Nanoscale materials applications in nanosensors: Insights from a comprehensive landscape analysis

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Abstract

Nanosensors are devices having a nanoscale dimension designed to detect, record, and transmit signals to provide valuable data and information. In this report we present our findings resulting from analysis of more than 250,000 publications in the field of nanosensors spanning a period of two decades (2003-2203) extracted from the CAS Content Collection, one of the largest repositories of scientific information. We have examined the landscape of published research in nanosensors to provide insights into the types of nanosensors as well as the common nanomorphology utilized. This in combination with our access to CAS Registry, enabled identification of emerging materials across various substance classes (polymers, small molecules, elements) associated with nanosensors. Our analysis indicates that a major application of nanosensors appears to be biomedical in nature including in cancer diagnosis and testing and drug discovery, other applications of importance are in agriculture and food industry. We also provide a snapshot of commercial interest in the development of nanosensors for a wide range of applications. It is our hope that this report provides a comprehensive overview of the field and serves as a valuable guide to researchers/scientists.

Keywords: Nanosensor, biosensor, nanomaterial-based sensor, health monitor, wearable sensor

Introduction

Sensors have played a pivotal role in revolutionizing 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 and are capable of converting physical, chemical, or environmental stimuli into measurable signals which can be interpreted, with the resulting information used to monitor, understand, or modulate the target.[1] 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.[2] 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.[3, 4] Incorporating nanomaterials such as nanoparticles, nanowires, nanotubes, or quantum dots enhances the specificity and sensitivity of sensors, enabling precise measurement.[4-7] Moreover, nanomaterials provide a high surface area to volume ratio, thereby amplifying the interactions between sensor and target.

Among the most commonly used nanosensors are temperature, proximity, motion, pressure, light, gas, sound, and humidity sensors. Biological nanosensors are a specialized subcategory of nanosensors that effectively combine biological components with nanoscale materials to detect biomolecules such as nucleic acids, proteins, antibodies, enzymes, biomarkers, entities such as pathogens, etc. allowing monitoring of biological processes. Biological nanosensors are used in medical diagnostics, bioassays, and for monitoring drug delivery and disease progression.[8-10] 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 report we present our findings resulting from analysis of more than 250,000 publications in the field of nanosensors spanning a period of two decades (2003-2203) extracted from the CAS Content Collection [11], one of the largest repositories of scientific information. We have examined the landscape of published research in nanosensors to provide insights into the types of nanosensors as well as the common nanomorphology utilized. This, in combination with our access to CAS Registry [12], enabled identification of emerging materials across various substance classes (polymers, small molecules, elements) associated with nanosensors. Our analysis indicates that a major application of nanosensors appears to be biomedical in nature including in cancer diagnosis and testing and drug discovery, other applications of importance are in agriculture and food industry. We also provide a snapshot of commercial interest in the development of nanosensors for a wide range of applications. It is our hope that this report provides a comprehensive overview of the field and serves as a valuable guide to researchers/scientists.

Journal and Patent publication trends

The number of journal publications related to nanosensors shows a steady increase over the last 20 years (Figure 1), 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.

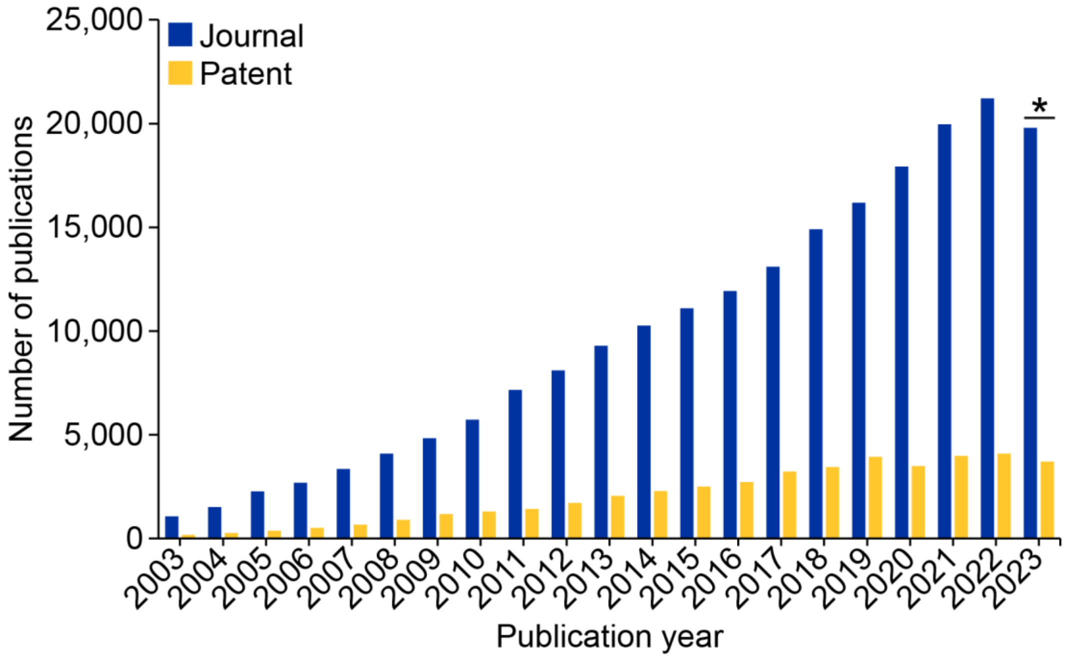

Figure 1. Publication trends for nanosensor related research over the last two decades. Data includes journal and patent publications from the CAS Content Collection for the period 2003-2023. *Indicates data is partial encompassing data from January to June 2023.

We identified leading scientific journals that are prolific both in terms of volume of output (number of publications) as well as citations to those publications, a rough quantification of their influence (Figure 2). 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 2). 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[13-15] as well as wearable[16] including epidermal sensors.[13-15, 17, 18]

