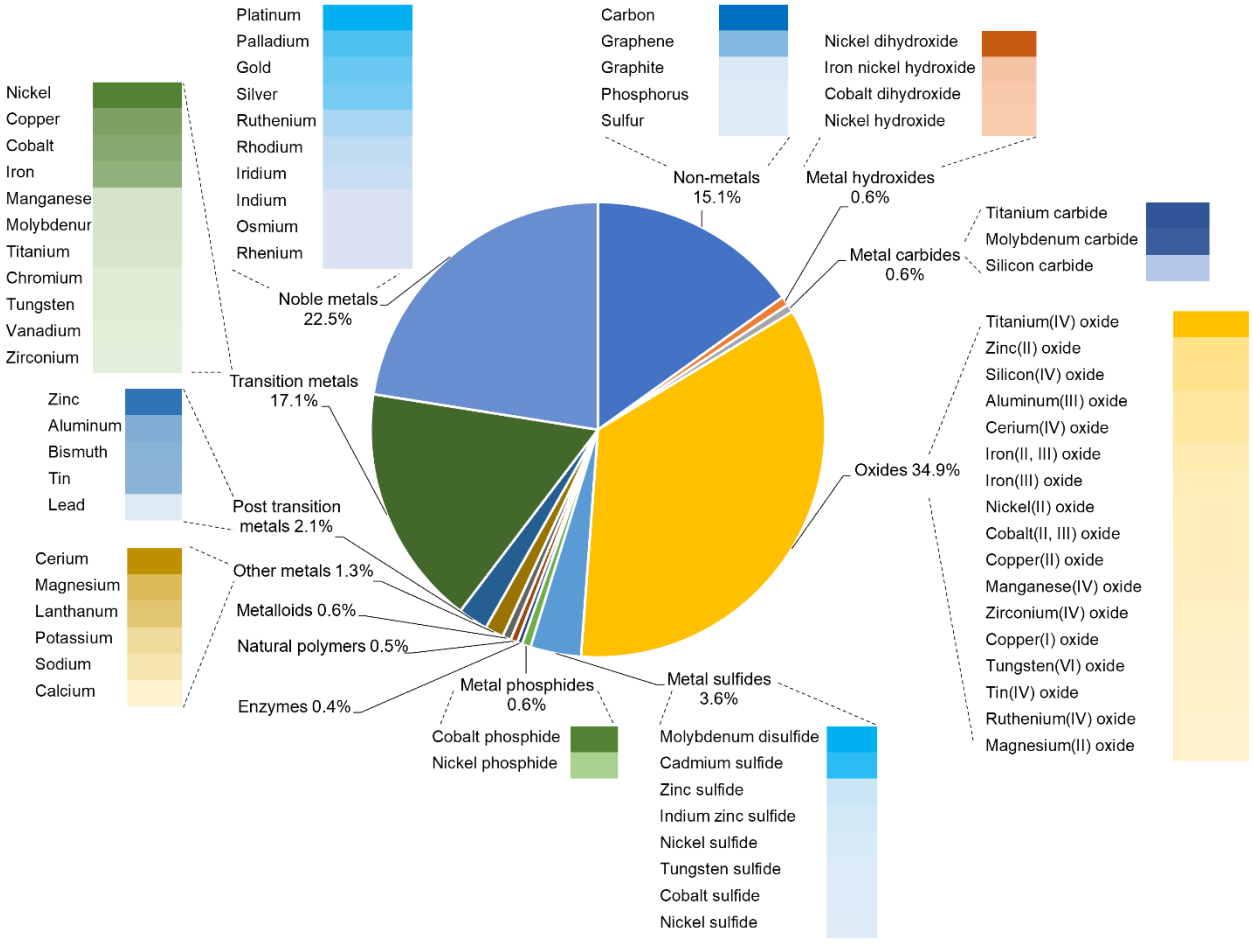

Figure 29: Top categories of substances used as catalysts. The percentages given in this chart are within the top 150 substances with the catalyst role in the nanocatalyst dataset and does not show the entire list of substances. The heat maps for each substance category show the top substances in each, with intensity of color directly proportional to the number of documents.

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Depending on their structure, we classified the nanomaterials into 6 categories. Zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) which contain 0, 1 and 2 dimensions respectively in the 1-100 nm range. In addition, we also have categories such as nanocomposites, nanoporous materials, and quantum dots (QD). Unlike the rest of the 0D nanostructures, properties such as band gap, band position, and melting point of QDs are highly dependent on size,[664] due to which we did not include QDs within the 0D category. Depending on the presence of indexed nanotypes which belong to these 6 nanostructure types, we obtained 6 sets of documents belonging to each of these nanostructure types from the nanocatalysts dataset.

We can gain better knowledge about a substance and the nanostructure type by looking into how much substances contribute within a nanostructure type and how the percent contribution of substances varies across nanostructure types. We did this by collecting the top substances in the nanocatalyst dataset and obtained the number of publications in which these substances were used, within each nanostructure type. Then the percentage contribution by each substance within a nanostructure type is calculated (Figure 30). The percentage contribution by substances within a nanostructure type and across the 6 nanostructure types provides meaningful insights. The overall percentage contribution in the entire nanocatalyst dataset is also calculated and the substances are arranged in the increasing order of this percentage contribution from top to bottom. Any deviation from the overall percentage indicates the substances' pros or cons with respect to the specific nanostructure type.

Carbon tops the list followed by titanium dioxide, in the overall contribution. Since carbon contributes nearly 15% to the overall numbers, the share of carbon is the highest in QD, nanoporous and 1D structure types. Share of carbon in the QD, nanoporous and 1D categories is higher than its overall share, due to the presence of carbon quantum dots and use of porous carbon as catalyst support and as catalyst.[665, 666] The highest contribution from carbon is of around 20% is in the 1D materials due to the widespread use of carbon nanotubes. Also, the share of carbon in 0D and nanocomposite categories are slightly less than its overall share, indicating that these 2 structure types are less common than other types of carbon. TiO_2, platinum, and palladium are the next largest components of the 0D nanostructure category, with contributions proportionate to their overall occurrence. Gold has a disproportionate contribution to the 0D category, suggesting that nanoparticles are a preferred form for gold nanocatalysts.

Other than carbon, the other top contributors to the 1D category are TiO_2, platinum and nickel. TiO_2 is widely used as nanowires[667] and nanotubes.[668] Noble metals and transition metals make large contributions to this category due to the loading of their NPs on other nanorods, tubes, fibers, wires, etc., for catalytic applications.

In the nanocomposites category, the maximum contributors are metal oxides such as TiO_2, and carbon-based materials such as graphene, carbon nitride and carbon. TiO_2 based composites are made by mixing other photocatalysts with TiO_2,[669-671] for environmental remediation, water splitting. Graphene, carbon nitride and carbon are used as supports in electrocatalytic and other applications. Polymeric carbon nitride-CeO_2 quantum dot composite photocatalysts are used for the visible light photocatalytic inactivation of bacteria.[672] Carbon nitride has emerged as a promising visible light photocatalyst in the nanocomposites form.[673, 674] Polymeric carbon nitride-CeO_2 quantum dot composite photocatalysts are used for the visible light photocatalytic inactivation of bacteria.[672] Carbon nitride has emerged as a promising visible light photocatalyst in the nanocomposites form.[673, 674]

Owing to their layered structures, molybdenum disulfide, carbon nitride and graphene make up large fractions of substances found in both 2D nanostructures and in QDs.[675]

Carbon makes the largest substance contribution to the nanoporous materials category due to the large variety of nanoporous carbon materials such as the ordered mesoporous carbon CMK-3, and 3D

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graphene.[676] Silica is also a common nanoporous material because of the widespread catalytic applications of ordered mesoporous materials such as MCM-41 and SBA-15, The high contribution from noble metals and transition metals to nonporous materials is probably due to their use as supported catalysts on or as dopants for porous materials such as zeolites, carbon and silica for catalytic applications. For example, single atom Pt catalysts loaded on nitrogen-doped carbon are used for electrocatalytic hydrogen evolution reactions.[677]

In the 0D category, most of the common substances occur with similar frequencies to their overall nanocatalysts frequencies except for gold, MoS_2 and carbon nitride. Gold seems to be predominantly made as nanoparticles while MoS_2 and carbon nitride disfavor 0D structure types.

Another notable substance with high percentage contribution across various nanostructure types is graphene. Graphene has the highest share in the QDs, followed by nanocomposites, and has the 3rd highest contribution in the 2D nanostructures category.

Among the noble metals, platinum is the most used catalyst, as seen by its high overall contribution. Though there are higher number of nanomaterials reported using gold, many of them do not involve catalytic applications and hence gold has less overall contribution than platinum. Gold has its highest contribution in the 0D category due to its widespread use of catalyst in the nanoparticles (NPs) form, followed by QD. Platinum is most prevalent in 0D nanostructures, nanoporous materials, and in 2D nanostructures. Platinum is not commonly found in nanoporous materials, 1D and 2D shapes and its higher contribution in these nanostructure types is due to the loading of Pt NPs on another material with these nanostructure type such as graphene, carbon,[678] and MoS_2.[679] Nanocomposites and 0D nanomaterials are the most prevalent silver-containing materials. By making nanocomposites with silver NPs, which exhibit surface plasmon resonance,[680] the visible light photocatalytic active of metal oxide photocatalysts were improved.[681] [678] and MoS_2.[679] Nanocomposites and 0D nanomaterials are the most prevalent silver-containing materials. By making nanocomposites with silver NPs, which exhibit surface plasmon resonance,[680] the visible light photocatalytic active of metal oxide photocatalysts were improved.[681] Nanocomposites made with Ag NPs and magnetic iron(III, IV) oxide bases catalysts performed well in the catalytic reduction of aqueous pollutants.[682] Palladium is highly prevalent in nanoparticles and in nanoporous structures. Palladium NPs have many catalytic applications such as in electrocatalytic oxygen evolution, electrocatalytic CO_2 reduction,[683, 684] and thermal catalytic hydrogenation of CO_2.[685] Pd NPs have been immobilized on the pores of nanoporous materials to prevent sintering[686, 687]Nanocomposites made with Ag NPs and magnetic iron(III, IV) oxide bases catalysts performed well in the catalytic reduction of aqueous pollutants.[682] Palladium is highly prevalent in nanoparticles and in nanoporous structures. Palladium NPs have many catalytic applications such as in electrocatalytic oxygen evolution, electrocatalytic CO_2 reduction,[683, 684] and thermal catalytic hydrogenation of CO_2.[685] Pd NPs have been immobilized on the pores of nanoporous materials to prevent sintering[686, 687] as well as to explore the synergistic effects of metal-support combinations.

Among the oxides, zinc oxide and titanium dioxide are widely used in nanocomposites. Titanium dioxide is widely studied in photocatalysis for water splitting and pollutant degradation applicationsj.[688] Zinc oxide despite its large bandgap is widely studied in optical applications, in heterojunctions, as a dopant, and in composites.[689]

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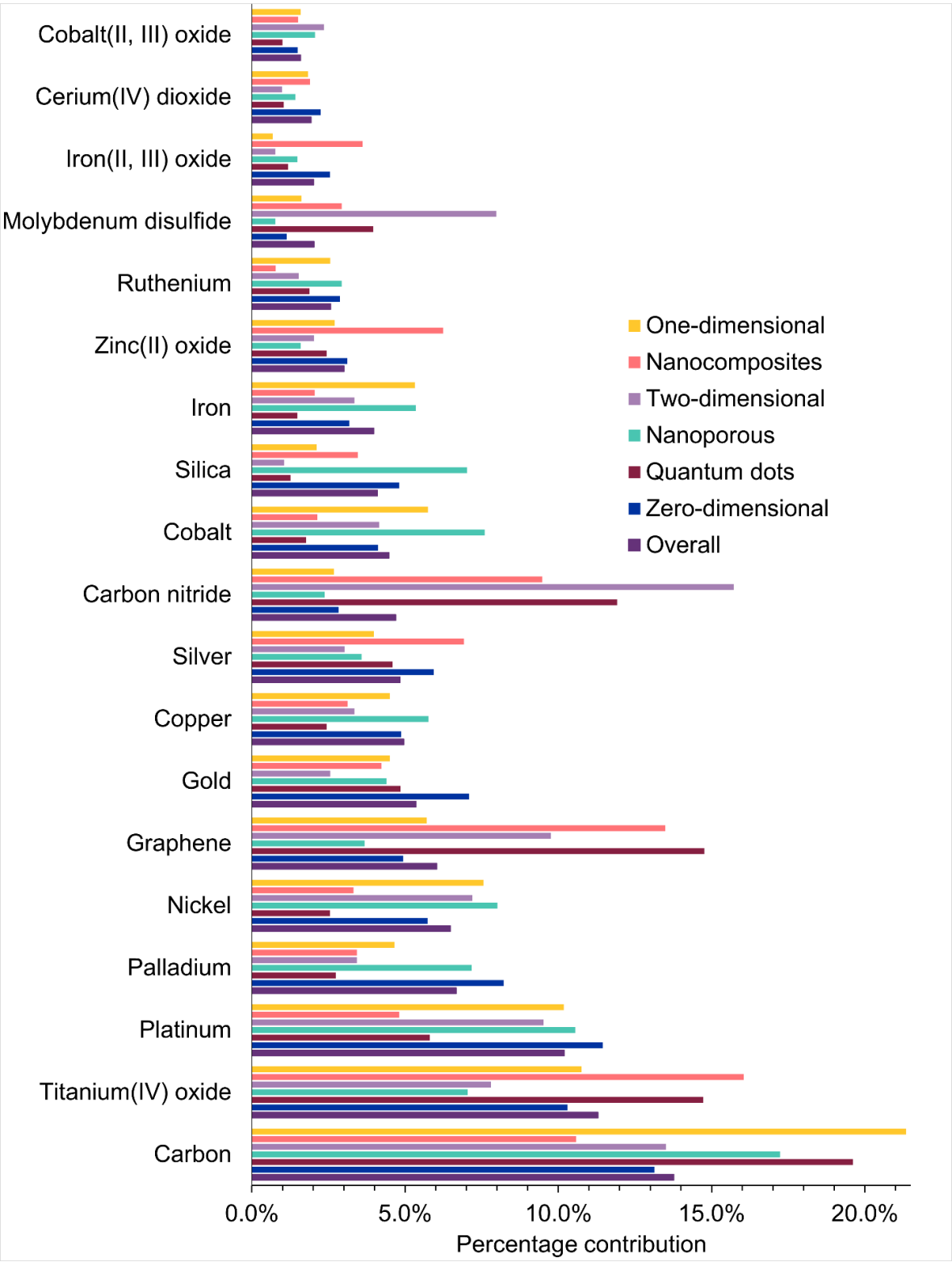

Figure 30. Percentage contribution of top catalyst substances within each nanostructure type and their comparison across the various nanostructure types. The percentages in this chart are calculated by

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considering the documents from these 19 selected substances as the total and does not include the numbers from the entire list of substances.

In addition to indexing substances, CAS Content Collection also indexes substance groups. Substance groups provide additional information, as groups such as metal-organic frameworks, layered double hydroxides, and MXenes, have varying compositions and do not appear in the top substances list, though their overall use is high. Substance groups also give a better overall understanding of the contribution from various groups of substances. A heatmap displaying the catalytic substance groups in the nanocatalysts category is also provided on the right side of Figure 31. The top 4 substance groups overall reflect the top substances seen in Figure 29. Substance groups such as synthetic zeolites, layered double hydroxides (LDH), polyoxyalkylenes, enzymes, heteropoly acids, alloys, and MXenes, did not feature in the top substances since they have varying compositions. The top substance groups in the 1D category are carbon-based materials, metals, oxides, zeolites, polyoxyalkylenes and LDH. As discussed in the previous section, carbon is present in the 1D category due to the use of CNTs as catalysts and supports. Metal nanoparticles are loaded onto 1D materials to improve their catalytic performance.[690] Carbon, oxides, metals, zeolites, and LDH are the top contributors in 0D category. LDH is the top contributor to 2D nanocatalysts, followed by MXenes, and carbon fiber fabrics. Layered double hydroxides are 2D materials widely used as electrocatalysts[691] and in other catalytic applications.[692] Zeolites, MCM-41 porous silica, and inorganic oxides are the most prevalent nanoporous materials. Porous materials which have attracted high interest in recent years such as metal-organic frameworks (MOF), and covalent organic frameworks (COF), did not appear in the top substance groups list as most of the MOFs have pore size in the micropore range (<2 nm), whereas COFs are fairly recent materials which also have some pore sizes in the micropore range. Nanocomposites are comprised of LDH,[693] polyanilines, carbon, aluminoxanes and various other substance groups. The other major contributors to QDs are MXenes, metals, oxides, LDH, and others.

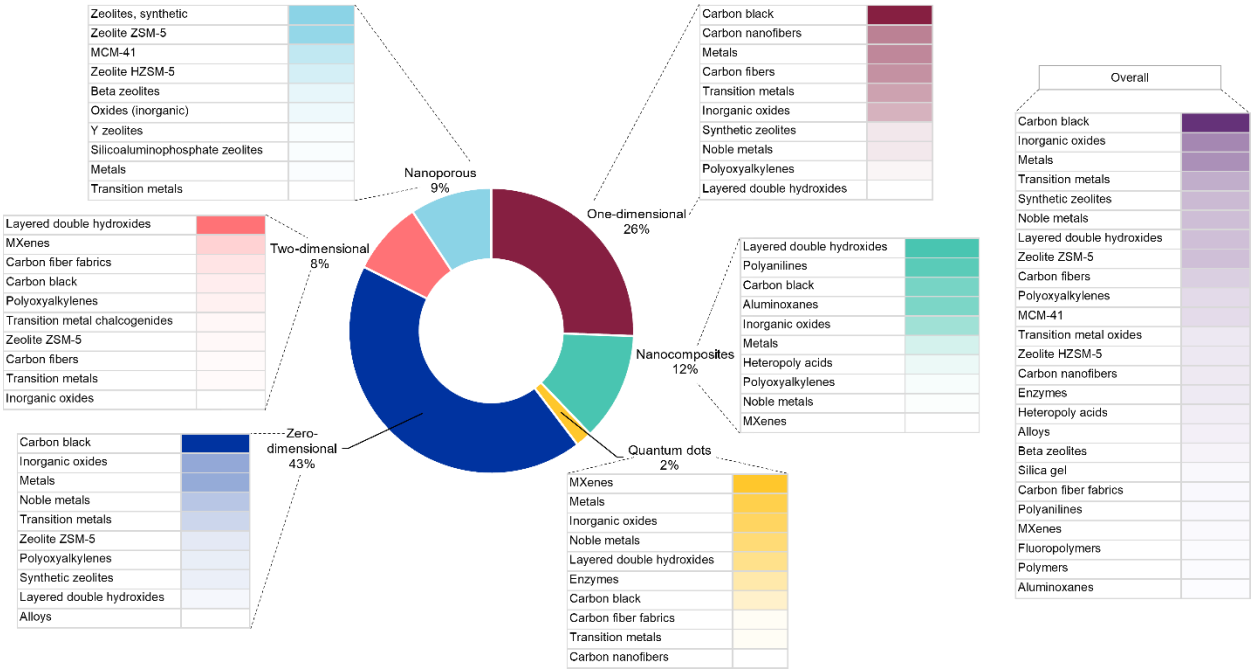

Figure 31: Top substance groups within the nanostructure types.

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Reaction Type Data Trends

CAS indexes the various reaction types found in the documents. We selected 20 unique reaction types from the list of reactions mentioned frequently in the naocatalysts dataset. The number of documents reporting these 20 reaction types were then extracted from each of the six nanostructure type datasets and entire nanocatalysts dataset. This data is tabulated in Figure 32 and the reaction types are arranged from left to right in the descending order of the number of documents in nanocatalysts dataset. Changes in reaction preference with nanostructure likely indicate the preferences of reactions for specific catalyst nanostructures.

Overall, the top reaction types are dominated by photocatalytic, electrochemical, and heterogeneous catalytic reactions. Photocatalysis tops the list of overall reaction types followed by electrochemical reactions. In all nanostructure types, photocatalysis reactions have the highest share. In the nanocomposites category, the top three reaction types are related to photocatalysis for water splitting and degradation of pollutants, followed by electrochemical reactions. The high use of composites in photocatalysis can be attributed to the use of heterojunction photocatalysts to improve the visible light absorption,[694] efficiency[695] and to achieve band positions favorable for a reaction.[696] followed by electrochemical reactions. The high use of composites in photocatalysis can be attributed to the use of heterojunction photocatalysts to improve the visible light absorption,[694] efficiency[695] and to achieve band positions favorable for a reaction.[696] Other than following the overall trend of high share from photocatalysts, nanoporous catalysts are useful for shape selective heterogeneous catalysis as seen by the high share of oxidation catalysts,[697, 698] hydrogenation,[699] reduction, dehydrogenation, bifunctional catalysts, and heterogeneous catalysts. Synthesis of nanoparticles inside the nanopores prevents sintering of the nanoparticles during high temperatures required for the heterogeneous catalytic reactions.[700] Contribution of 1D materials to electrocatalytic reactions such as hydrogen evolution reaction, and oxygen evolution reaction is higher than the overall trends, indicating a preference for such a structure type. The majority of the 1D nanocatalysts used in electrocatalytic applications are based on carbon nanotubes,[691, 697, 698, 701] hydrogenation,[699] reduction, dehydrogenation, bifunctional catalysts, and heterogeneous catalysts. Synthesis of nanoparticles inside the nanopores prevents sintering of the nanoparticles during high temperatures required for the heterogeneous catalytic reactions.[700] Contribution of 1D materials to electrocatalytic reactions such as hydrogen evolution reaction, and oxygen evolution reaction is higher than the overall trends, indicating a preference for such a structure type. The majority of the 1D nanocatalysts used in electrocatalytic applications are based on carbon nanotubes,[691, 701] and the other contributors include noble,[702, 703] metal chalcogenide nanowires,[704, 705] and TiO_2 nanotubes.[706] QD catalysts are most commonly used for photochemical reactions because of their semiconducting nature and their ability to absorb and transmit light energy.[704, 705] and TiO_2 nanotubes.[706] QD catalysts are most commonly used for photochemical reactions because of their semiconducting nature and their ability to absorb and transmit light energy. Notable contributors to QDs used in photocatalytic applications include carbon quantum dots,[707, 708] CeO_2,[672] and boron nitride.[709] The share of the reactions contributing to 2D is very similar to the overall trend, except the negligible contribution from heterogeneous catalytic reactions and the slightly higher contribution from electrocatalytic reaction types. [707, 708] CeO_2,[672] and boron nitride.[709] The share of the reactions contributing to 2D is very similar to the overall trend, except the negligible contribution from heterogeneous catalytic reactions and the slightly higher contribution from electrocatalytic reaction types.

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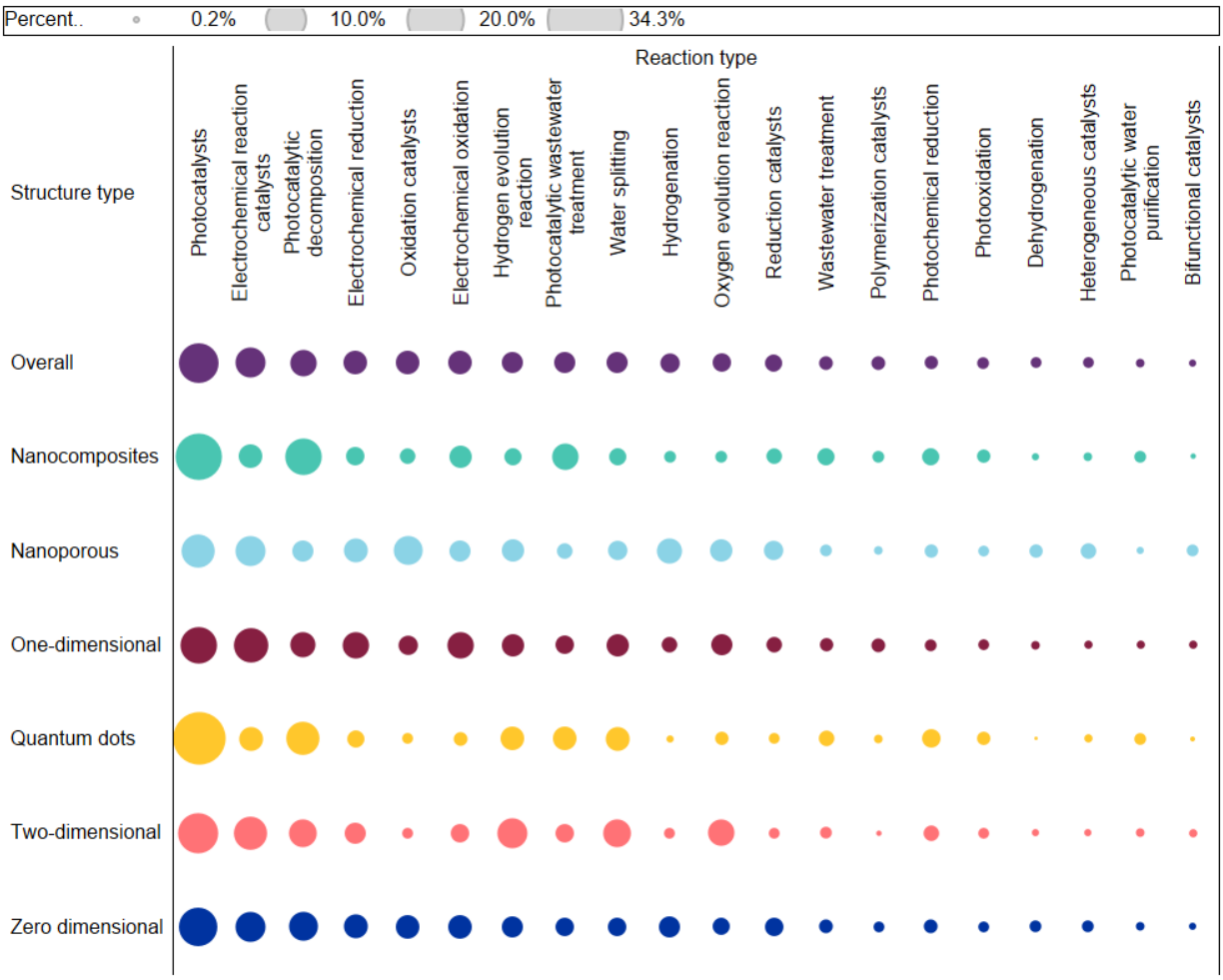

Figure 32: Percentage contribution of top reaction types within each nanostructure type and their comparison across the various nanostructure types. The percentages in this chart are calculated by considering the documents from these 20 selected reaction types as the total and does not include the numbers from the entire list of reaction types. The percentage contribution is visualized by the circle's size.

Apparatus/Application Data Trends

CAS indexes the various apparatus reported in the documents. An apparatus has a specific purpose and includes a device and its components. We extracted the indexed apparatuses from the nanocatalysts dataset and selected 20 unique ones present in high number of documents. The number of documents reporting these top apparatuses were then extracted from each of the six nanostructure type datasets and entire nanoscience-catalyst dataset. This data is tabulated in Figure 33 and the apparatus types are arranged from top to bottom in the descending order of the number of documents in overall nanoscience-catalyst dataset. Variations in the order of apparatuses for a given nanostructure indicates the advantages and disadvantages of a nanostructure for a given use.

The top apparatuses in the nanocatalyst dataset are related to electrodes, fuel cells, sensors, batteries, and photoelectrodes. The high usage of nanocatalysts in various sensors is due to use of nanomaterials to catalyze the reactions responsible for the sensing.[710-713] The share of contribution by various apparatus in the 0D category are very similar to their overall contributions, except the slightly higher contribution from proton exchange membrane fuel cells, direct methanol fuel cells, immunosensors, and engine

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exhaust systems. The two apparatus which contributed less than overall to the 0D category are molecular sieves, and biochemical fuel cells. In the 1D category, the contribution from biochemical fuel cells and semiconductor devices are higher than the overall, whereas the contribution from immunosensors and nanoreactors is less than the overall contribution. The higher than overall contribution from biochemical fuel cells to 1D is due to the use of CNTs as electrode materials.[714-716] Contributions from all types of sensors to nanocomposites category are notably higher than their contribution to the overall, whereas fuel cells and electrodes contributed less than their contribution to overall. Molecular sieves and engine exhaust systems are the notable high contributors in the nanoporous category, whereas solar cells and photoelectrodes contributed less than their contribution to overall.

The distribution of 2D materials in specific device types differed significantly from their overall distribution. Despite the high contribution from electrodes, the contribution of 2D materials to fuel cells is considerably lower than overall. Catalysts in the fuel cell electrodes are usually dispersed on porous carbon materials or nickel foam, due to which they have less contribution to layered 2D materials. The contribution of battery related apparatus and supercapacitors to 2D category is considerably higher than their contribution to overall. The layered nature allows the storage of charges and ions, which is important in batteries and supercapacitors

Quantum dots also had considerably different trends in contribution from the overall. The highest contributor to QDs are solar cells, photoelectrodes, and electroluminescent devices since QDs are mostly made of semiconductors, which due to their suitable bandgap are used in optical and solar energy conversion applications.

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Total documents		42.7%	25.6%	12.2%	9.3%	8.3%	1.8%
Apparatus	Overall	Zero-dimensional	One-dimensional	Nanocomposites	Nanoporous	Two-dimensional	Quantum dots
Electrodes	10.51%	10.00%	10.67%	9.09%	8.79%	14.83%	8.35%
Fuel cells	8.72%	8.74%	8.56%	4.75%	6.96%	4.40%	2.59%
Chemically modified electrodes	8.09%	9.24%	8.55%	13.59%	6.91%	7.00%	6.78%
Electrochemical sensors	4.13%	4.87%	3.89%	10.14%	4.73%	4.16%	4.27%
Biosensors	3.95%	4.45%	3.38%	5.24%	3.09%	2.67%	8.35%
Sensors	3.14%	3.00%	2.83%	3.70%	3.42%	2.42%	4.92%
Lithium secondary batteries	3.04%	2.48%	3.63%	2.62%	2.66%	4.18%	1.75%
Proton exchange membrane fuel cells	2.97%	3.51%	2.70%	1.20%	2.16%	0.83%	0.42%
Photoanodes	2.74%	2.31%	3.36%	2.16%	1.82%	3.64%	7.66%
Fuel cell cathodes	2.62%	2.55%	2.57%	1.50%	2.01%	1.03%	0.23%
Battery cathodes	2.59%	2.52%	3.15%	1.47%	3.70%	4.41%	1.11%
Fuel cell anodes	2.43%	2.42%	2.28%	1.81%	1.33%	0.92%	0.27%
Solar cells	2.33%	1.83%	2.27%	1.47%	1.28%	2.15%	10.37%
Dye-sensitized solar cells	2.25%	2.21%	2.25%	2.41%	1.32%	2.81%	2.59%
Secondary batteries	2.19%	1.92%	2.64%	1.16%	3.52%	3.66%	0.72%
Supercapacitors	2.18%	1.53%	2.19%	2.60%	2.63%	4.40%	2.44%
Direct methanol fuel cells	2.01%	2.92%	1.96%	1.96%	1.54%	1.35%	1.14%
Gas sensors	2.00%	1.88%	2.03%	1.69%	1.63%	1.38%	0.80%
Equivalent electric circuits	2.00%	2.20%	1.84%	2.41%	1.86%	4.58%	2.71%
Electrochemical biosensors	1.86%	2.14%	1.68%	3.76%	2.07%	1.80%	2.82%
Polymer electrolyte fuel cells	1.82%	1.88%	1.69%	0.59%	1.01%	0.62%	0.15%
Battery anodes	1.80%	1.58%	2.23%	1.46%	1.67%	2.57%	0.65%
Battery electrodes	1.56%	1.38%	1.91%	0.98%	1.82%	2.61%	0.76%
Photoelectrodes	1.52%	1.33%	1.75%	1.76%	0.98%	1.98%	3.54%
Amperometric biosensors	1.39%	1.43%	1.79%	2.92%	1.08%	1.04%	1.30%
Molecular sieves	1.35%	0.77%	0.95%	0.46%	9.28%	0.50%	0.30%
Glucose sensors	1.34%	1.36%	1.45%	2.56%	1.47%	1.35%	1.22%
Electrolytic cells	1.32%	1.33%	1.10%	0.56%	1.35%	1.98%	0.53%
Photoelectrochemical cells	1.31%	1.13%	1.28%	1.35%	0.78%	1.61%	3.01%
Batteries	1.23%	1.26%	1.24%	0.53%	1.85%	2.16%	0.99%
Biochemical fuel cells	1.18%	0.83%	1.78%	1.16%	0.91%	0.68%	0.69%
Electroluminescent devices	1.17%	1.14%	0.96%	1.04%	0.61%	0.79%	4.54%
Metal-air electrochemical cells	1.13%	1.36%	1.24%	0.72%	2.27%	1.85%	0.50%
Nanoreactors	1.09%	1.16%	0.27%	0.50%	2.58%	0.25%	0.46%
Semiconductor devices	1.07%	0.85%	1.19%	1.08%	0.61%	1.26%	2.36%
Immunosensors	1.01%	1.62%	0.70%	1.80%	0.89%	0.95%	2.29%
Filters	1.00%	0.60%	0.70%	0.21%	1.43%	0.14%	0.46%
Amperometric sensors	0.96%	1.00%	1.13%	2.24%	0.80%	0.64%	0.61%
Photoelectric devices	0.96%	0.82%	0.94%	0.69%	0.48%	0.62%	2.97%
Solid oxide fuel cells	0.95%	0.99%	0.18%	0.76%	0.38%	0.04%	0.04%
Heterojunction semiconductor devices	0.85%	0.83%	0.93%	1.03%	0.44%	1.96%	1.71%
Engine exhaust systems	0.76%	1.19%	0.29%	0.19%	2.07%	0.05%	0.00%
Membrane electrodes	0.76%	0.66%	0.95%	0.26%	0.72%	0.27%	0.04%
Lithium-sulfur secondary batteries	0.72%	0.80%	0.95%	0.39%	1.08%	1.45%	0.61%

Figure 33: Percentage contribution of top apparatus types within each nanostructure type and their comparison across the various nanostructure types. The percentages in this chart are calculated by considering the documents from these selected apparatus as the total and does not include the numbers from the entire list of apparatus.

Nanostructure Types Data Trends

We analyzed nanocatalyst documents for relationships between nanostructure and indexed properties. Some of the characterization methods used to study the properties are also indexed under properties. This data is tabulated in Figure 34 and the properties are arranged from top to bottom in the descending order of the number of documents in overall nanoscience-catalyst dataset.