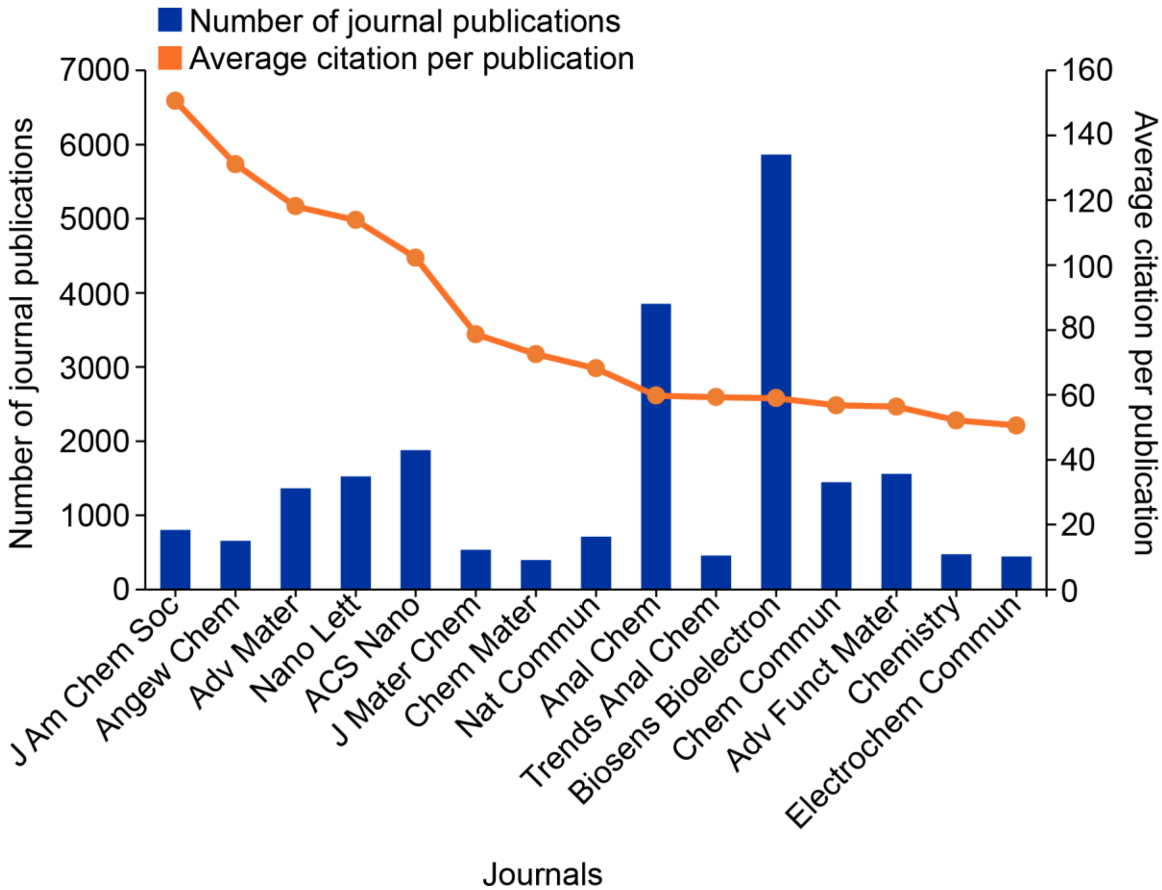

Figure 2. Leading scientific journals in the field of nanosensors based on data from the CAS Content Collection for the period 2003-2023. Data for 2023 is partial encompassing data from January to June 2023. Blue bars represent number of journal publications while the orange line represents average number 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). Academic institutions from China (CHN) tend to lead 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 the United States (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 3). Examples of highly cited journal articles originating from these research organizations revolve around the use of nanosensors in wearable electronics,[19] agriculture,[20] and detection and/or monitoring of neurotransmitters[21] among other applications.

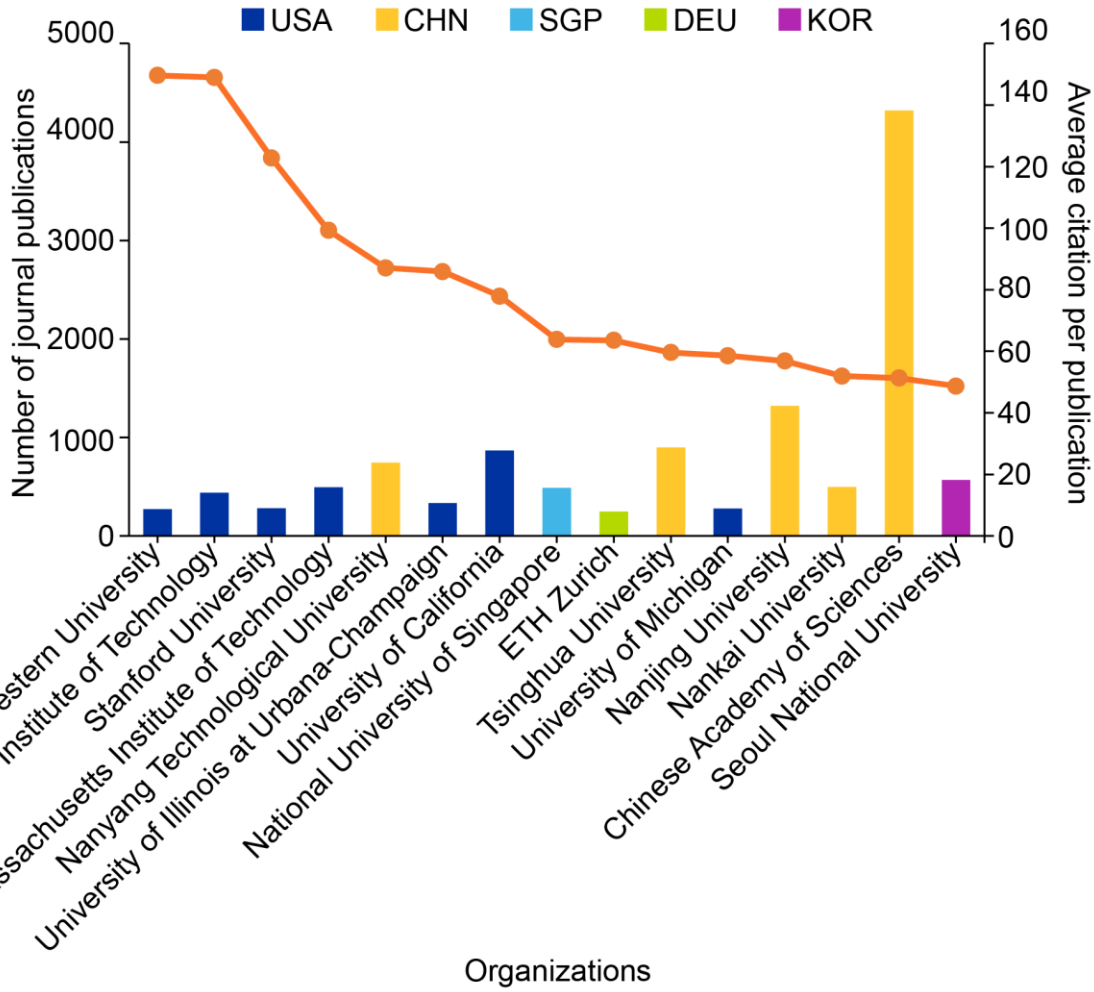

Figure 3. Leading research organizations in the field of nanosensors based on journal publication data from the CAS Content Collection for the period 2003-2023. Data for 2023 is partial encompassing data from January to June 2023. Colored bars represent number of journal publications while the orange 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).

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 4A). 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 4B). 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 multinational company Samsung Electronics involve image sensors,[22, 23] and their application in electronic devices as well as examples of acoustic sensors,[24] strain sensors,[25] and sensors for biometric inputs.[26] The Japanese multinational conglomerate, Fujifilm, appears to have patents related primarily to image sensors[27-29] 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,[30-32] as well as sensors with potential use in wound dressings.[33] Finally, Toray Industries, the Japanese multinational company specializing in chemicals, has filed patents related to gas sensors[34, 35] as well as flexible wearable biomedical sensors that can be utilized in monitoring heart activity in last few years.[36]

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 4B). Examples of patents by University of Jinan in recent years include those related to flexible wearable sensors,[37, 38] nanoprobes for cancer detection and imaging[39] and a fluorescent sensor to detect chemicals.[40] The only two non-commercial entities based outside of China are the Korean Universities - Korea Advanced Institute of Science & Technology (KAIST) and Korea Institute of Science & Technology (KIST). Examples of recent patents by KAIST involve gas sensors,[41, 42] a cerium oxide-based sensor that can be used to detect hydrogen peroxide (H_2O_2) [43] and a carbon nanotube (CNT)-based sensor for virus detection.[44] Similarly, patents filed by KIST cover a range of sensors including colorimetric sensors based on gold nanoparticles,[45] wearable sensors utilizing silver nanowire and single-walled caron nanotube (SWCNT)[46] and nitrogen dioxide gas sensors using SWCNTs decorated with carbon dots,[47] among many others.