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Overall and across the nanostructure types, surface structure and surface area are the most studied properties, as these are most important properties for determining the functionality of the nanomaterials. Overall, Microstructure, XPS, particle size, and X-ray diffraction are the next most prevalent properties, likely because of their use in identifying and understanding the nanocatalysts. As the 0D class mostly contains nanoparticles, properties such as particle size, particle size distribution, particle shape and zeta potential occur frequently for this nanostructure type.

Electric current potential, Raman spectra, electrical impedance, current density, electrical conductivity, and luminescence occur more frequently with 1D materials than for all nanomaterials. This can be attributed to the presence of CNTs in the 1D category, which are known for their electrical properties and Raman spectra is used in their characterization. Since nanocomposites are associated with photocatalysis and photoelectrochemistry applications (Figure 32 and 33), spectral properties such as bandgap, photoluminescence, photocurrent, and UV-Visible diffuse reflectance are more often associated with nanocomposites than other types of nanomaterials. For obvious reasons, properties such as surface area, pore size distribution, pore size, and porosity are more often found in documents discussing nanoporous materials than in documents discussing other structure types.

In the case of 2D nanomaterials, electrical properties such as electrical impedance, current density, photocurrent and overvoltage are more prevalent in documents discussing 2D materials than in nanocatalyst documents. Properties such as band gap, UV visible spectrum, photoluminescence, and photocurrent are more common in documents discussing QDs than in the overall pool of documents, as QDs are made of semiconducting materials.

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Total documents		42.7%	25.6%	12.2%	9.3%	8.3%	1.8%
Properties	Overall	Zero-dimensional	One-dimensional	Nanocomposites	Nanoporous	Two-dimensional	Quantum dots
Surface structure	9.0%	9.1%	10.0%	8.4%	7.1%	8.1%	7.0%
Surface area	8.6%	8.4%	7.9%	8.0%	13.6%	8.1%	5.1%
Microstructure	5.0%	4.4%	7.0%	3.9%	4.0%	4.4%	3.6%
XPS	4.5%	4.4%	4.8%	4.2%	4.0%	5.7%	5.0%
Particle size	4.2%	5.2%	2.7%	3.1%	3.5%	1.4%	2.6%
X-ray diffraction	3.9%	3.8%	3.8%	4.0%	3.8%	3.8%	3.1%
Electric current-potential	3.8%	3.5%	5.7%	2.9%	2.5%	4.5%	3.4%
Pore size distribution	3.4%	3.4%	2.9%	3.3%	8.0%	3.7%	2.1%
Binding energy	3.3%	3.3%	3.1%	3.4%	2.6%	4.4%	3.8%
Particle size distribution	2.8%	3.9%	1.8%	1.9%	2.3%	0.9%	2.7%
Pore size	2.8%	2.7%	2.2%	2.6%	7.3%	1.9%	1.3%
Stability	2.8%	2.9%	2.8%	2.4%	2.8%	3.1%	2.6%
Band gap	2.7%	2.5%	2.3%	4.1%	1.2%	3.2%	4.5%
Raman spectra	2.6%	2.2%	4.1%	2.5%	1.9%	3.1%	2.7%
Crystallinity	2.6%	2.7%	2.5%	2.6%	3.1%	2.2%	2.0%
Crystal structure	2.5%	2.4%	2.3%	2.3%	1.9%	2.7%	2.2%
IR spectra	2.5%	2.6%	1.9%	3.5%	2.7%	2.2%	3.0%
UV and visible spectra	2.4%	2.7%	2.1%	2.8%	1.6%	2.0%	4.9%
Electric impedance	2.4%	2.0%	3.0%	2.8%	1.9%	3.9%	3.3%
Current density	2.2%	2.1%	3.0%	1.2%	1.9%	3.8%	1.9%
Temperature	1.9%	2.0%	1.9%	1.4%	1.5%	1.1%	1.3%
Photoluminescence	1.9%	1.8%	1.7%	3.4%	0.9%	3.1%	6.4%
Thermal stability	1.8%	1.8%	1.4%	2.5%	2.3%	0.9%	0.8%
Grain size	1.7%	1.9%	1.1%	1.7%	1.2%	0.7%	0.8%
Porosity	1.6%	1.5%	1.4%	1.2%	4.0%	1.0%	0.7%
Photocurrent	1.5%	1.1%	1.9%	2.6%	1.0%	2.6%	4.2%
Particle shape	1.5%	1.9%	1.4%	1.2%	1.5%	1.7%	1.4%
Electric conductivity	1.5%	1.2%	2.5%	1.7%	1.1%	1.9%	1.5%
Synergism	1.3%	1.4%	1.3%	1.7%	1.4%	1.9%	1.5%
Nanoscale particle size	1.2%	1.7%	0.7%	0.9%	1.0%	0.4%	1.3%
Light	1.2%	1.1%	1.0%	1.7%	0.6%	1.5%	2.4%
Optical band gap	1.1%	1.1%	0.9%	2.4%	0.7%	1.5%	2.1%
Zeta potential	1.1%	1.4%	0.6%	1.1%	0.6%	0.9%	1.7%
Overvoltage	1.0%	0.8%	1.2%	0.5%	1.1%	2.2%	0.6%
Activation energy	1.0%	1.0%	0.8%	0.7%	0.8%	0.5%	0.2%
Reaction kinetics	0.9%	1.0%	0.8%	0.9%	0.7%	0.9%	0.7%
UV-visible DRS	0.9%	0.8%	0.8%	1.9%	0.8%	1.4%	1.3%
Luminescence	0.9%	0.6%	1.4%	1.0%	0.3%	0.5%	2.0%
Lattice parameters	0.9%	1.0%	0.7%	0.6%	0.5%	0.6%	0.5%
Band structure	0.9%	0.6%	0.9%	1.2%	0.4%	1.7%	1.9%

Figure 34: Percentage contribution of top properties within each nanostructure type and their comparison across the various nanostructure types. The percentages in this chart are calculated by considering the documents from these selected properties as the total and does not include the numbers from the entire list of properties.

General Publication Trends

Figure 35 shows the yearly publication trends in the catalysis related publications in nanoscience, which shows a steady increase in the number of journal publications. In general, the number of patents per year also increased between 2003-2022. However, the upward trend in patents is not as consistent as the journals due to dip in the numbers between 2010 and 2020. Overall, during this period the ratio of journals to patents (orange line in the figure) remained between 3.5 and 5. The similar trends in patent and journal publication implies that a consistent fraction of the academic research in this area is commercializable, as seen in the filing of patent applications.

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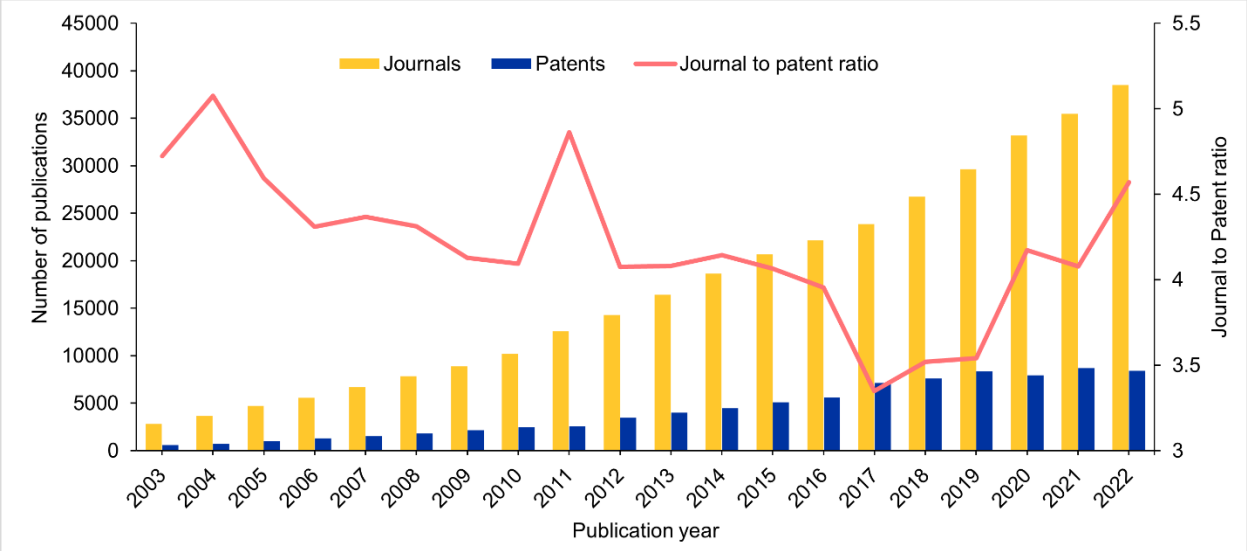

Figure 35: Number of catalysis related publications in journals and patents from 2003-2022. The line shows the journal to patent ratio.

Finding a suitable journal in which to publish research is an important step. Figure 36A shows the 20 journals which published the highest number of articles related to catalytic nanomaterials, and the average citations per article. In addition, to put the publication numbers and numbers of citations in context, Figure 36B shows the 20 journals with the highest average number of citations per article selected from the top 100 journals in terms of total publications on nanocatalysts (the same analysis presented in the other sub-sections). It is noteworthy that only five journals with the highest number of publications (Figure 36A) are present in the journals with the highest average citations per article (Figure 36B). The journals Angewandte Chemie and JACS have the most numbers of citations per article among both top 20 (Figure 36A) and top 100 (Figure 36B) journals with the most publications, which indicates that their publications are relevant despite the high numbers. ACS Nano ranks high in terms of the number of citations per article among the top 100 journals with the most publications (Figure 36B).

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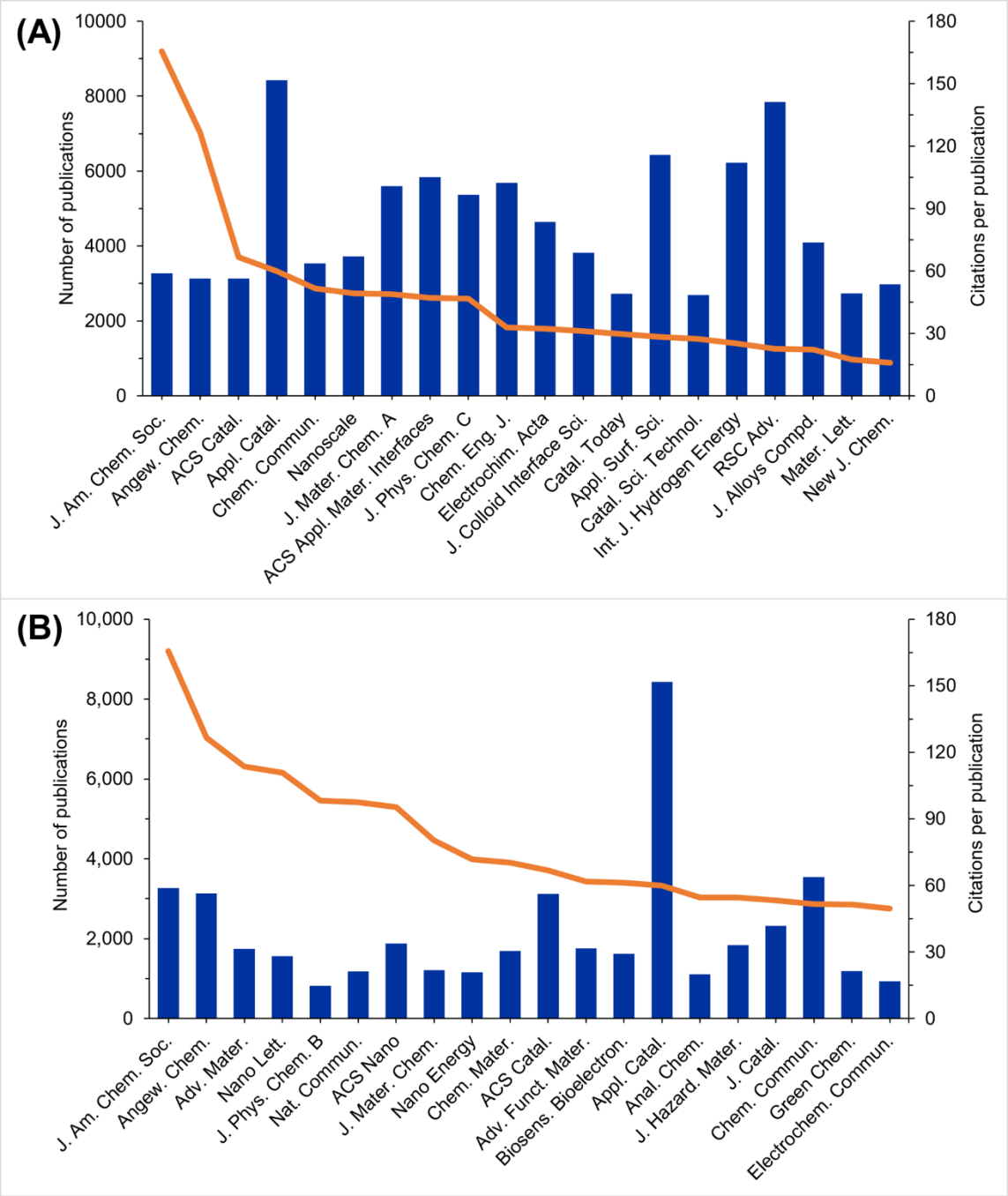

Figure 36: (A) 20 journals with the highest number of publications in catalytic nanomaterials and their average citations per article, and (B) journals with the highest citations per article selected from the top 100 journals in terms of total number of publications on catalytic nanomaterials. The average citations per article is calculated only for the articles related to catalytic nanomaterials covered in our search query for this section.

Figure 37 shows the top 20 universities with the highest number of journal articles related to catalytic nanomaterials. The Chinese Academy of Sciences published the highest number of articles followed by the Islamic Azad University of Iran. The remainder of the universities in the top 20 are in China. It is worth

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mentioning that the Chinese Academy of Sciences is an umbrella organization including 124 institutions[166] and hence has a very high number of journal publications. In terms of the average number of citations per publication, Tsinghua University tops the list followed by University of Science and Technology of China and Fuzhou University, all from China.

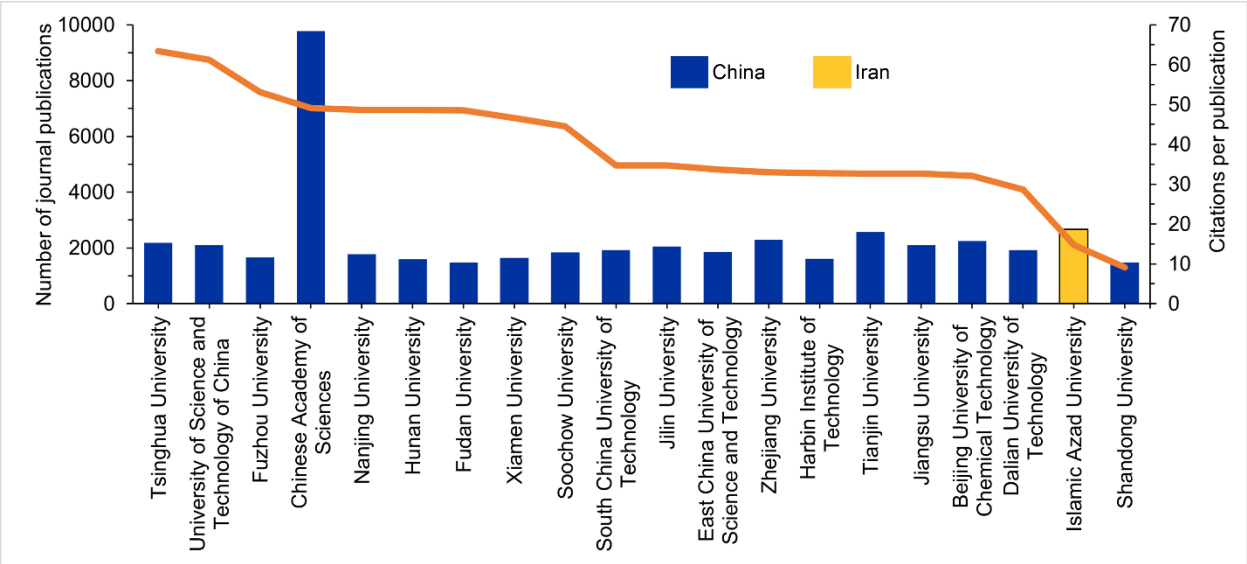

Figure 37: Top institutions with the highest number of journal publications in catalytic nanomaterials and their average number of citations per publication.

The number of patent applications in research area is an indicator for the interest in commercialization of the research. We investigated the patent activity in nanocatalyst-related work. Figure 38A and 38B shows the top 20 entities having the highest number of patent publications in the commercial and non-commercial categories. China Petroleum and Chemicals Limited tops the list of commercial entities followed by Samsung Electronics and Toyota Motors. It is interesting to note that the commercial entities belong to various categories of industry such as petroleum, automobiles, electronics, chemicals, etc., which highlights the wide-ranging applications of catalytic nanomaterials. China and Japan have 5 commercial organizations each in the top 20, followed by Republic of Korea with 3 organizations.

The top 20 non-commercial entities are all academic institutions from China showing the extent of interest in nanocatalyst research in China. Dalian Institute of Chemical Physics tops the non-commercial category followed by Zhejiang University and the Beijing University of Chemical Technology. Dalian Institute of Chemical Physics did not appear in the top 20 institutions with the highest number of journal publications as they seem to be publishing in journals under the institutional umbrella of Chinese Academy of Sciences.

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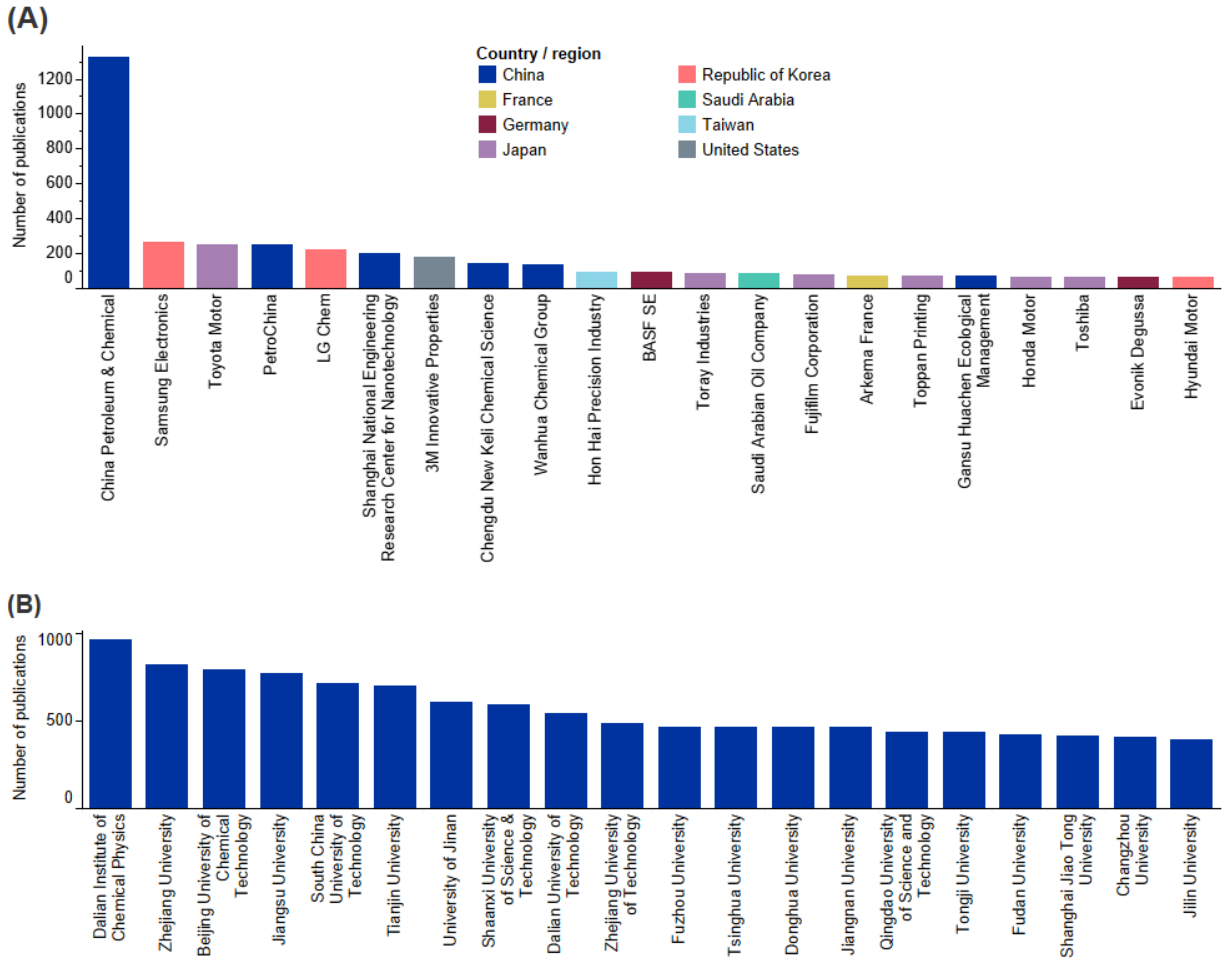

Figure 38: Patent assignees with the largest number of publications in both commercial (A) and non-commercial (B) categories.

Summary and outlook:

In this section, we provided an overview of the substances used as nanocatalysts, the reactions in which they are applied, the types of apparatuses in which these nanocatalysts are utilized, and the properties / methods used to understand and study them. By looking into trends in the above-mentioned parameters within six nanostructure types, we presented deeper insights about nanocatalysts. We believe these scientific insights backed by data provide reliable and faster understanding of this area. In addition, we provided publication trends in journals / patents, commercial and non-commercial organizations along with citations per publication for journals.

Catalysis is an application which seems to reap plenty of benefits from the advancements in nanoscience, as seen from the diversity of the commercial organizations publishing on nanocatalysts. The number of journal publications and patents is expected to grow in coming years, primarily driven by the need for clean energy, and pollution abatement.

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Applications of Nanoscale Materials in Energy

Introduction

Global energy consumption is on the rise, particularly in countries with quickly growing populations and incomes[717]. The COVID-19 pandemic, geopolitical issues, and weather conditions have caused disruptions in the fossil fuel industry, resulting in a situation which the International Energy Agency has characterized as a global energy crisis.[718] Meanwhile, these fossil fuels account for over 75% of global greenhouse gas emissions.[719] Nanotechnology and nanomaterials are part of the solution to satisfy rising energy demand while lowering greenhouse gas emissions. Nanotechnology can improve the efficiency of energy use, energy production, energy storage and energy transmission.[720-723]Global energy consumption is on the rise, particularly in countries with quickly growing populations and incomes[717]. The COVID-19 pandemic, geopolitical issues, and weather conditions have caused disruptions in the fossil fuel industry, resulting in a situation which the International Energy Agency has characterized as a global energy crisis.[718] Meanwhile, these fossil fuels account for over 75% of global greenhouse gas emissions.[719] Nanotechnology and nanomaterials are part of the solution to satisfy rising energy demand while lowering greenhouse gas emissions. Nanotechnology can improve the efficiency of energy use, energy production, energy storage and energy transmission.[720-723] Nanoscale materials have also been used in a wide number of renewable energy applications.[724, 725] In this section we present a landscape view of nanoscale materials in energy applications through the analysis of both journal and patent documents in order to represent academic and commercial research, development efforts, and the growth of this field during the last two decades.

Querying the CAS Content Collection for publications related to the use of nanoscale materials in energy applications (see Methods section for query details) resulted in over 240,000 journals and almost 80,000 patents spanning from 2003 to 2023. In this section, we perform a landscape analysis of publication trends throughout these years, along with a summary of the journals that have published the most highly cited articles in this area, the most prolific research organizations in terms of journal and patent publications, along with a geographic breakdown of these organizations. We also discuss the distribution of publications across several selected energy-related applications, which reflect three general and interconnected areas of interest in the energy sector: production, storage, and sustainability. Lastly, we will analyze trends in the substances and nanoscale forms used in energy applications, with an emphasis on emerging materials and applications.

Publication Trends

The number of journal publications in the field of energy and nanoscale materials shows an exponential increase from 2003 to 2014 (Figure 39), a slow increase in publications in 2015 and 2016, followed by a steadier increase from 2017 to 2022. Journal publications grew by a yearly average of 118% from 2003 to 2023. As is typically seen in emerging areas of science and technology, the total number of patent publications is less than behind journal publications, have grown at roughly the same rate (119%) between 2003 and 2023. Most of the growth in patent publications occurred between 2003 and 2014 with reduced growth in annual publication between 2015 and 2022.

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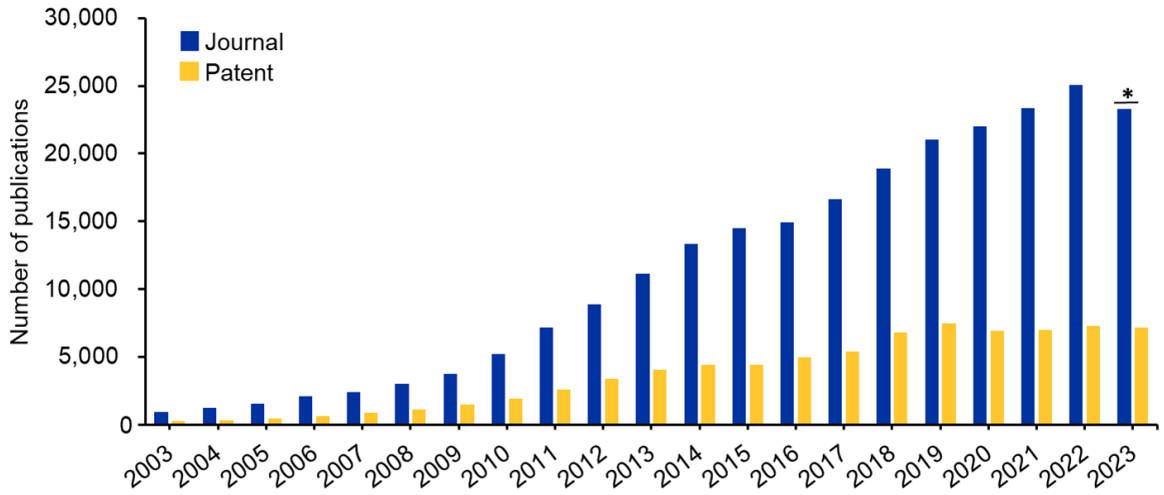

Figure 39. Publication frequency in the area of nanoscale materials in energy related research over the last two decades. Data includes journal and patent publications from the CAS Content Collection for the period 2003-2023. *Year 2023 has incomplete data due to date of data acquisition.

The journals which have published the largest number and most highly cited articles in the area of nanoscience energy-related applications between 2003 and 2022 (using the approach described in previous sections of first selecting the top 100 journals in terms of total publications in this area, then ranking by average number of citations per article) are shown in Figure 40. The journals with the highest number of average citations to their publications are J. Amer. Chem. Soc., Nano Lett., Energy Environ. Sci., Angew. Chem. Int. Ed., and ACS Nano. These last results include journals with reviews and perspectives, which tend to be more highly cited. Topics of highly cited article from J. Amer. Chem. Soc. in the past two years include: co-solvent electrolyte for stable anode free zinc batteries,[726] use of Cu-single atoms for electrochemical reduction of ammonia (which can be applied for hydrogen storage),[727] the preparation of high entropy alloy electrocatalytic anodes for glycerol oxidation reaction (an alternative anodic reaction for oxygen evolution reaction (OER)) that can then be applied to acidic hydrogen production,[728] and carbon vacancy Pt traps for Hydrogen Evolution Reaction (HER) catalysts.[729] In the case ACS Nano, the highest recently cited articles include piezoelectric composite hydrogels for triboelectric nanogenerators,[730] different materials for dendrite-free zinc anodes,[731, 732] reversible Zn metal anodes for flexible Zn-MnO_2 batteries,[733] and ginkgo leaf-like Co_4N coupled with trace Pt as HER catalysts.[734] The journals with the highest number of publications in this area overall are J. Mater. Chem. A, Electrochim. Acta, and ACS Appl. Mater. Interfaces (See SI Figure SI21).

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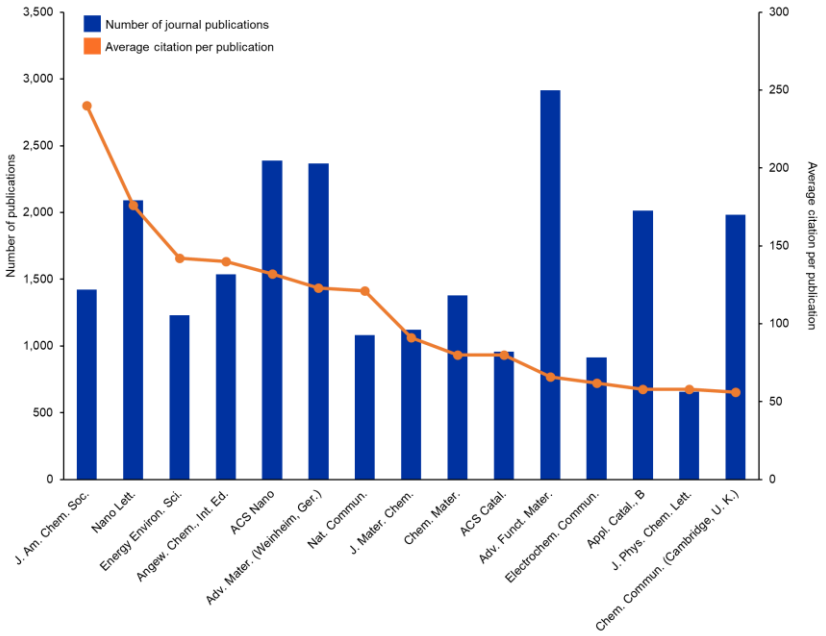

Figure 40. Leading scientific journals in the field of energy in association with nanoscience based on journal publication data from the CAS Content Collection for the period 2003-2023.

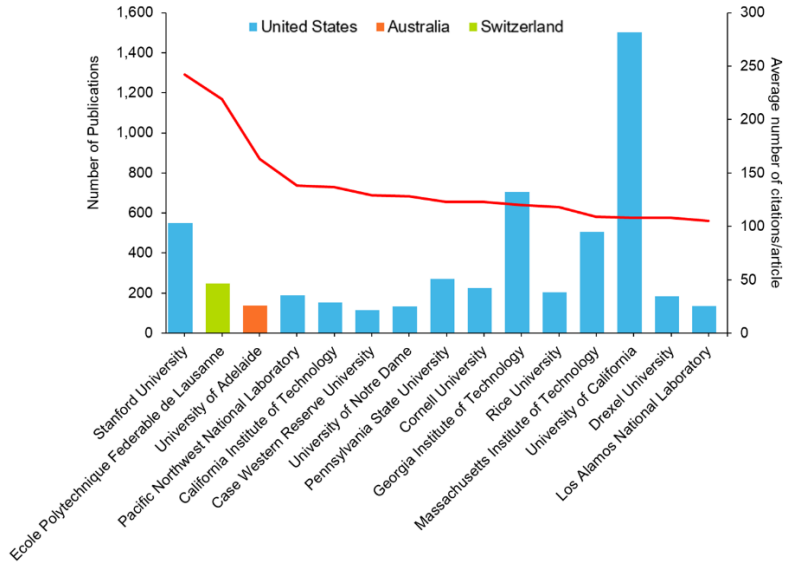

Figure 41. Leading research organizations in the field of energy in association with nanoscience based on journal publication data from the CAS Content Collection for the period 2003-2023.

The same approach was used to identify the most active and influential research organizations in nanoscience energy research. When it comes to the top 15 organizations with the most journal publications, China dominates with the Chinese Academy of Sciences coming firmly in first place with 5x more publications than the only US organization that made it to the top 15, the University of California (See SI Fig SI3). This is the same observation made in the Sensors section of this paper. We followed up by observing which of the top 100 organizations by highest number of journal publications had the highest number of average citations per article. In this case, organizations from USA dominate with 13 out of the

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top 15 organizations with highest average citations being located in the US. Stanford University took 1st place, followed by the Swiss Federal Institute of Technology Lausanne (École Polytechnique Federale de Lausanne) in 2nd place, and the University of Adelaide from Australia placing in 3rd (Figure 41).

The top three most cited papers from Stanford University published in 2022 and 2023 focus on the electrolytes of lithium metal batteries,[735, 736] and stretchable all-polymer light-emitting diodes achieving both on-skin wireless powering and real-time displaying of pulse signals.[737] A recent highly cited publication from the Swiss Federal Institute of Technology Lausanne demonstrates that efficient CO_2 electroreduction can be conducted in an acidic medium by suppression of the otherwise predominant hydrogen evolution via the use of alkali cations,[738] while the most recent highly cited paper from the University of Adelaide presents the synthesis of 2D $FePS_3$ (FPS) nanosheets anchored with TiO_2 nanoparticles for photocatalytic HER.[739]

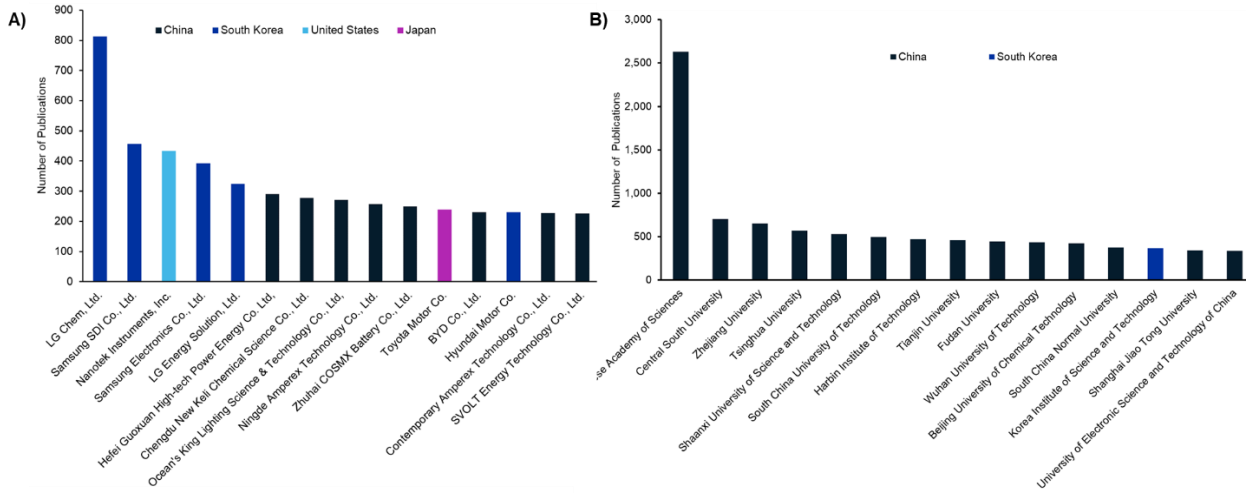

Figure 42. A) Leading commercial patent assignees in the field of energy in association with nanoscience in terms of number of patent publications between 2003-2023 based on data from the CAS Content Collection. **B)** Leading non-commercial patent assignees in the field of energy in association with nanoscience in terms of number of patent publications between 2003-2023 based on data from the CAS Content Collection.