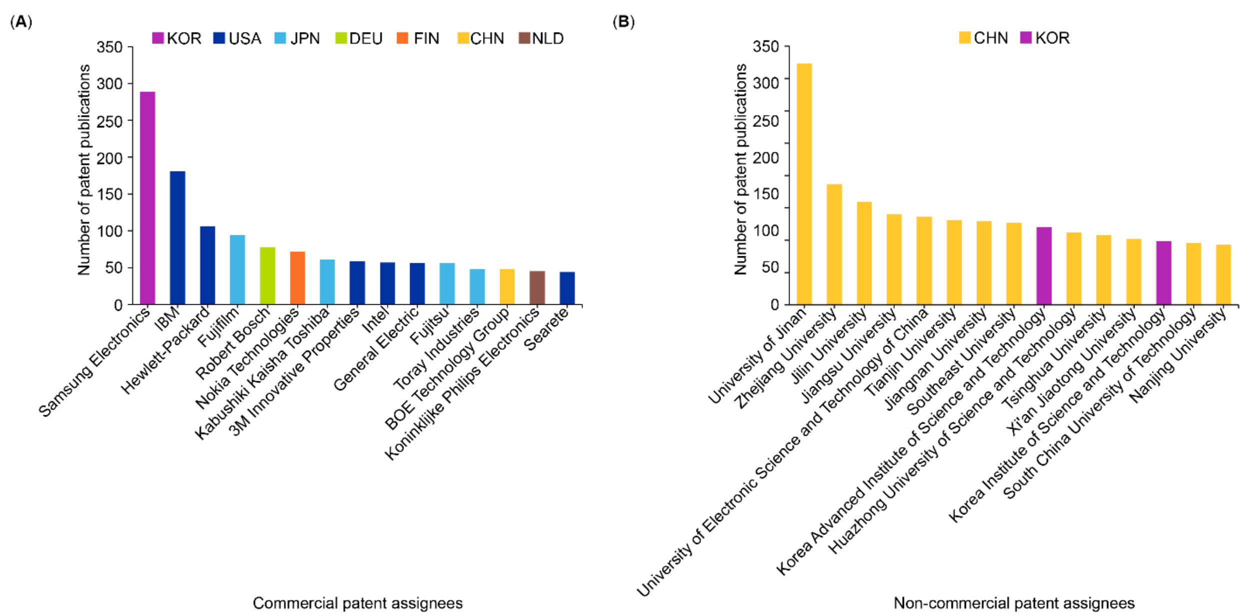

Figure 4. Leading patent assignees in the field of nanosensors in terms of numbers of patent publications between 2003-2023 based on data from the CAS Content Collection. Data for 2023 is partial encompassing data from January to June 2023. Patent assignees have been categorized into (**A**) commercial 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).

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 coordination compounds, nucleic acid sequences, alloys, and protein/peptide sequences (Figures 5 and 6).

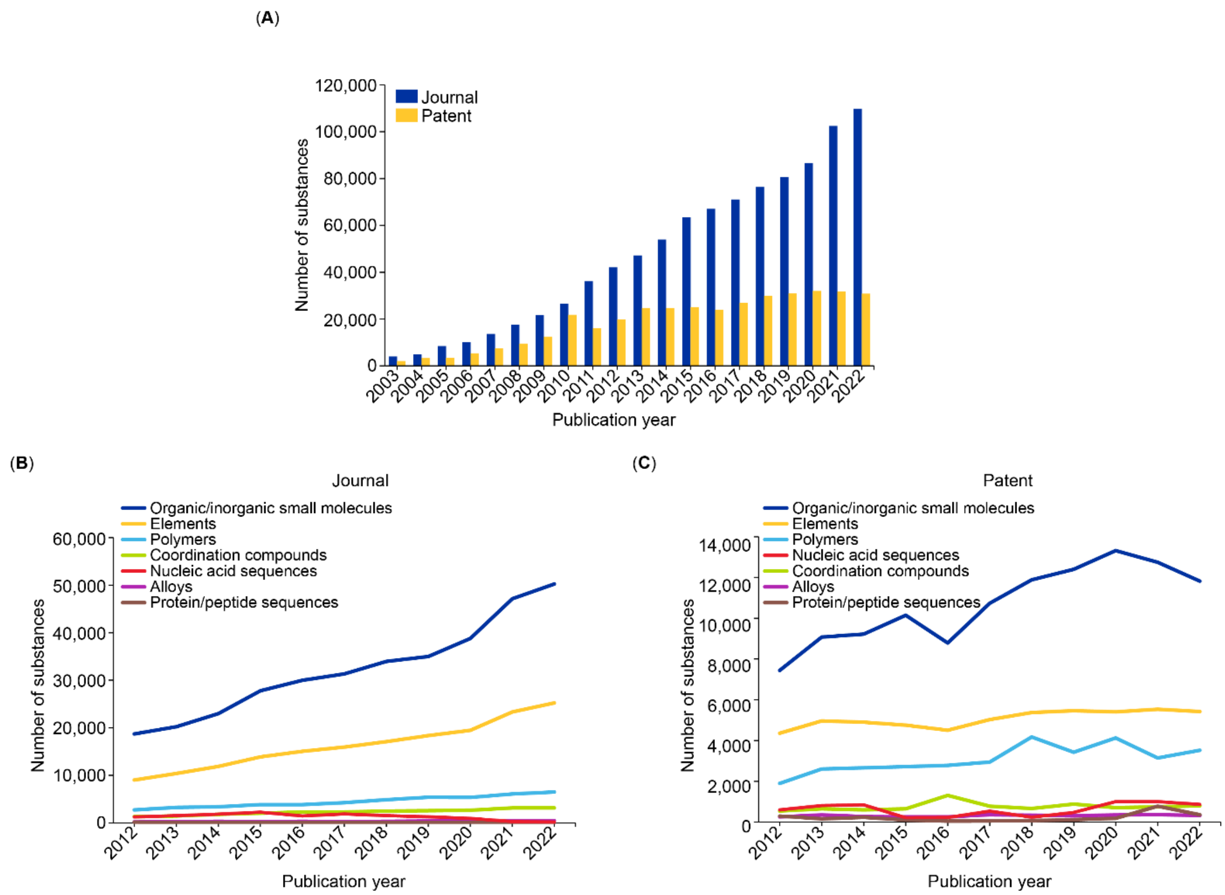

Figure 5. (**A**) Number of substances associated with journal and patent publications. Breakdown across various substance classes (organic/inorganic small molecules, elements, polymers, coordination compounds, nucleic acid sequences, alloys, and protein/peptide sequences) associated with (**B**) journal 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. Data for 2023 is partial encompassing data from January to June 2023.

Highlighted in Figure 6 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).

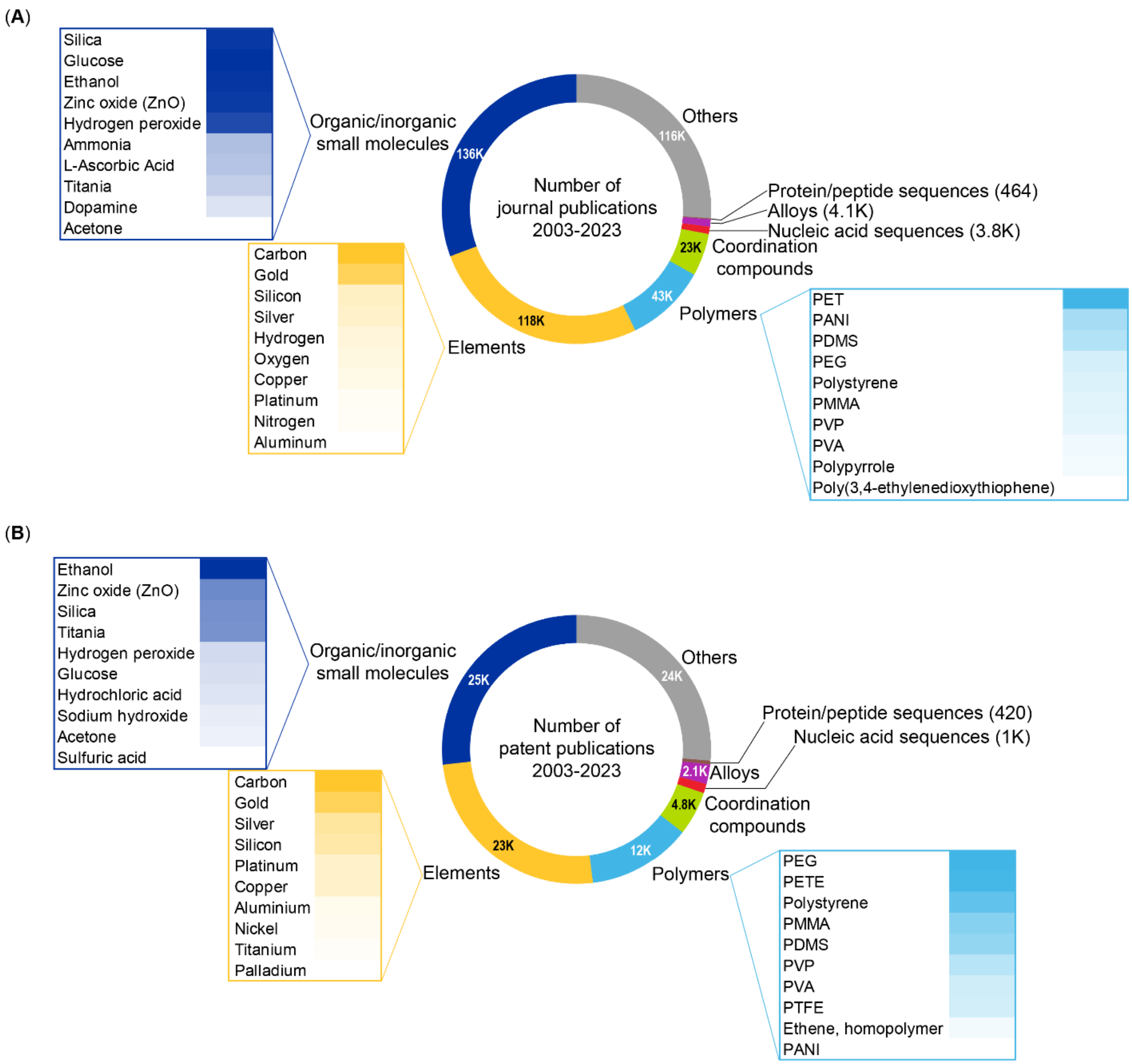

Figure 6. Leading substances in each individual substance class – organic/inorganic small molecules, elements and polymers associated with (**A**) journal and (**B**) patent publications shown as heat map tables with the intensity of the colors corresponding to number of publications associated with that substance. Included are substance and publication data from CAS Registry and CAS Content Collection associated with journal and patent publications for 2003-2023. Data for 2023 is partial encompassing data from January to June 2023.

Leveraging our access to extensive substance and bibliographic data, we identified emerging substances in each substance class highlighted in Figure 7. 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, followed closely by the element subclass. The organic/inorganic small molecule subclass shows the highest degree of divergence with only a few emerging substances common between journal and patent publications.

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[48] and colorimetric nanosensors[49] 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.[50] Other examples include alcohol sensors[51] and carbon monoxide sensors.[52] 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,[53] Cu/Al electrodes in strain sensors[54] and $NiCo_2S_4$ nanosheets for sensing glucose and ascorbic acid.[55] Examples of latter include zinc oxide nanotube-based NO_2 gas sensors[56] and N-doped molybdenum oxide quantum dots-based fluorescence sensor for detection of Cu^{2+}.[57]

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 7). Examples include journal publications describing the use of cellulose in electrochemical,[58] flexible strain[59] and chemosensors[60] often as nanofibers and in combination with other materials (including synthetic polymers) used for applications such as health monitoring,[61] heavy metal detection[60] and in the food industry[62] amongst others. The use of chitosan has been explored in sensors across several biomedical applications including in wearable sensors for health monitoring[63, 64] including continuous monitoring of the neurotransmitter serotonin considered a biomarker for depression.[65] Often chitosan is used in conjunction with other materials in the fabrication of these sensors including synthetic polymers such as polyaziridne[66] as well as metals[65] and metal oxides.[67] Patent publications show similar use/applicability of cellulose[68-70] and chitosan[71, 72] including metal organic framework (MOF)-multi-walled carbon nanotube (MWCNT)/chitosan composites for electrochemical detection of tryptophan enantiomers.[73]

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 7B). A type of semiconducting polymer, PDA is composed of repeating units of dihydroxyindole, indoledione and dopamine[74] and is synthesized by subjecting dopamine to oxidation. Often fabricated as nanoparticles, [75-77] PDA is also frequently used as coating to modify surface properties of a wide variety of materials.[78 79] In the context of nanosensors, PDA coated CNTs were embedded in a PVA-PEG hydrogel matrix to fabricate flexible wearable sensors.[80] In another instance, PDA-gold 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 [75-77] PDA is also frequently used as coating to modify surface properties of a wide variety of materials.[78 79] Use of PDA reported in patent applications appears to be similar to those reported in journal publications including use of PDA-multi-walled CNTs in electrochemical sensors.[81]

Another well-known semi-conducting polymer, PEDOT, shows consistent and increasing growth in journal and patent publications since 2008 (Figure 7). 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,[82] sensors composed of wood sponge decorated with SWCNT/PEDOT:PSS capable of detecting pulse and temperature[83] and MXene-PEDOT:PSS-PPy nanosheets used as wearable sensors for real-time monitoring of sweat in terms of sodium and creatinine levels.[83] PANI has been utilized to detect small molecules such as formaldehyde[84] in the form of PANI/Zn bismuthate nanocomposite decorated carbon electrodes; amoxicillin, a penicillin antibiotic, in water bodies as PANI-silver bromide composites[85]; as mesoporous silicon-PANI nanocomposite to detect levels 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,[86] monitoring humidity[87] and colorimetric sensors for pH measurement.[88] Many PANI-based sensors are electrochemical sensors that utilize the excellent conducting properties of PANI.