Next, we considered patent publications assigned to commercial and non-commercial entities (Figure 42A and Figure 42B) and their countries of origin. In the case of the top 15 commercial organizations (Figure 42A) with the highest number of patent publications 8 are located in China, 5 in South Korea, 1 in the US and 1 in Japan. Interestingly though Chinese companies made the majority of the top 15, the top three companies with the highest number of patents are LG Chem, Ltd. and Samsung SDI Co., Ltd. from South Korea, and Nanotek Instruments, Inc. from the US. Some examples of patent applications published in 2023 assigned to LG Chem discuss an electrode for a lithium secondary battery and its manufacturing method with enhanced adhesion between the electrode current collector and the electrode active material layer[740], a cathode additive made out of a lithium transition metal oxide for lithium secondary batteries[741], and a pre-lithiated cathode with a Si-based active material that demonstrates high energy density and capacity when used in a lithium ion secondary battery.[742] Overall, patents assigned to LG Chem seem to focus on electrodes or electrode additives for secondary batteries, mostly lithium, and for all-solid-state batteries.[743] Most of Samsung SDI's recent patent applications also relate to lithium ion and all-solid-state secondary batteries, with some examples being separators for lithium[744-746] and all-solid-state secondary batteries, electrodes, other structure components, and their methods of manufacturing.[747-749] Unlike the previous companies, the US based Nanotek Instruments, Inc. stopped being a patent assignee

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in 2021 and most of their 2021 patent applications were re-assigned to the Global Graphene Group, a holding company for a variety of subsidiaries including Angstron Materials, Nanotek Instruments, Honeycomb Battery, and the Taiwan Graphene Company.[750] As the name of their holding company suggests, Nanotek Instruments 2021 patent applications focus on graphene-enhanced batteries and battery components.[751-753]

Moving to patents assigned to non-commercial organizations (Fig 42B), we see that there is a clear dominance by Chinese organizations, with the Chinese Academy of Sciences coming in first place with more than three times the number of patents from 2003-2023 than the next highest-ranked organization. Some examples of recently (2023) published patent applications from the Chinese Academy of Sciences are for the invention of: a composite separator using MOF nanoparticles with excellent electrochemistry, higher stability, increased migration of lithium ions, and the ability to inhibit the growth of lithium dendrites[754]; a method for preparing hollow polyacrylonitrile-based carbon fiber electrode material for flow battery by using electrospinning, oxidation and carbonization[755]; and a carbon-supported catalyst containing platinum and platinum alloy that demonstrates improved active area, catalytic activity and stability, and used as an oxygen reduction catalyst for fuel cells.[756] Due to the Chinese Academy of Sciences being a conglomeration of different research institutions, their recent patent publications span a variety of topics including materials for different battery components for a variety of battery types, components and catalysts for different kinds of fuel cells, materials for solar cells and other photovoltaic devices. A recent patent application from the Central South University of China include inventions for zinc ion battery negative electrode coating that contained graphene-coated spherical copper powder,[757] a metal chalcogenide nanoparticle @ nitrogen-doped carbon hollow sphere material for the use in lithium metal battery negative electrodes,[758] and the preparation method and application of a negative electrode current collector.[759] Most of their recent patent applications are related to alkali metal batteries, electrodes and composite materials for different applications. Lastly, Zheijang University's most recent patent applications vary in topics and include: a plant fiber-based and improved triboelectric negative material based nanogenerator,[760] the preparation and application of an artificial fiber protective film modified metal zinc negative electrode rich in functional groups,[761] and solar photovoltaic-concentrating photothermal comprehensive utilization system.[762]

Energy Applications in relation to nanoscience

Definitions and Scope

Based on a combination of manually indexed concepts and NLP analysis as described in the Methods section, we identified ten areas of focus for the use of nanoscale materials in energy applications. These applications were categorized and defined as following:

- **Batteries** are the most common and traditional form of energy storage and usually work through electrochemical mechanisms. This category is very broad and includes both primary and secondary batteries, batteries that utilize different chemistries, including flow batteries.
- Photovoltaic cells, most commonly **solar cells**, are one of the most well-known and popular devices used to produce green energy. This category includes publications on a variety of solar cells such as quantum dot solar cells, organic solar cells, perovskite solar cells, solid-state solar cells, among others. It also includes all nanoscience publications containing the term "photovoltaic".
- **Supercapacitors** are energy storage devices, similar to batteries, that store electrostatic energy. This category also includes documents discussing supercapatteries, a hybrid electrochemical energy storage device that combines the characteristics of rechargeable batteries and supercapacitors.[763]

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- **Water Splitting,** commonly using electrolysis or photocatalysis, is the process of producing hydrogen via the breakdown of water molecules. This energy application contains documents containing terms related to electrolysis, electrolysis catalysts, electrolyzers, hydrogen evolution reaction, and oxygen evolution reaction. Note that, while this is considered an energy application in this section, it contains significant overlap with documents analyzed in the catalyst section. (This is also true, to a lesser extent, for other energy applications.)
- **Hydrogen Storage** refers to methods of storing H_2 via mechanical, physical, or chemical approaches and is closely tied to water splitting and fuel cells. Hydrogen is a desirable energy storage carrier with the highest energy per mass (142 kJ/g) of any fuel, but is difficult to store because it is a gas at temperatures above –252 °C at ambient pressure[764] and thus has low mass density leading to a low energy per unit volume; it also forms explosive mixtures with air over a wide range of compositions.[765] The widespread use of hydrogen will thus require the development of advanced, safe, and efficient storage methods with the potential for high energy densities, methods which can be achieved using nanomaterials such as carbon nanotubes.[766]
- **Fuel Cells** are electrochemical devices that convert chemical energy into electrical energy via a fuel and an oxidizing agent; with hydrogen and oxygen being the most common fuel-oxidizer combination. Though similar to batteries, fuel can be supplied continuously to fuel cells, which allows fuel cells to provide uninterrupted electrical energy. This application is closely tied to water splitting and hydrogen storage[766] and includes publications on polymer electrolyte fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs), reversible fuel cells among others. Flow batteries, included in the battery category, are also closely tied to fuel cell applications.
- **Thermoelectrics** are solid-state devices that convert thermal energy into electrical energy by utilizing the Seebeck effect,[767] the electromotive force (emf) that develops across two points of an electrically conducting material when there is a temperature difference between them.[768] This category contains publications related to photothermoelectricity, piezothermoelectricity, Seebeck effect, thermoelectric cooling, thermoelectric power, thermoelectric materials, and thermoelectric electrodes.
- **Triboelectric** objects and devices undergo triboelectrification, the process by which two initially uncharged bodies become charged when brought into contact and then separated.[769] This application category includes publications discussing nanomaterials for triboelectric devices such as triboelectric nanogenerators.
- **Thermal Energy Storage** or heat storage involves the use of engineered materials to store energy in the form of heat to be used later.[770] It is closely tied to solar cells and solar thermal applications. This application category includes phase change materials, heat storage, thermal energy storage and latent heat energy storage.
- **Solar thermal** systems generate or use solar thermal energy. This category includes publications on solar cooling, solar heaters, solar collectors, solar concentrators, Brayton solar engines, solar heated reactors, solar engines, and other similar topics and applications.

In the following sections, we will examine publication trends and other material-related trends according to these application groups.

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Energy Applications Publication Trends

The top application group in terms of total number of publications is batteries. With the rise in demand of batteries for electric vehicles[771] and stationary storage of renewable energy,[772] it is of no surprise that total battery publications are almost twice as high than that of the next highest application (Figure 43A). This is followed by solar cells, again emphasizing the interest in green energy, followed by supercapacitors, fuel cells, and water splitting.

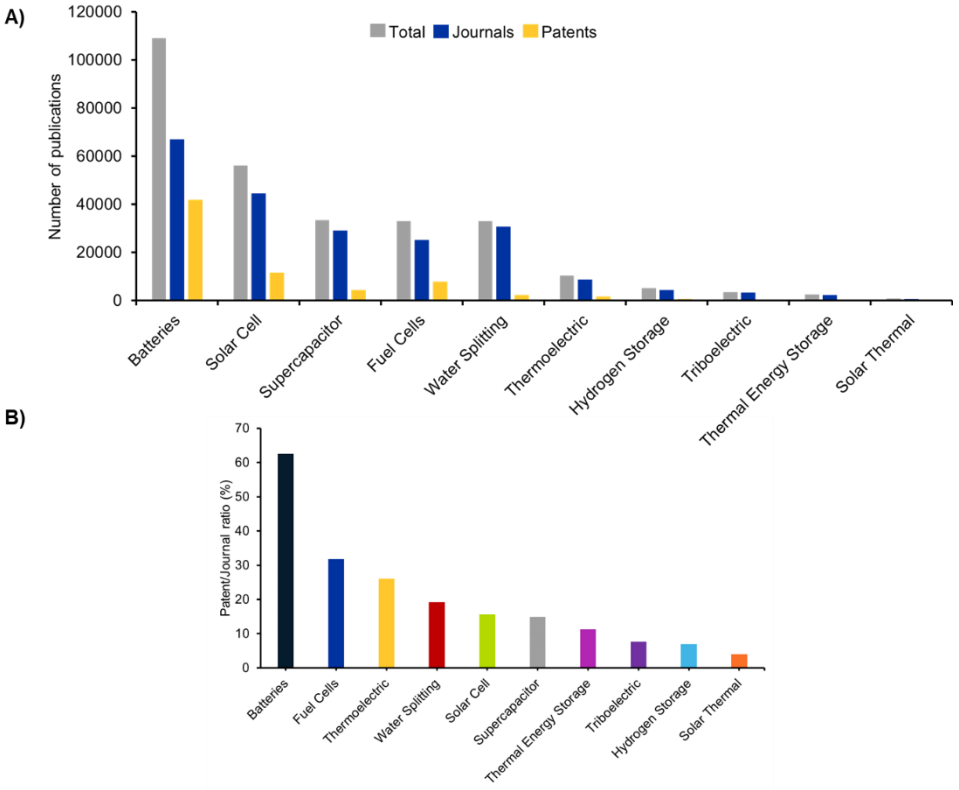

Figure 43. A) Number of total publications, total journal publications and total patent publications by energy application category from 2003-2023. B) Total patent to journal ratio of publications from 2003-2023 by application category

The ranking of topics by the ratio of patents to journal articles differs from the ranking by total publications. While batteries have the highest patent-to-journal ratio of the nanoscience energy topics, fuel cells and thermoelectric are ranked second and third despite having fewer publications. There are more total patents on fuel cells than supercapacitors, which suggests that the latter has not matured enough for commercialization, or that there is relatively more active research at the academic stage. In the case of solar cells, though it has higher number of total patent publications than fuel cells, it has a lower patent-to-journal publication ratio, suggesting again that much of the research in relation to this technology has yet to reach high levels of commercialization. Likewise, the high patent to journal ratio in thermoelectrics, despite a low number of overall publications, may signify a high degree of commercialization potential, though the field itself is not as widely studied as other, more mature applications.

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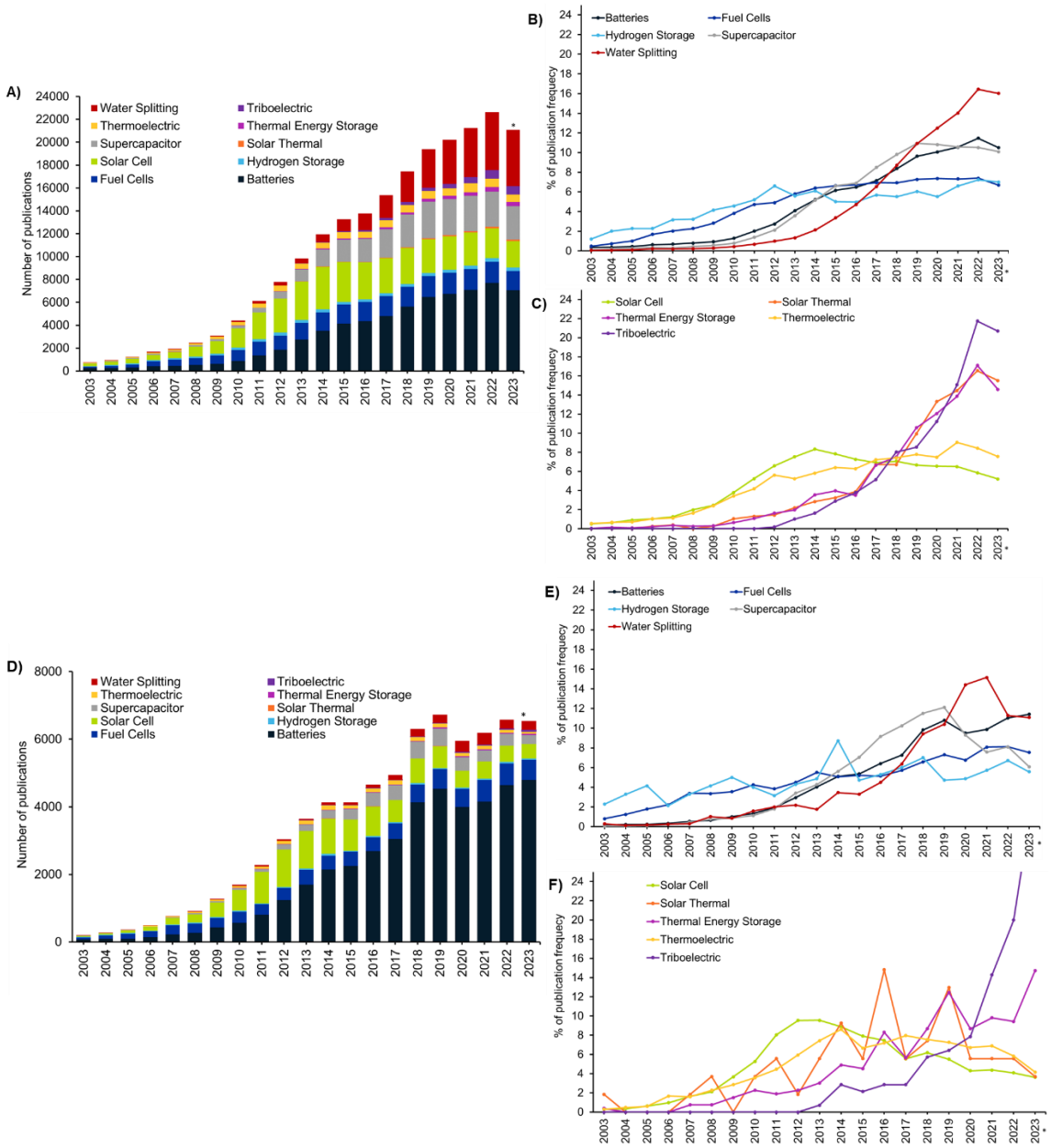

Figure 44. A) Number of journal publications by energy application category from 2003-2023. B) & C) Normalized publication frequency for journal publications by year from 2003-2023 by application category. D) Number of patent publications by energy application category from 2003-2023. E) & F) Percentage of patent publications by year by total journal publication from 2003-2023 by application category

A more detailed picture of publication trends, broken down by application group, is shown in Figure 44 A-F. The overall journal publications related to the energy applications of nanoscience grew exponentially from 2003-2015 with growth slowing in 2016 and 2017 and steadying from 2018 onwards. Much of this overall growth is due to the research interest in batteries, solar cells, and fuel cells during the first ten years, and interest in supercapacitors and water splitting from 2013 onwards. To be more specific, solar cell publications were in the majority from 2003-2014 (fig SI4), but publication numbers and frequency (Figure 44B-C) began to decline starting in 2015. Battery publications grew sharply starting in 2010,

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surpassing solar cells after 2015 and continuing to dominate in number of total publications, though its publication frequency has been slowing. Fuel cells experienced a rise in publications from 2003-2011, reaching a steady plateau starting in 2013. Interestingly, water splitting shares a similar growth trend to batteries, though with lower publication numbers, and its publication frequency surpassed that of batteries. A surge of supercapacitor publications occurred from 2009-2018 but has plateaued in 2019. Thermoelectric publications have grown all throughout the two decades, though its publication frequency has stabilized. Lastly, the journal publication frequency of solar thermal, thermal energy storage and triboelectric sharply rose at the end of the second decade, though publication numbers remain low in comparison to other categories.