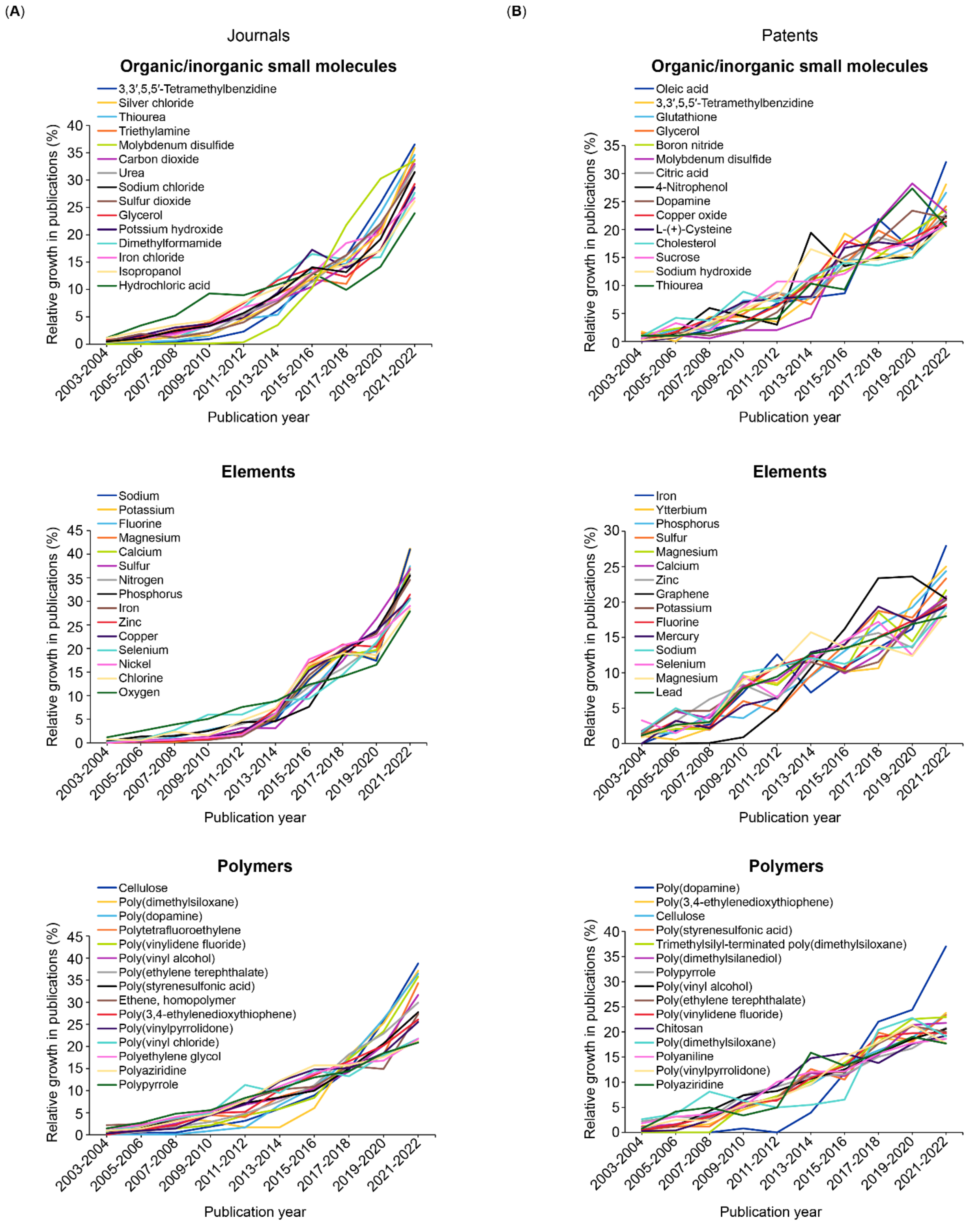

Figure 7. Relative growth in publications associated with emerging substances in each individual substance class – organic/inorganic small molecules, elements and polymers associated with (**A**) journal and (**B**) patent publications. Included are substance and publication data from CAS Registry and CAS Content Collection associated with journal and patent publications for 2003-2023. Data for 2023 is partial encompassing data from January to June 2023.

The organic/inorganic small molecule subclass of substances show the least 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[89-91] as well as components of hydrogels[92] and in some instances as protectant against temperature induced changes.[93] Similarly, thiourea is often mentioned as part of synthesis of nanomaterials.[94, 95] Another context in which thiourea often appears is in terms of development of nanosensors for its detection.[96-99] Molybdenum disulfide (MoS_2) nanoparticles appears to be often employed in a variety of different nanostructures including quantum dots,[100] nanoroses[101]/flower-like structures,[102, 103] and nanosheets[104] for environmental applications including monitoring water quality[101] and detection of volatile organic compounds[103] as well as biomedical applications such as detection of biomolecules[100, 105, 106] and health monitoring[107] to name a few. MoS_2 is also often used as a modifier of CNTs[106, 108, 109] 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.[110, 111]

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[112-114] and as components of nanocomposites.[115] Nanosensors have been tested for their sensitivity in the presence of varying concentrations of sodium chloride (NaCl).[116, 117] Iron chloride ($FeCl_3$) appears in the context of synthesis and may be utilized in the synthesis of both ferric oxide nanoparticles[118, 119] and Fe-MOF nanocomposites.[120] Similarly, urea has also been used in the synthesis of nanocomposites.[121, 122] Triethylamine can be used as a solvent in the synthesis of nano-based materials.[123, 124] Nanosensors have also been developed to detect presence and levels of triethylamine considered an environmental pollutant.[125, 126] Dimethylformamide (DMF)[127, 128] 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.[129] KOH has also been used in the synthesis of nanocomposites.[130, 131] Other small molecules associated with journal publications are toxic gases such as carbon dioxide[132, 133] and sulfur dioxide[134, 135] and isopropanol,[136-139] 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.

Types of nanostructures

Figure 8 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,[140] 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 CNTs, 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 CNTs, 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 is likely to be necessary for broader usage.[141] 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.[142]

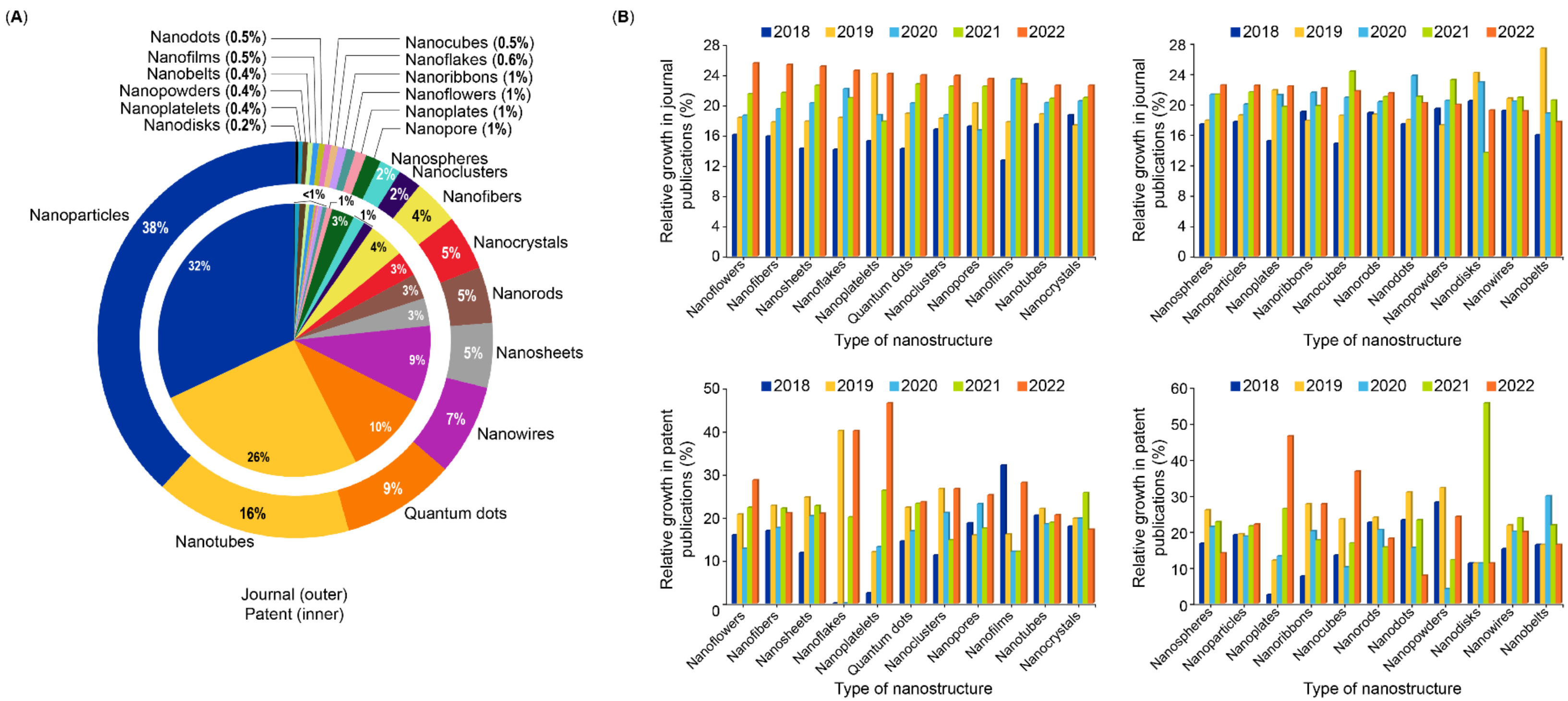

Figure 8. (**A**) Distribution of nanostructures in the field of nanosensors in journal (outer donut chart) and patent (inner pie chart) publications and (**B**) their relative growth in journal (left panel) and patent (right panel) publications over the last 5 years (2018-2022).

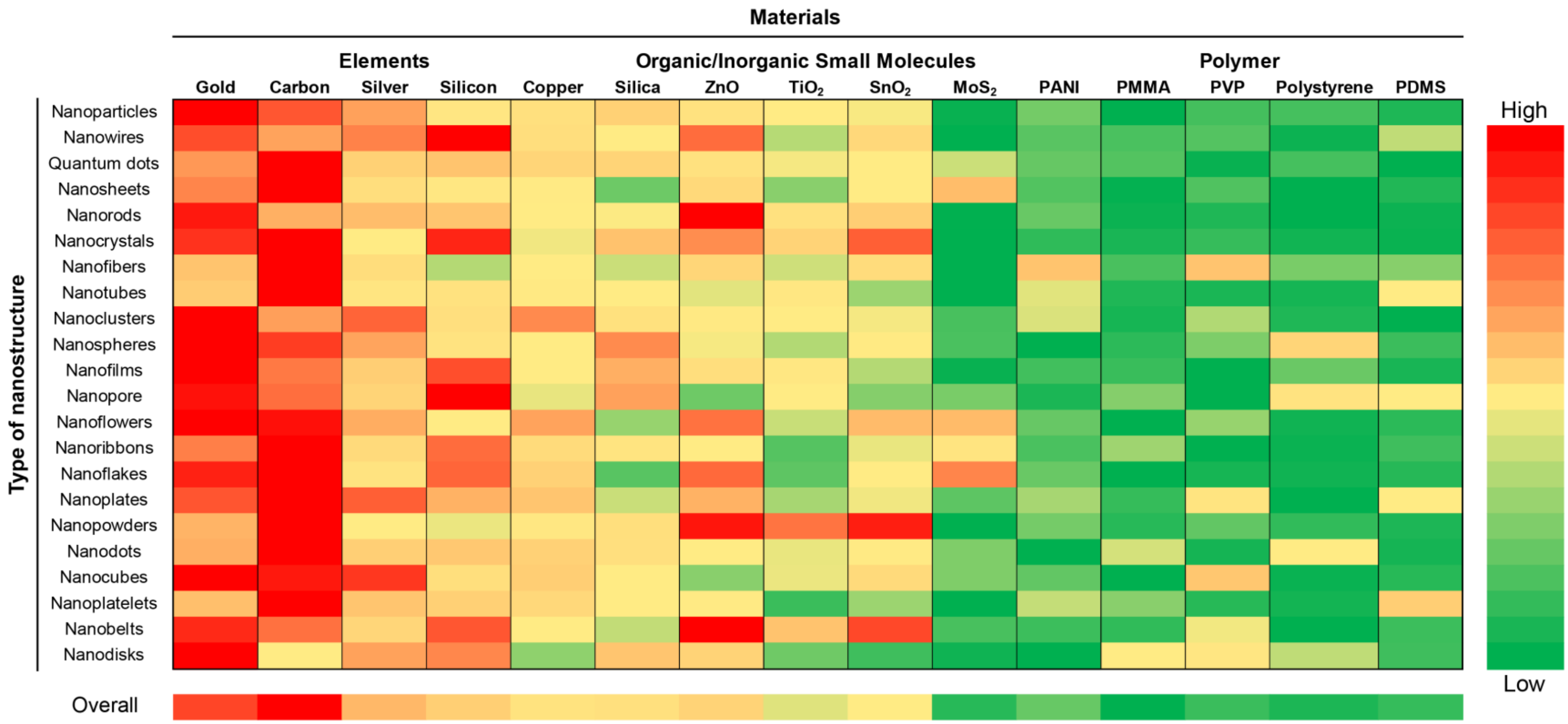

Figure 9. Heat map showing co-occurrences of specific types of nanostructure vs substances for journal publications. The substances shown here are the leading substances identified in each individual substance class (elements, organic/inorganic small molecules, polymer) shown in Figure 6A. Included are substance and publication data from CAS Registry and CAS Content Collection associated with journal publications for 2003-2023. Data for 2023 is partial encompassing data from January to June 2023.

Figures 9 and S1 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. CNTs 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.[143] 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.[144] 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[145]; 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[146]; 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 PANI and polyvinyl pyrrolidinone. PANI 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.

Types of nanosensors

For most stimuli, the fraction of journal publications and the fractions of patent publications are similar, implying similar proportions of exploratory and commercial interest (Figure 10). 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,[147] CO,[148] and NO_2[149] 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.[150-152]

Surface plasmon resonance (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.[153, 154] 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.[155] 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.

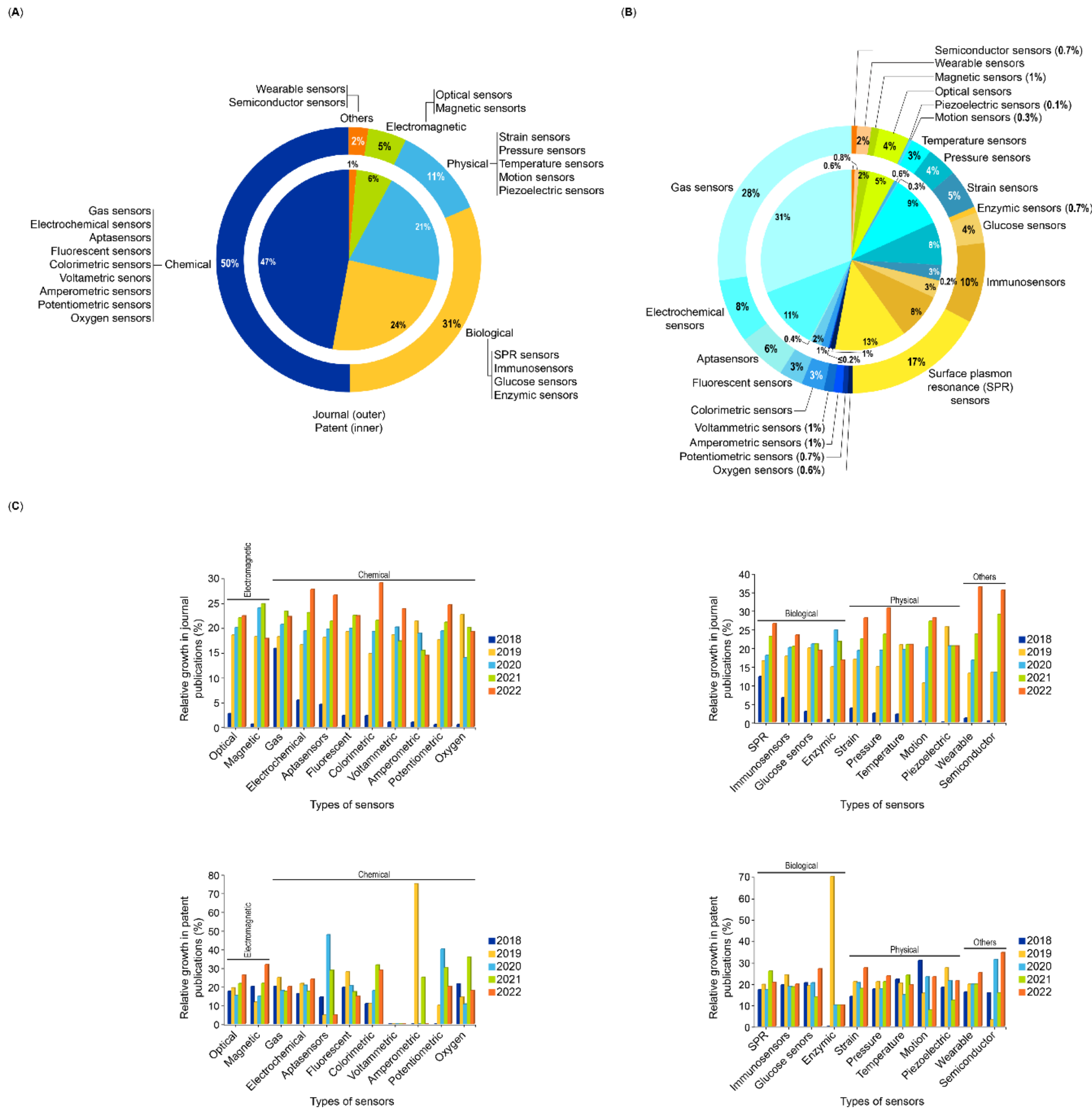

Figure 10. Distribution across (**A**) broader categories of nanosensors, (**B**) their breakdown into individual subtypes for the period 2003-2023 and (**C**) growth in publications (2018-2022). In (**A**) and (**B**), the outer donut chart represents journal publications while the inner pie chart represents patent publications. Data includes journal and patent publications from the CAS Content Collection for 2003-2023. Data for 2023 is partial encompassing data from January to June 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 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.