In the case of overall patent publications related to the energy applications of nanoscience exponential growth lasted up to 2014 (Figure 44D). Afterwards, there is a small drop in 2015, a sharp rise in 2018-2019 with another drop in 2020 followed by slow growth in 2021 and 2022. The main driver for this growth is due to the batteries sector, whose publication number and publication frequency rose consistently until 2019, declined in 2020-2021, and then rose again in 2022 onwards (Figures SI5 and 43E). Fuel cells and solar cells also influenced the rise in publication numbers during the beginning of the first decade, fuel cells from 2003 to 2008 and solar cells from 2003 to 2011 (Figure SI54). Upon closer reflection, one can see that solar cell patent interest declined drastically after 2013, both in total publications and frequency (Figure 44F), demonstrating that nanoscience application in solar cell technologies may be a mature commercial technology. The publication number and frequency of fuel cells has steadily risen throughout the two decades, showing that though slow in growth, interest in applying nanomaterials for this application continues. Despite low numbers of patent publication, publications related to supercapacitors and water splitting have increased substantially until the last two to four years. Thermoelectric patents had also seen a rise in interest up to 2014, then slowly began to decline. Lastly, patent publication frequency for solar thermal applications shows a pattern or rising and falling every few years then continuing down while triboelectric sharply rose at the end of the second decade, and thermal energy storage interest is also overall on a rise with only a bit of a dip in 2017 and the Covid-19 pandemic years (2020-2022).

As previously mentioned, in relation to scientific publications, batteries are the most popular and continuously growing application of nanoscience in the energy field. Due to this a more detailed analysis of publication trends in this category was merited. There is a large variety of types of batteries but in this article, we will mainly categorize them by their battery chemistry (See Figure 45). The top seven battery chemistries are Li-ion, Na-ion, Li-S, Zn-air, Zn-ion, Al-ion and K-ion. When comparing number of patents vs journals we observed that, though lower in total publications, Li-S has more patents than Na-ion. This higher number in patents is likely due to the high energy density of Li-S batteries, their low cost, and the natural abundance of sulfur material.[773] We also observed that Al-ion has more patents that the Zn-air and Zn-ion, and K-ion has more journals than Al-ion.

While we found that the largest number of publications is associated with Li-ion batteries, many of the publications (particularly in journals) use Li-ion batteries as standards with which to compare other battery types rather than as the main objects of interest. Still, new materials for Li-ion batteries are being explored, for example: using nanosheet-assembled porous $MnCo_2O_{4.5}$ microflowers as electrode material,[774] porous Co_2VO_4 nanodisk as a high-energy and fast-charging anode,[775] and phosphorus-doped $NiMoO_4$ nanorods (P-$NiMoO_4$) on anodes for high lithium storage.[776] More examples of these materials will be further elaborated in the next section.

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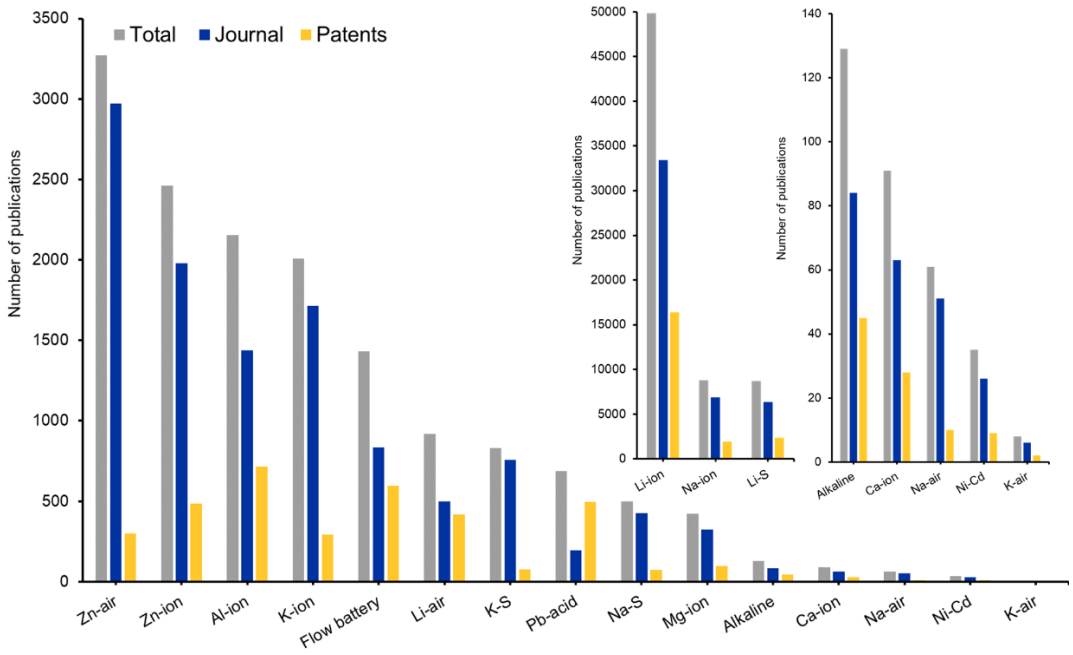

Figure 45. Number of publications associated with different types of battery chemistries.

LG Energy Solutions has the highest number of patent publications in the area of batteries from 2021-2023 (Fig. SI6). The main focus of these publications appears to be rechargeable/secondary batteries, with approximately 66% of 2023 patents describing lithium secondary batteries or their components. The use of carbon nanotubes as conductive materials in electrodes is a theme in many of these patents, for example a negative electrode with single-walled carbon nanotubes for a secondary battery with a lithium transition metal oxide cathode,[777] a lithium nickel-based oxide bimodal carbon nanotube cathode material having both large and small particle diameters[778], and the development of a manufacturing method for cathodes composed of lithium iron phosphate and carbon nanotube conductive material.[779]

Substance Data Trends related to Energy in Nanoscience

In this section, we will examine the most prominent substances used in nanomaterials in energy applications, and the forms in which they are used. Figure 46 lists the most prominent materials used in nanoscale forms in each of the ten energy applications. The numbers in the figure refer to the number of journal or patent references in which the material was described as being in nano form or nanoscale, or where the material had a dimension between 0.05 and 100 nm. Across all journal and patent publications, there are roughly 28,000 such unique substances.

Based on this analysis, the most commonly used nanoscale substances in almost all categories are carbon-based. The only exception is in solar cells, where TiO_2 is used more commonly. Examples of carbon-based nanoscale materials in energy include nanoporous carbon[780] with incorporated metals and other dopants, which are used in batteries, supercapacitors, fuel cells, and water splitting. There are also numerous examples of 0-, 1-, and 2-dimensional carbon nanomaterials in energy applications. These include carbon nanospheres, which can be used to support single-atom HER catalysts in water splitting,[657] and carbon nanotubes, used in batteries and other electrochemical applications that leverage their strength, electrical

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conductivity, and high surface area.[781, 782] CNTs are also used in triboelectric generators to improve performance through their increased surface area and electrostatic effects,[783] and in thermoelectrics.[784] Carbon nanosheets and graphene are also used in electrochemical applications, where they can be combined with other materials either in their atomic level structure (by doping with metals and nonmetals), [785] or by stacking them with other materials.[786]

Of particular importance are nitrogen-doped carbon nanomaterials, which have been extensively tested in electrochemical applications. Here, the incorporation of nitrogen in the structure (and similarly boron, phosphorous, and sulfur) alters the electronic and chemical behavior of carbon nanomaterials, improving their performance in fuel cells, batteries, hydrogen storage, and other applications.[787, 788]

Several transition metal oxides are commonly used in supercapacitor electrodes, with MnO_2 being the most prominent nanoscale material among them,[789] due to its high specific capacitance, low cost, and chemical stability. This includes the use of MnO_2 in the form of pure nanowires,[790] core-shell nanowires,[791] and nanosheets.[792]

Titania (TiO_2) nanomaterials appear prominently in both water splitting and solar cell applications (notably dye-sensitized solar cells[793]) due to its photocatalytic properties,[794] which can be leveraged, for example, to enhance water splitting and CO_2 reduction in the form of nanosheets,[795] nanofibers,[796] and composite nanoparticles.[797] TiO_2 nanoparticles have also been used in combination with perovskites to make high efficiency, stable solar cells.[798, 799] Zinc oxide (ZnO) is also used to perform multiple functions in photovoltaics, including the use of ZnO nanoparticles in the electron transport layers of thin-film photovoltaics.[800, 801]

The noble metals platinum[802] and palladium[803] are used extensively in nanoscale forms in hydrogen fuel cells, where they catalyze the oxygen reduction reaction (ORR). They are also used in methanol,[804] ethanol,[805] and formic acid fuel cells.[806] In some cases, as combinations of Pt and Pd have been used in the same structure, in the form of core/shell nanowires and hierarchical nanoscale dendrites.[807, 808] Silver nanowires are used commonly in triboelectric nanogenerators, as well as in strain and pressure sensors, to make stretchable and flexible conductive pathways for electrical signals or harvested electrical energy.[809, 810]

MgH_2 is used for hydrogen storage due to its high volumetric and gravimetric hydrogen storage capacity; forming it into nanoscale particles, or supporting it on carbon nanotubes or other nanomaterials, speeds up the uptake and release of hydrogen.[811, 812]

After carbon-based materials, bismuth telluride is the second-most commonly used nanoscale material in thermoelectric applications, due to its uniquely high thermoelectric figure of merit (a combination of its electrical conductivity, thermal conductivity, and Seebeck coefficient). The figure of merit can be increased further by using one-dimensional forms of Bi_2Te_3, which reduces the thermal conductivity disproportionately compared to the electrical conductivity.[813]

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Classification	Substance	Batteries	Supercapacitors	Fuel cells	Water splitting	H2 storage	Triboelectric	Solar cell	Solar Thermal	Thermal energy storage	Thermoelectric
Carbon	Carbon	32.46%	28.51%	22.34%	14.91%	24.25%	19.57%	8.13%	15.82%	18.44%	22.42%
	Graphene	13.91%	18.09%	8.03%	5.90%	9.13%	8.45%	4.61%	8.36%	14.87%	9.40%
	Graphite	1.34%	0.87%	0.81%	0.43%	1.29%	0.72%	0.27%	2.36%	4.07%	0.76%
Noble metals	Gold	0.89%	1.17%	4.30%	3.90%	1.63%	4.71%	5.18%	6.73%	1.12%	3.03%
	Iridium	0.13%	0.03%	1.18%	1.53%	0.48%	0.00%	0.09%	0.00%	0.00%	0.05%
	Palladium	0.46%	0.24%	7.25%	2.13%	10.09%	0.48%	0.54%	0.18%	0.28%	0.69%
	Platinum	0.78%	0.51%	20.54%	6.39%	4.73%	0.72%	1.75%	0.18%	0.07%	0.99%
	Platinum ruthenium alloy	0.01%	0.01%	0.94%	0.09%	0.07%	0.00%	0.01%	0.00%	0.00%	0.00%
	Ruthenium	0.34%	0.17%	2.07%	2.63%	2.07%	0.00%	0.20%	0.00%	0.07%	0.23%
	Silver	1.72%	2.23%	2.61%	2.69%	1.44%	16.55%	8.52%	10.55%	5.19%	3.95%
Transition metals	Cobalt	1.78%	1.27%	2.90%	4.44%	3.55%	0.24%	0.40%	1.09%	0.77%	0.99%
	Copper	1.50%	0.84%	2.09%	2.48%	2.44%	3.02%	1.80%	6.55%	4.63%	1.91%
	Iron	1.06%	0.67%	2.00%	2.13%	2.14%	0.12%	0.38%	0.73%	0.49%	0.76%
	Nickel	1.56%	2.88%	3.65%	6.37%	8.58%	0.72%	0.86%	3.09%	0.84%	1.43%
Other metals	Aluminum	0.65%	0.23%	0.20%	0.15%	0.92%	3.74%	1.47%	2.36%	1.05%	0.64%
	Bismuth	0.42%	0.07%	0.20%	0.33%	0.04%	0.00%	0.15%	0.18%	0.07%	2.42%
	Magnesium	0.24%	0.08%	0.10%	0.06%	5.21%	0.12%	0.12%	0.36%	0.14%	0.13%
Nonmetallic elements	Germanium	0.71%	0.05%	0.05%	0.03%	0.07%	0.00%	0.63%	0.36%	0.07%	1.83%
	Silicon	8.59%	0.75%	0.36%	0.95%	1.00%	1.09%	6.52%	1.64%	0.35%	9.38%
	Tellurium	0.09%	0.10%	0.13%	0.09%	0.07%	0.12%	0.06%	0.00%	0.00%	3.44%
Oxides	Alumina	1.66%	0.30%	0.81%	0.20%	1.07%	0.85%	1.54%	6.73%	9.12%	1.55%
	Barium titanate	0.17%	0.09%	0.02%	0.11%	0.00%	6.76%	0.25%	0.18%	0.00%	0.28%
	Ceria	0.36%	0.51%	2.29%	1.10%	1.15%	0.24%	0.32%	0.55%	0.42%	0.15%
	Cobalt oxide (Co_3O_4)	2.04%	3.95%	0.73%	3.68%	0.37%	0.36%	0.19%	0.36%	0.07%	0.18%
	Cobalt nickel oxide (Co_2NiO_4)	0.49%	2.93%	0.24%	0.86%	0.11%	0.12%	0.05%	0.00%	0.00%	0.00%
	Copper oxide (CuO)	0.77%	1.42%	0.46%	1.40%	0.78%	0.60%	0.76%	4.18%	6.24%	0.59%
	Iron oxide (Fe_2O_3)	1.77%	1.94%	0.50%	2.18%	0.52%	0.36%	0.41%	0.73%	0.70%	0.31%
	Iron oxide (Fe_3O_4)	1.43%	1.34%	0.55%	0.67%	0.26%	0.36%	0.20%	2.36%	3.30%	0.56%
	Manganese oxide (MnO2)	2.06%	8.66%	0.70%	0.88%	0.22%	0.48%	0.14%	0.36%	0.63%	0.13%
	Nickel monoxide	1.22%	3.56%	1.16%	2.38%	0.55%	0.48%	1.21%	0.18%	0.14%	0.33%
	Silica	3.67%	1.20%	2.13%	0.90%	1.37%	4.83%	3.09%	7.27%	9.12%	2.24%
	Tin oxide (SnO_2)	2.86%	0.88%	0.60%	0.76%	0.37%	0.24%	2.42%	0.36%	0.28%	0.43%
	Titania	5.34%	2.95%	3.39%	8.28%	2.77%	3.74%	23.15%	5.27%	6.31%	1.94%
	Tungsten oxide (WO3)	0.40%	0.72%	0.50%	1.83%	0.11%	0.12%	0.85%	0.36%	0.00%	0.15%
	Zinc oxide (ZnO)	1.75%	2.22%	0.84%	2.87%	0.92%	8.45%	12.91%	2.36%	2.95%	3.31%
	Zirconium dioxide	0.67%	0.16%	1.24%	0.29%	0.55%	0.00%	0.84%	0.73%	0.14%	0.59%
Calcogenides	Cadmium sulfide	0.09%	0.11%	0.16%	2.42%	0.07%	0.00%	3.26%	0.36%	0.00%	0.31%
	Lead sulfide (PbS)	0.04%	0.04%	0.01%	0.07%	0.04%	0.00%	1.79%	0.00%	0.00%	1.32%
	Molybdenum disulfide	2.03%	2.41%	0.37%	5.97%	0.52%	2.17%	0.73%	1.09%	0.28%	1.30%
	Cadmium selenide	0.03%	0.04%	0.06%	0.36%	0.11%	0.12%	2.80%	0.55%	0.00%	0.43%
	Antimony telluride (Sb_2Te_3)	0.02%	0.00%	0.00%	0.02%	0.00%	0.00%	0.03%	0.00%	0.07%	2.88%
	Bismuth telluride	0.04%	0.02%	0.03%	0.04%	0.04%	0.12%	0.09%	0.00%	0.14%	9.89%
	Lead telluride	0.01%	0.00%	0.00%	0.01%	0.04%	0.00%	0.20%	0.00%	0.00%	3.36%
Inorganic compounds	Boron nitride	0.31%	0.21%	0.21%	0.15%	1.77%	1.33%	0.17%	0.73%	1.75%	0.94%
	Carbon nitride (C3N4)	0.24%	0.56%	0.31%	2.38%	0.85%	0.36%	0.23%	0.18%	0.07%	0.10%
	Magnesium hydride	0.02%	0.01%	0.06%	0.01%	5.06%	0.00%	0.00%	0.00%	0.14%	0.00%
	Nickel dihydroxide	0.40%	2.70%	0.23%	1.82%	0.26%	0.24%	0.04%	0.00%	0.14%	0.00%
	Silicon monocarbide	0.33%	0.28%	0.19%	0.19%	0.55%	0.24%	0.39%	0.73%	1.61%	1.53%
	Titanium carbide (Ti_3C_2)	0.40%	0.83%	0.08%	0.42%	0.30%	1.57%	0.09%	1.82%	0.63%	0.08%
Other materials	Cellulose	0.71%	1.20%	0.38%	0.14%	0.04%	5.43%	0.19%	2.00%	3.23%	0.66%

Figure 46: Heat map of nanoscale substances used in energy applications.

Figure 47 shows a breakdown of different nanoscale forms referenced in journal and patent publications on energy applications. The top three forms are nanoparticles, nanotubes, and nanosheets, which account for >50% of all nanoscale forms. Interestingly, these are 0-, 1-, and 2-D forms, indicating that all three types of materials are used frequently in energy applications.