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 11A) accounting for nearly ~82% and ~80% of journal and patent publications. In the paragraphs that follow, we have described in detail a few of these applications.

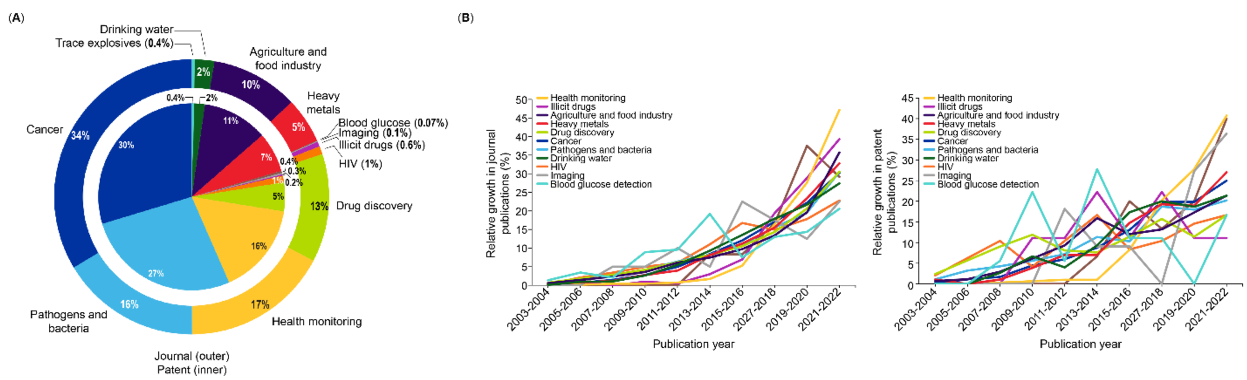

Figure 11. (**A**) Distribution of and (**B**) relative growth in publications (journals and patents) of various applications across which nanosensors appear to be utilized. Data includes journal and patent publications from the CAS Content Collection for the period 2003-2023. Data for 2023 is partial encompassing data from January to June 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 from exhaled breath of patients suffering from lung, breast, colorectal, and prostate cancers.[156] Nanosensors based on CNTs can be used to detect cancer-related biomolecules in trace amounts.[156-158] Highly sensitive sensors developed using silicon nanowires, silver nanowires, etc. can also be used to detect cancers. These nanosensors can detect subtle changes in electric conductivity upon their interaction with cancer biomarkers.[159, 160] 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.[161] 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.[162]

Nanosensors in pathogen and infectious diseases detection: Owing to their miniature size and ease of portability nanosensors play a pivotal role in the detection of pathogens including bacteria, fungi, viruses, and protozoans with high sensitivity and selectivity. 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,[163] metallic nanoparticles,[164] and metal-oxide-based nanoparticles[165] are used for bacterial detection and therapy. Certain metallic nanoparticle-based nanosensors, such as silver and gold experience localized changes in SPR.[166] Nanobiosensors are also being developed for fungi and viruses, especially for the COVID-19 virus.[167, 168] Specialized nanosensors are developed by coating nanomaterials with pathogen-specific recognition elements such as enzymes, aptamers, proteins, and peptides.[169] 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.[170] 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.[171] In addition, advancements in this field have led to the development of nanopore-based sensors for pathogen detection,[172] microfluidic nanosensors for high throughput pathogen detection,[173] and magnetic nanoparticles conjugated with aptamers or antibodies[174] 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.[175, 176] 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 such as cancers,[177] and cardiovascular disease.[178] For efficient management of diabetes, nanosensors can be injected into the skin or can be used as a wearable device for continuous glucose monitoring.[179, 180] Nanosensors are also being developed that can perform metabolite detection from bodily fluids such as sweat, blood, urine, plasma, etc.[181, 182] Nanofabricated sensors can also be implanted in eyes to monitor intraocular pressure which can be important for managing conditions such as glaucoma.[183] In addition, biotoxins such as anthrax and smallpox can be detected by nansosensors at minute levels with possible applications in 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[184] indicating 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 11A) and show a steady increase in publications perhaps more pronounced after 2014 (Figure 11B). Environmental monitoring consists of detecting levels of heavy metals[185-187] and monitoring of water quality.[188, 189] For an informative perspective on nanosensors for monitoring water quality please see Vikesland.[188-190] 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*[191] in food samples.

Use of sensors in the agricultural sector[192] includes PANI-based[193] and CNT-based[194] 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[195] and graphene dot-based electrochemical sensors[196] as well as monitoring soil quality in terms of moisture content[197] and bacterial flora.[198] 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.[199] 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.[199, 200] Therefore, accurate, rapid and highly sensitive detection of aflatoxin levels in food samples is an important area of development for nanosensors[201, 202] including aptasensors.[201, 202]

Nanosensors under development for commercial use

Data from Pitchbook [203], a database encompassing global capital markets, indicates robust economic investments in companies in the realm of nanosensors with more than 500 companies currently involved in this area (Figure 12A). In terms of geographical distribution, companies headquartered in the United States dominate accounting for 70% of the total capital invested and is followed by companies originating from United Kingdom (13%) (Figure 12B inset). The United States saw an especially large influx in capital investment in 2020 – nearly 2.2 billion USD (Figure 12B). Distribution across industry group indicates highest degree of interest from the healthcare devices and supplies sector, unsurprisingly, accounting for half of all capital invested, followed by the pharmaceutical and biotechnological sector (Figure 12C). This agrees with our analysis which indicated that the largest fraction of application of nanosensors is in the biomedical and other allied fields.