Examining the time trends of individual nanoscale forms, nanoflowers, nanosheets, and nanoclusters appear to be growing the fastest in journal publications, while nanoplatelets and nanoplates stand out as

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growing quickly in use in patent publications. This suggests that these 2-dimensional forms are growing more quickly in commercialization activity.

Recent examples of the use of these forms in journal publications include $Ni(OH)_2$ nanoflowers as precursors to generate Ni_2P plates decorated with CeO_2 nanoparticles[814] and mixed $TiO_2/ZnIn_2S_4$ nanoflowers,[815] both for photocatalytic water splitting, and N-doped graphitic nanoflowers as a support for Co/CoFe used as a bifunctional ORR and OER catalyst in Zinc-air batteries.[816] Nanosheet references are dominated by MXenes, with applications including Na-ion batteries using Nb_2CTx MXene and MoS_2,[817] Zn-ion batteries using MnO_2 and V_2CTx MXene,[818] and a triboelectric nanogenerator using composite PVDF nanofibers with Ti_3C_2Tx MXene.[819] Nanoclusters are used in battery electrodes, including FeS_2 nanoclusters in a carbon matrix for sodium storage,[820] sulfur nanoclusters that make up part of a pomegranate-like structure for Li-S batteries, where their nanoscale size is theorized to provide rapid kinetics.[821]

In recent industrial patent publications, nanoplates and nanoplatelets typically refer to graphite or graphene, used for example in a protective anode coating[822] or a cathode[823] for a Li-S battery, cathode for a Li-ion battery,[824] as a heat dissipation layer in an electric vehicle battery in combination with copper,[825] a separator for fuel cell,[826] and an electron transport layer for a photovoltaic device, in combination with TiO_2.[827]

Other materials are also used in nanoplatelet form in industrial patent publications. Examples of these include boron nitride nanoplatelets as a protective coating for batteries, fuel cells, or supercapacitors,[828] MXenes in a Na-ion battery cathode,[829] and bismuth tellurium in a thermoelectric device, in combination with carbon nanotubes.[830]

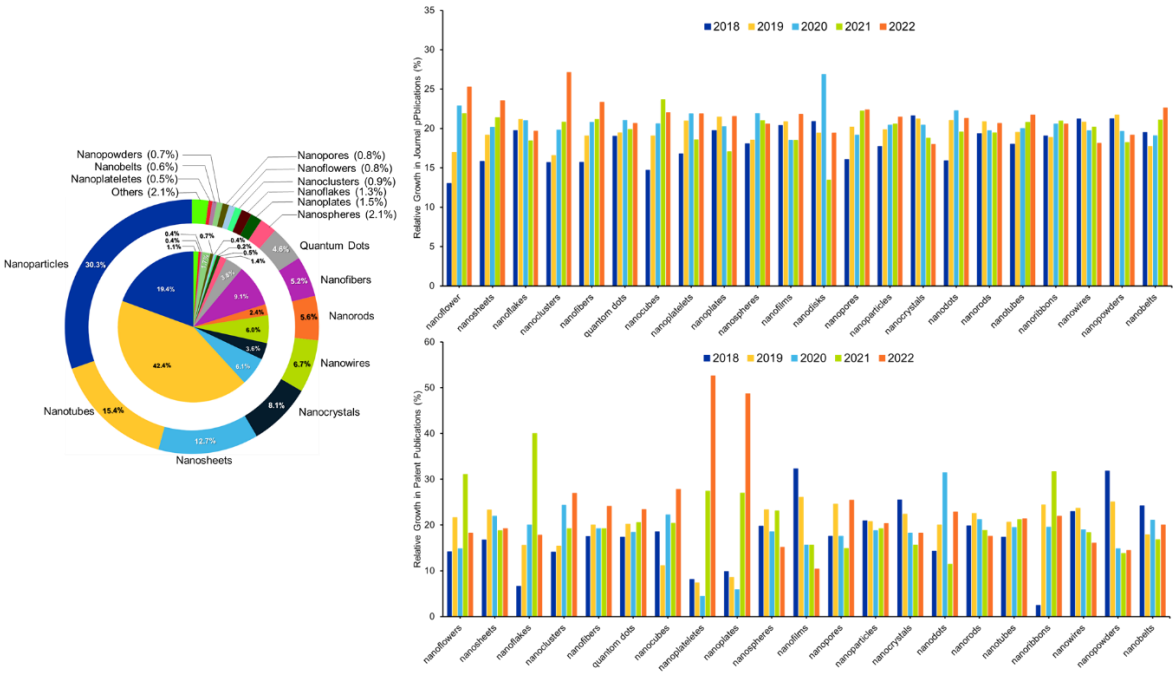

Figure 47. (A) Distribution of nanostructures in the field of energy in journal (outer donut chart) and patent (inner pie chart) publications and (B) their relative growth in journal and patent (left panel) publications over the last 5 years (2019-2023).

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Figure 48 shows a breakdown of substance classes (as described in the catalyst section) by energy application, for publications with a nanomaterial component. Reading vertically down each energy application indicates how frequently each material class is used (square size) and their relative use in journal versus patent publications.

Taking the battery category as an example, we see that carbon black, fluoropolymers, and general polymers are heavily used, and that they appear frequently in patent publications. Carbon nanofibers, ionomers, and MXenes are used less frequently, mostly in journal publications. These comparisons likely represent a combination of how different materials are used within each application, and the relative technical maturity of each field.

Notable trends that can be observed in Figure 48 include the use of layered double hydroxides (LDHs) in supercapacitor electrodes, which includes the use of Ni-Co LDHs supported on reduced graphene oxide,[831] hollow spheres made of Ni-Co LDH sheets,[832] and nanowires with a core consisting of the high specific capacitance material $MgCo_2O_4$, and Co-Fe LDH as the shell.[833] Porous and hollow carbon nanofibers synthesized through carbonizing electrospun polymers, are also used fairly commonly in supercapacitors as electrodes,[834] or as supporting templates for other materials such as metal phosphides[835] or even Zn-Mg-Al LDH nanosheets.[836]

MXenes have been studied in all of the energy applications discussed in this section, which in part is a reflection of the great potential and general interest of these materials. This is due mainly to their morphology, electrical properties, and the ability for customizability as discussed in previous sections. Prominent applications for MXenes in energy include their use in supercapacitors, for example in flexible electrodes[837] and composite electrodes with graphene.[838] MXenes have also been used as a skeleton for phase change material in solar thermal and thermal energy storage applications,[839-841] due to their high thermal conductivity and photothermal conversion efficiency.[842] MXenes have been studied in all of the energy applications discussed in this section, which in part is a reflection of the great potential and general interest of these materials. This is due mainly to their morphology, electrical properties, and the ability for customizability as discussed in previous sections.

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Figure 48. Distribution of substance classes within each application. Square size represents the relative number of total publications (normalized within each application), square color represents the fraction of publications which are patents.

Conclusions

The use of nanoscale materials in energy applications saw significant, sustained growth from 2003 to 2023, becoming a well-developed and expansive field over this time. The more mature topics within this field, characterized by relatively slower growth in publication frequency combined with higher patent publication activity, include batteries (dominated by Li-ion, Na-ion, and Li-S), fuel cells, and photovoltaics.

Growth in the field has been driven by new interest in applications such as triboelectric and other nanogenerators, solar thermal, and thermal energy storage technologies. These appear to mainly be related to heightened research activity into self-powered wearable sensors and sustainable energy sources.

The most highly cited academic publications in this area are in journals focused on nanotechnology (Nano Letters, ACS Nano), energy (Energy Environ. Sci.), and those with a wider interest (JACS, Angew. Chem. IE). These high impact journals have each published between roughly 1,000 and 3,000 articles that combine nanoscale materials and energy applications in the last 20 years. There has also been a high amount of interest in commercialization of nanoscale materials in energy applications, with over 80,000 patent documents published in this area since 2003. The top industrial patent assignees, which are based in China, South Korea, the US, and Japan, represent a number of industries, including chemical, electronics, battery, and automotive.

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With only a few exceptions, the nanoscale materials used across all areas are most commonly carbon-based (CNTs, graphene, fullerenes, nanofibers). Other materials used in nanoscale forms include noble metals in fuel cells and hydrogen storage, TiO_2 and ZnO in photovoltaics, silver in triboelectrics, and Si and other specialized chalcogenides in thermoelectrics. MXenes are a material of especially high research interest, and are being actively studied in almost all energy applications discussed in this section.

In energy applications, these materials are commonly used in 0-, 1-, and 2-D forms. In journal publications, complex forms including nanoflowers and nanoclusters have seen the highest growth in the last 5 years, while 2-D forms appear to be favored in patent publications.

The use of nanoscale materials in mature and emerging application areas has been motivated by several diverse factors, including their strength, electrical and thermal transport properties, high surface area, and their high degree of chemical and morphological customizability. In many cases, nanoscale materials offer unique properties not available in bulk materials. In emerging applications, these include the flexibility and conductivity of silver nanowires, and the high thermoelectric figure of merit of chalcogenide and Si nanoscale materials. For these reasons, nanoscale materials are expected to maintain their common use in existing and new energy applications in the future.

Applications of artificial intelligence in prominent nanotechnology

Artificial intelligence (AI) can play a significant role in nano-related research by helping researchers discover novel nanomaterials with desired features, predicting properties and applications of nanomaterials, and reducing time to analyze output data from nanomachines. Our analysis within the CAS Content Collection shows that there have been roughly 1600 scientific publications (including journal articles, patents, and conference publications) related to the use of AI in nanoscience-associated research. **Figure 49** shows the yearly distribution of these publications. Overall, the number of publications has steadily increased in the last two decades, indicating continuous growth in research, development, and commercialization efforts being made in this field. Journal publications dominate the field, with their total number being ~7 times higher than patent publications. However, the overall patent-to-journal ratio has shown a steady increase in the last five years indicating the onset and progression towards commercialization of research in this field.

In terms of geographical distribution, China dominates the field of journals followed by Iran, India, and the United States. China also leads patent publications with ~70% of these originating from China. The remaining 30% of patent publications are contributed by India, the United States, and South Korea among others.

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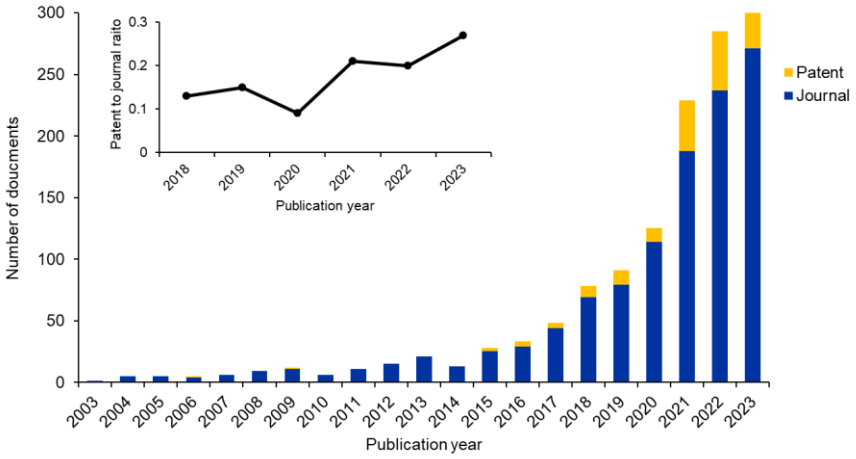

Figure 49: Number of journal and patent publications published per year from the CAS Content Collection that are related to the use of AI in nanoscience-related research areas (shown as blue and yellow bars, respectively) over the last two decades (2003-2022). The inset shows the trend for the patent-to-journal ratio for the last five years (2018-2023)

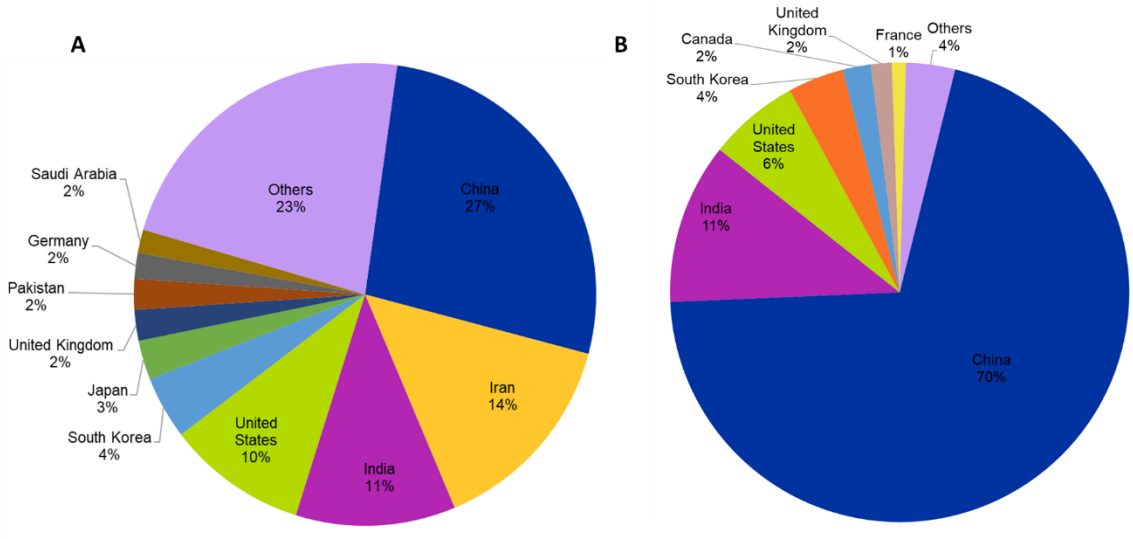

Figure 50: Geographic distribution of **(A)** journal **(B)** patent publications related to the use of AI in the field of nanoscience from 2003-2023 from the CAS Content Collection

Figure 51A shows a Sankey diagram illustrating the correlation of AI and its different applications in the field of nano-related research where we see that sensors, energy, catalysis, and drug delivery are prominent areas that show maximum co-occurrence with the use of AI. The use of AI also shows a high correlation with other applications such as environmental, agricultural, tissue engineering-related applications and disease areas where AI is being used for detection, diagnosis, and treatment. Amongst these 4 prominent fields- sensors, energy, catalysis, and drug delivery, the use of nanomaterials in energy and sensors is the highest as demonstrated by a high percentage (44% and 28% respectively) of scientific publications in these areas **(Figure 51B)**. Further investigation into the prominent fields of nanoscience reveals that the use of artificial

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intelligence has increased in publications related to the application of nanomaterials in energy and sensors (**Figure 51C**). A steady increase in the number of scientific publications in the last decade can be seen in relation to these applications, indicating the rising interest of the scientific community in this field. Interestingly, the number of publications discussing the involvement of AI in the other two prominent nano-related areas - catalysts and drug delivery systems also show a steady increase till 2022.

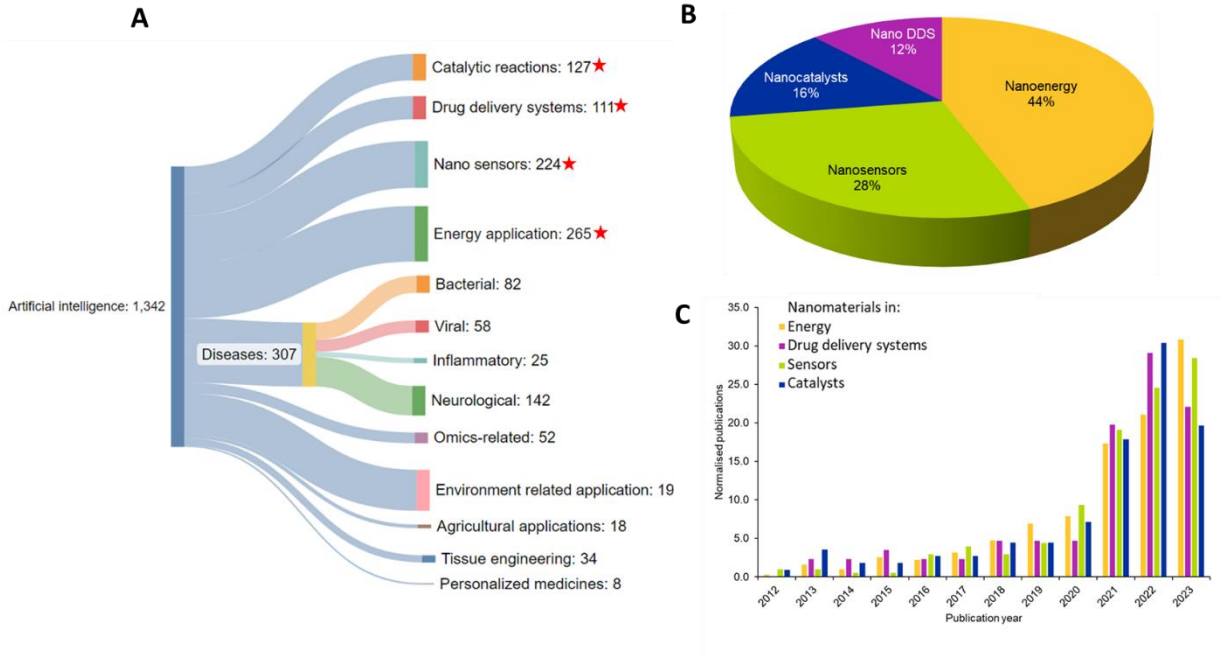

Figure 51: **(A)** Sankey diagram showing correlations between uses of artificial intelligence with applications in several nano-related fields derived from the CAS Content Collection (Branched marked with a red asterisk are explored in panels B and C. (**B**) Percentage distribution of AI use in prominent nano-related fields (Note: Nano DDS is used for nano drug delivery systems) (**C)** Yearly growth for the use of AI in prominent nano-related fields from 2003-2023.