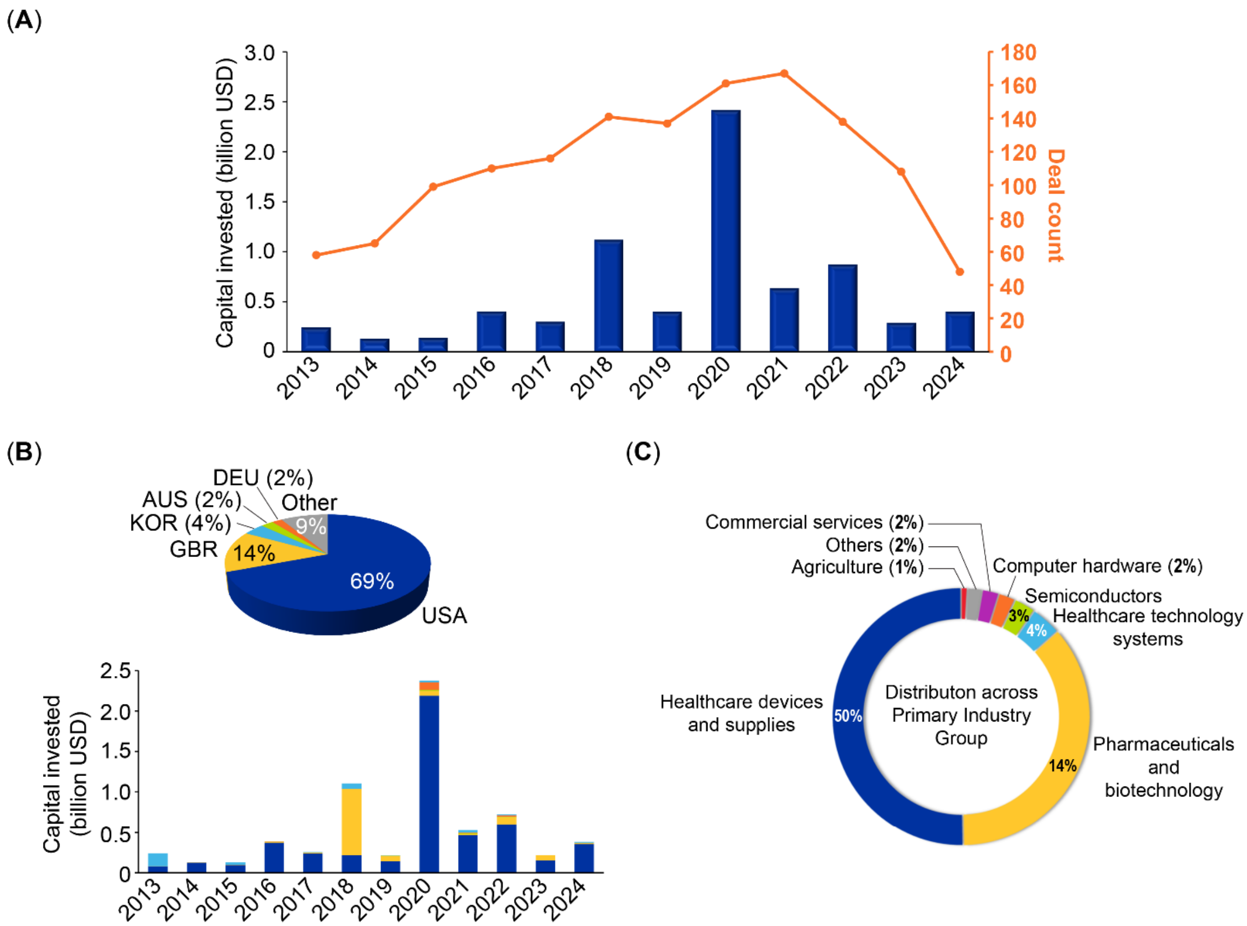

Figure 12. (**A**) Capital invested and number of deals over the last decade, (**B**) geographical distribution of companies and (**C**) distribution of companies across primary industry group in the field of nanosensors. Data extracted from Pitchbook for the period 2013-2024.

Tables 1 and 2 list details of nanosensor-based products that are being pursued commercially and clinical trials involving nanosensors registered on clinicaltrials.gov, respectively.

Table 1. A few examples of nanosensors under development for commercial use

Name of product	Company	Type of sensor	Brief description
LipidSense	Lime Therapeutics [204]	CNT-based optical sensor	A sensor used to detect lipid accumulation inside living cells [205, 206]
LiveOne	LiveMetric [207]	Wearable sensor (pressure sensor)	Real-time blood pressure monitoring [207]
NanoDx	NanoDx [208]		Silicon nanowires-based sensor for biomarker detection in blood samples [208]
NEXOS (Nanoparticle EXOsome Sensing)	Mursla Bio [209]	Electro-optical sensor [210]	Detection of liver-specific extracellular vesicles as biomarkers of liver function [211]

Rosewell ME chip [212]	Roswell Biotechnologies [212]	Single molecule sensor embedded in semiconductor chip	Capable of detecting biomolecules such as DNA, proteins, antibodies etc. [213]
SimpleSense	Nanowear [214]	Wearable sensor	Textile-based sensor for blood pressure monitoring [215]
	Pinpoint Science [216]	Aptasensor	Fast, accurate detection by non-invasive means of SARS-Cov-2
	OncoNano Medicine [217]	Fluorescent sensor	pH sensitive fluorescent sensor that lights up and cancer cells only allowing for easier removal by surgery [218]

Table 2. List of clinical trials registered utilizing nanosensors on clinicaltrials.gov.

Study ID (Study start year)	Status	Study title	Sponsor	Condition	Type of nanosensor
NCT04086329 (2023)	Recruiting	The development of minimally invasive nanosensor technology to quantify mitochondrial function in human muscle	Children's Hospital of Philadelphia	Mitochondrial myopathies, mitochondrial diseases	Electrochemical oxygen sensor
NCT04074629 (2019)	Completed	Novel nanosensor array for detection of volatile biomarkers from skin in multiple sclerosis	Carmel Medical Center	Multiple sclerosis	Chemical sensor [219]
NCT04119154 (2019)	Completed	Feasibility and accuracy of nanosensor-based cancer diagnosis at the point-of-care (Chedza)	Harvard School of Public Health (HSPH)	Breast neoplasms, lymphoma	contrast microhalography (CEM) device
NCT04022109 (2019)	Recruiting	Screening of gastric cancer via breath volatile organic compounds by hybrid sensing approach	University of Latvia	Gastric cancer, atrophic gastritis, gastric dysplasia, *H. pylori* infection	
NCT02332213 (2014)	Completed	Volatile marker testing for digestive cancer and precancerous lesion detection, evaluation of confounding factors	University of Latvia	Colorectal cancer, colorectal adenoma, gastric cancer, peptic ulcer disease, atrophic gastritis, intestinal metaplasia, *H. pylori* infection	Gold nanoparticle-based sensor [220]
NCT03053453 (2016)	Terminated	Evaluation of the patient reported outcomes after sensor-guided total knee arthroplasty under spinal anesthesia with limited motor-block.	NYU Langone Health	Knee injuries	Verasense Knee System device

Conclusions: Outlook, challenges, and perspectives

Publications related to nanosensors have shown consistent and accelerated growth over the last twenty years. The highest numbers of citations per journal publications were found for articles published by primarily institutions in the United States or China. Patents in the field of nanosensors exhibit a much more sedate pace of growth over time more or less leveling off 2019 onwards. Technology and engineering companies hailing mostly from the United States and Japan are the primary entities interested in commercial sensor research.

With respect to materials nanosensors appear to be associated most commonly with organic and inorganic substances, particularly titanium, silicon, and zinc oxides, as well as elements such as carbon, gold, and silicon to a lesser extent. Small molecules such as glucose, H_2O_2, ethanol, and ammonia are frequently associated with sensors, and all are important analytes in biological systems. The other major class of substance important in the context of nanosensors are polymers with specific examples including PEG and PANI likely to control nonspecific protein absorption and for conditional conductivity, respectively.

In terms of morphology, nanoparticles remain the most commonly explored in nanosensors followed by nanotubes. The conductivity, high surface area and ease of functionalization make CNTs particularly useful in nanosensors. Among the various types of sensors, chemical sensors dominate accounting for nearly half of journal and patent publications.

As research endeavors continue, we can aim for increasingly sophisticated nanosensors which utilize nanomaterials in novel ways. However, the major challenges in this field that still persist are:

- Ensuring the stability of nanomaterial-based sensors in a harsh environment. This is especially true in the context of biosensors/sensors used for biomedical applications wherein stability has to be tempered with compatibility.
- Integrating nanosensors into devices and instruments poses several challenges such as miniaturization and packaging, interfacing with electronics while minimizing noise and signal interference, designing power-efficient circuits, and efficient calibration and maintenance.
- 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.

In conclusion, nanosensors have been explored in various categories due to their unparalleled sensitivity, selectivity, and miniature size. Despite the challenges listed above, the future of nanosensors appears promising and they have a potential to revolutionize various realms of science including healthcare and other industries. 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.

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Supporting Information

Figure S1. 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. Data for 2023 is partial encompassing data from January to June 2023.

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