Applications

AI has revolutionized various scientific fields; additionally, advancements in computational approaches and nanomaterials have helped synergize these fields for various applications across diverse domains. For instance, advanced sensors such as image, vision, and wearable sensors, use AI-based algorithms such as machine learning and neural networks to analyze complex and multidimensional data output generated by them [843, 844] AI-enabled nanosensors monitor data in real time, improving the ability of healthcare providers to detect diseases, track disease onset and development, and continuously monitor health conditions.[845] For drug delivery using nanoparticles, AI can help optimize various aspects of drug delivery such as drug design, optimizing drug formulation, controlled drug release, enhancing localized drug delivery, and target penetration, etc.[846-848] The use of AI-enabled sensing technologies can help in designing nanoparticle-based personalized medicine and treatment optimization in the future with real-

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time monitoring and feedback capabilities. AI-enhanced nanogenerators such as piezoelectric nanogenerators (PENG) and triboelectric nanogenerators (TENG) can bring paradigm shifts to the sector of energy harvesting[849 845] For drug delivery using nanoparticles, AI can help optimize various aspects of drug delivery such as drug design, optimizing drug formulation, controlled drug release, enhancing localized drug delivery, and target penetration, etc.[846-848] The use of AI-enabled sensing technologies can help in designing nanoparticle-based personalized medicine and treatment optimization in the future with real-time monitoring and feedback capabilities. AI-enhanced nanogenerators such as piezoelectric nanogenerators (PENG) and triboelectric nanogenerators (TENG) can bring paradigm shifts to the sector of energy harvesting[849] PENG and TENG can capture mechanical energy from various sources. By using AI algorithms, these nanogenerators can optimize energy harvesting efficiency. AI-enhanced nanogenerators can use predictive analytics to efficiently manage energy generation. AI can also benefit the field of nanocatalysts where AI-enabled algorithms analyze vast datasets of nanomaterials to predict catalyst reactivity, performance, and reaction mechanisms.[850, 851] In addition, AI-based programs can explore chemical repositories to identify novel nanomaterial compositions and/or combinations with unprecedented catalytic activity. In conclusion, AI has the potential to significantly accelerate nanoscience and nanomaterial development.

Conclusions

Publications

Nanoscience publications have generally increased over time but the rate and monotonicity of the increases varies with subtopic. Publications about nanoscience catalysts, sensors, and nano-drug delivery systems (nano-DDS) have increased consistently over the last twenty years, while the growth of publications related to energy have slowed after 2018 and publications related to AI in nanoscience have increased rapidly after 2015 and less rapidly after 2018. The largest numbers of journal articles related to nanoscience were published in subtopic-specific journals such as Applied Catalysis, Nano letters, ACS Nano, and Advanced Functional Materials while publications with the highest number of citations per document are most commonly published in general chemistry journals (often those incorporating review or perspective articles) such as J. Am. Chem. Soc. and Angewandte Chem. Intl. Ed. Research organizations based in China published the largest number of journal articles in nanocatalysis, sensors, nano-DDS, and AI, while institutions in the United States, Europe and Australia published the most articles in energy-related topics in nanoscience. The highest numbers of citations per article were found for articles published by institutions in the United States or by US and European institutions in energy, sensors, and nano-DDS.

Patent publication in the fields of nanoscience studied in this paper has increased over time but leveled off in the period between 2017 and 2019. The distribution of patent publications differs significantly between noncommercial (particularly academic) and commercial entities. Patent publication from noncommercial entities is dominated by Chinese universities and academies such as the Chinese Academy of Science in catalysts, energy, sensors, and AI and contribute significantly to patent publication in nano-DDS. Commercial entities show a broader geographic distribution; while nanoscale catalyst patenting has a significant contribution from petroleum companies in China, patenting in the energy and sensor fields

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and in nano-DDS is distributed mainly in the United States and Europe. Petrochemical company interest in catalysts is likely motivated by pollution reduction and for optimizing the efficiency and scope of petroleum use. Technology and engineering companies are the primary entities interested in commercial sensor research. Nano-DDS research is, not surprisingly, focused on disease diagnosis and treatment and in controlled release applications, which provide commercial opportunities outside of medicine.

Applications

Nanoscience catalysis and energy are unsurprisingly focused on energy applications. While catalysis is (by its nature) focused on reactions, the use of nanoscale materials in catalysis (nanocatalysis) focused primarily on reactions to provide energy such as catalysts for fuel cells and battery components. The use of nanoscale materials in energy is centered on hydrogen generation from water, energy storage in batteries, supercapacitors, and fuel cells, and on the generation of electricity from other sources such as heat and friction (thermal energy storage, thermoelectric materials, and triboelectric materials). The shift of energy source from fossil fuels to electricity, particularly for transportation, is likely necessary to improve the efficiency of energy use and reduce the emissions costs of transportation, and is an important interest of both governments and businesses.

Sensor work in nanoscience is primarily devoted to disease diagnosis and detection of pathogens and heavy metals. The ability to reduce risks to human health through sensor technology is likely to improve health outcomes through early detection of threats and is also likely to be commercially viable. Nanosensors are more likely to be developed using chemical and biological stimuli; the applications of interest are most amenable to chemical and biological detection, while physical stimuli may already have successful technologies available on conventional length scales and thus require either significant improvements over current technology or a broader scope of uses (for example, strain and pressure sensors using nanoscale materials may provide highly localized data on structural integrity that cannot be obtained easily by other methods). .

Nano-DDS are (perhaps unremarkably) dominated by disease treatments and diagnostics, areas in which there are many unmet needs, significant scientific advances in biological knowledge and technology on the nanoscale, and commercial interest. Much of drug delivery development using nanoscale materials involves oral formulations of difficult-to-deliver treatments such as nucleic acids and genes, proteins and peptides, and polymers; oral drugs are more convenient to deliver and do not require syringes, specialized equipment, or medical professionals to administer. Drug delivery technology for controlled release has been explored; a variety of consumer products would benefit from controlled release technologies and provide alternative markets and allows for diversification of businesses.

AI technologies in nanoscience are focused on energy, sensors, catalysis, and drug delivery. Energy and sensors likely deliver large volumes of data and require some autonomy in modifying systems to respond to circumstances, tasks for which AI is well suited. While technologies to study catalysis and biological systems on small scale have been and continue to be developed, the volume of data is likely smaller and the need for autonomy lower in those fields than for energy and sensors.

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Nanoobject morphology

The most common morphologies seen in nanoscale objects in the fields discussed here are nanoparticles. A larger number of substances have been used to form nanoparticles than other morphologies such as nanosheets, nanoplatelets, or nanotubes; in addition, nanoparticles are readily prepared by solution methods, making their production easier on laboratory and commercial scales.

For energy, sensor, and catalyst applications, the next most common morphology is nanotubes. The most common and known nanotube material is carbon; carbon nanotubes are commercially available, are strong, and can be either conducting or semiconducting. The focuses of energy and catalysis in nanoscience are in electricity generation and storage, technologies for which CNT are useful, while the conductivity or semiconductivity of CNT, their high surface area, and their ready functionalization makes them useful for sensors. Nanotubes are also easier to immobilize on surfaces and thus more likely to be used as part of a device rather than as a reagent. Nano-DDS rely on controlled release morphologies more than nanotubes. DDS are intended to disappear controllably upon administration, making the structural stability of a morphology a liability rather than a benefit; in addition, the incomplete knowledge of CNT toxicology likely reduces their use in DDS.

Composition

The materials most often used for nanoscale objects depend on the applications to which they are put. Carbon is the most common material associated with energy and catalysis documents in nanoscience, while titanium dioxide is also common in both applications. Silicon and iron oxides are frequently associated with energy applications, while platinum and palladium are associated with catalysis. Carbon, titanium dioxide, and silicon dioxide are readily available and can assume a variety of morphologies; in addition, nanoscale carbon can be conducting, semiconducting, or insulating, can be functionalized in a variety of ways, and can absorb light, while titanium dioxide can absorb light and generate energy or chemical work. The ability of substances to assume multiple morphologies and roles and the ability to interconvert forms of energy is important for catalytic and energy applications. Platinum and palladium are costly but have significant capabilities that other materials are not known to have. Palladium reversibly absorbs hydrogen, catalyzes many reactions, and is used on significant scale in catalytic converters for internal combustion engines, while platinum has been used often in industry as a catalyst. The use of costly catalysts allows and requires the use of lower amounts of catalyst.

For sensors, the most common classes of materials are organic and inorganic substances, particularly titanium, silicon, and zinc oxides, with elements such as carbon, gold, and silicon less common. Polymers such as poly(ethylene glycol) and polyaniline are also seen, likely for specific purposes (poly(ethylene glycol) likely to control nonspecific protein absorption and polyaniline for conditional conductivity. Glucose, hydrogen peroxide, ethanol, and ammonia are frequently associated with sensors, and all are important analytes in biological systems.

Drug delivery systems are associated most often with polymers, followed by metals and their oxides (primarily gold and magnetic materials), lipids, and silica and calcium phosphate. As noted earlier, materials for drug delivery must be biocompatible, with structures that are reversible and components

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that can either be cleared easily or which degrade to nontoxic fragments. Polymers incorporated into DDS are often natural polysaccharides or polyesters that readily degrade, while gold is a noble metal and unreactive under biological conditions, and magnetic components such as magnetite are nontoxic at useful concentrations.[852] Lipids, calcium phosphate, and silicon dioxide are (if not inhaled) biocompatible.

One significant factor in the materials used in nanoscience is economy. Most of the materials used in nanoscience are inexpensive; one of the important goals of nanoscience is to generate functionality from simple materials through control of their properties at small scale. Technologies that are capable of being used widely likely need to incorporate materials that are readily available and that are not costly, while the economic incentives for their development militate towards lower-cost materials. Rarer or more expensive materials are used only for applications where either the materials cost is less relevant (gold in nano-DDS) or where they have properties that cannot replicated by less expensive materials (palladium and platinum in nanocatalysis).

Further opportunities

While this article discusses the capabilities of nanoscience, there are also opportunities for improvement. The morphologies and sizes of nanoscale objects are determinants of their functionality, but in many cases the morphology of nanostructures depends strongly on the materials used. While gold and carbon can be fashioned into a broad range of nanostructures, other materials are significantly more limited in the structures they can assume. The ability to control nanostructures for a given material would allow replacement of expensive materials with less expensive ones, or to incorporate the functions of one material into another. While the atomic structure and composition of a material may determine the structures it can form, templating or stabilizing components may allow nominally unstable structures to be obtained for a given material. A more readily attainable goal would be to control the structures of carbon nanotubes (and potentially of carbon nanostructures in general). While carbon nanotubes are readily available, single-walled and multi-walled nanotubes require either high temperatures, corrosive reagents, or difficult separation and purification steps[853] and thus high costs. The ability to generate conducting or semiconducting CNT would make a variety of applications more available. CNT may be formed in a variety of diameters and stereochemistries, many of which are not currently available but which would likely to be useful in sensors. Incorporation of methods for nano-DDS systems into nanomaterial synthesis may also allow the formation of materials with atypical morphologies. The ability to generate morphologies with less dependence on the source material would likely expand the scope of nanomaterial use.

This article outlines current research trends in nanoscience, particularly those related to catalysis, energy, drug delivery, sensors, and artificial intelligence, and proposes explanations for them. We hope that our work will help to place nanoscience research in a helpful context and that it will inspire further research.

Methods

NLP analysis

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Using a custom-made search query ("?nano? and (conference/dt and acs/so) and (journal/dt) and (patent/dt)"), we identified around 3 million documents related to nanoscience and nanotechnology in the CAS Content Collection. The documents include journal articles, patents, conference proceedings, and preprints published from the year 2003 onwards. We then used a novel Natural Language Processing (NLP) to identify the emerging topics within these documents. For identifying candidate phrases, Natural Language Toolkit (NLTK) procedures lemmatization and removal of English stop words by using the python library implementation of NLTK were performed on all n-grams containing 2 to 6 words from the abstract and title of the documents. In addition, we only considered phrases that were found in at least 100 documents.[28]

Applying the two NLTK procedures described above and the >100 documents constraint, 306,353 candidate phrases were identified. For each phrase, the NLP method calculated the publication rates and number of documents in which a particular phrase appeared. Publication rate for a given year is the difference in the number of documents compared to the previous year. We used the top 20,000 phrases with the highest average of the publication rates for the years 2020, 2021 and 2022 for further analysis. From these 20,000 phrases, we manually picked those phrases which can be identified with an application or material or property. For example, phrases such as "play crucial" and "highlight potential" which cannot be connected with any application or material or property are ignored. The selected phrases are then grouped into topics. For example, "solar cells", "photovoltaics", and "perovskite solar" are grouped under 'solar cells'. Then these grouped topics are categorized into applications, materials, and properties.
Out of the various applications which were identified, we selected four applications with the most number of documents for an in-depth analysis.

Co-occurrence analysis

To calculate the rate of co-occurrence (Figures 4, 5, and 6), the same grouped topics that were identified using the NLP analysis described above and shown in the mind maps in Figures 2 and 3 were used. For each pair of topics, the number of document title and abstract in which any phrase in one topic appeared in the same sentence as any phrase in another topic was counted. For example, a document where the term "solar cells", "photovoltaics", or "perovskite solar" appeared in the same abstract sentence as "nanocavities" or "nanocavity" was counted as a co-occurrence of the topics "solar cells" and "nanocavities".

This analysis was conducted for journal and patent documents published between 2019 and 2022. The average rate of increase (y-axis of Figures 4, 5, and 6) was calculated as the average year-over-year change in co-occurring document count over that period.

Search strings

The following search strings were used to identify documents in the CAS content collection for further analysis in the five sub-sections.

<u>Drug delivery</u>

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?nano? and (((?drug? or gene or “nucleic acid” or mRNA or siRNA or DNA or ?RNA or ?vaccine or pharmaceutic?) and (delivery or administration or release or target? or ?carrier? or ?encapsulation? or formulation or bioavailability or pharmacokinetic? or therap?) or (lipid and nanoparticle) or (silica and nanoparticle) or (metal and nanoparticle) or (silver nanoparticle) or (gold and nanoparticle) or (“iron oxide” and nanoparticle) or (magnetic and nanoparticle) or (polymer? and nanoparticle) or (“core-shell” and nanoparticle) or (“stimuli-responsive” and nanoparticle) or exosome or “extracellular vesicle” or liposome or niosome or polymersome)) and PY>2002

Results: 611712 doc

Sensors

L1 ((?NANO? OR CNTS OR CNT OR SWCNT? OR MWCNT? OR GRAPHENE? OR QUANTUM DOT?) AND (?SENSOR? OR ?DETECTOR? OR NANOPROBE? OR NANO-PROBE?)) AND PY>2002

L2 L1 NOT (NANOSECOND? OR SENSORY)

Results: 272661

Catalysis:

s ?nano? and ?catal? and PY>2002

Results: 495188

Energy

L1 (?NANO? OR CNTS OR CNT OR SWCNT? OR MWCNT? OR GRAPHENE? OR QUANTUM DOT?) AND (?BATTER? OR ?CAPACITOR? OR SOLAR(W)CELL? OR SOLAR(W)ENERGY OR PHOTOVOLTAIC? OR TRIBOELECTRIC? OR FUEL(W)CELL? OR NANOGENERATOR? OR ENERGY(W)CONVER? OR THERMOELECTRIC? OR CURRENT COLLECTOR? OR HYDROGEN(W)SYNTHES? OR HYDROGEN(W)STOR? OR HYDROGEN(W)PRODUCTION OR WATER(W)SPLIT? OR ELECTROLYSIS OR OXYGEN EVOLUTION REACTION? OR HYDROGEN EVOLUTION REACTION? OR ENERGY HARVEST? OR OXYGEN REDUCTION REACTION? OR ENERGY(W)STOR?) AND PY>2002

L2 L1 AND (67 OR 76 OR 77 OR 52 OR 71 OR 51 OR 59)/SC

L3 L1 AND (67 OR 76 OR 77 OR 52 OR 71 OR 51 OR 59)/SX

L4 L2OR L3

L5 L4 NOT (NANOSECOND? OR MITOCHONDRIA?)

Results: 347585

AI

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s ("artificial intelligence" or "machine learning" or "support vector machine" or "neural network" or "natural language process"or "cognitive computing" or "deep learning" or "machine intelligence") and "nano"

s l1 AND (JOURNAL/DT OR PATENT/DT OR CONFERENCE/DT) AND PY>2002

aprox 1700

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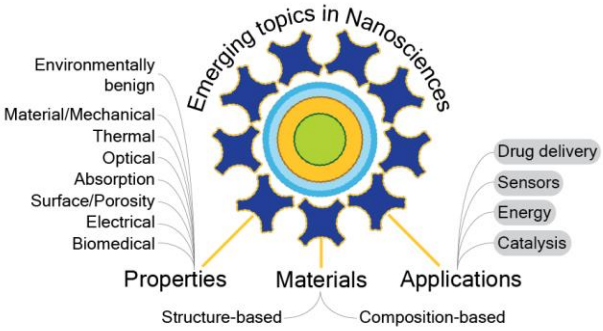

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