P-Band Intermediate States Mediate Electron Transfer at Confined Nanoscale

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Abstract

In this perspective article, mainly based on the model of structural water molecules (SWs) as bright color emitters, we briefly summarize the development and theoretical elaboration of P-band intermediate state (PBIS) theory and its application in catalysis, especially in several representative redox reactions. In particular, with a simple equation ($\mathbf{2\int\psi^2{}_{\sigma1'} + \int\psi^2{}_{\sigma2} + \int\psi^2{}_{\pi} = 1}$), we define how the interface sate correlate with the three basic parameters of heterogenous catalysis (conversion, selectivity and stability), and what is the dynamic nature of catalytic active sites. Overall, the proposal of SWs dominated PBIS theory provides new insights into the physical origin of photoluminescence emission of low-dimensional quantum nanodots and the physical nature of nanoconfinement and nanoconfined catalysis.

Key words: P-band intermediate state, Interfacial water structure, Photoluminescence, Nano-confined catalysis, Confinement, Metal nanoclusters, Three-dimensional free electron gas model

Introduction

The molecules and molecular aggregates confined at nanoscale or sub-nanoscale exhibit the abnormal physic-chemical properties, in particular in the field of photoluminescence (PL) and heterogeneous catalysis. However, the physical origin of nanoconfinement for PL and nanocatalysis remains elusive, in particular when the low-dimensional quantum nanodots were used as a confined host. The main difficulties currently limiting the development of this field lie in the lack of high spatiotemporal resolution spectroscopic methods and effective theoretical calculation methods, as the sub-nanometer or nanometer scale just falls at the boundary between the micro- and macro-scales.

It seems that there is no significant correlation between the luminescence and catalytic effects of noble metal nanoclusters, but surprisingly consistent, their optical properties and catalytic performance strongly depend on the type, density, and packing mode of surface protective ligands, as well as the size, shape, and composition of metal core, suggesting the same surface state dominates the Electron transfer behavior at nanoscale interface. Of course, more energy levels mean more possibilities for electron transitions, yielding the multi-color PL emissions. In fact, from an electronic perspective, improving the luminescence efficiency and catalytic performance of precious metal nanoclusters, especially for redox reactions, is essentially how to manipulate the relaxation and transfer processes of interface electrons at the molecular level. Obviously, through the spatial interaction of atomic orbital, the construction of three-dimensional surface state or delocalized state at confined nanoscale interfaces can promote the interface electron transfer, thus enhancing the reaction kinetics through the inner sphere electron transfer process. In a word, the observations of optoelectronic properties of low-dimensional quantum nanodots by stead and ultra-fast time-resolved optical spectroscopy provides an indirect tool or means for understanding the nature of the surface (or interface) state of heterogeneous catalysis or the catalytic active site on the molecule level.

In this report, taking the debate on the origin of the PL of noble metal nanoclusters (NCs) as a starting point, a new concept of P-band intermediate state (PBIS) theory was introduced to elucidate the physical origin of the luminescence of metal NCs, and based on solid experimental evidence, we confirmed that the structural water molecules (SWs) adsorbed on the surface of NCs core was the emitter center, not the metal center. Generally, the physical origin of PL of low-dimensional quantum nanodots is attributed to the quantum nanoconfinement effect. Then, with the cylindrical free electron gas model though resolving the Schrödinger equation, interfacial delocalized state or three-dimensional surface state of the confined electrons were calculated, which is consistent with the experimental observation, further proving the reliability of PBIS model. Finally, we very briefly reviewed the practice of PBIS theory in several typical nanoconfined catalytic reactions, in particular for redox reactions involving interfacial electron transfer, such as the selective reduction of 4-nitrophenol (4-NP), the selective hydrogenation of cinnamaldehyde, hydrogen evolution reaction (HER) and the gas-phase selective catalytic oxidation of benzyl alcohol at high temperature.

Anomalous PL properties of noble metal NCs protected by surface organic ligands or confined in the inorganic scaffold

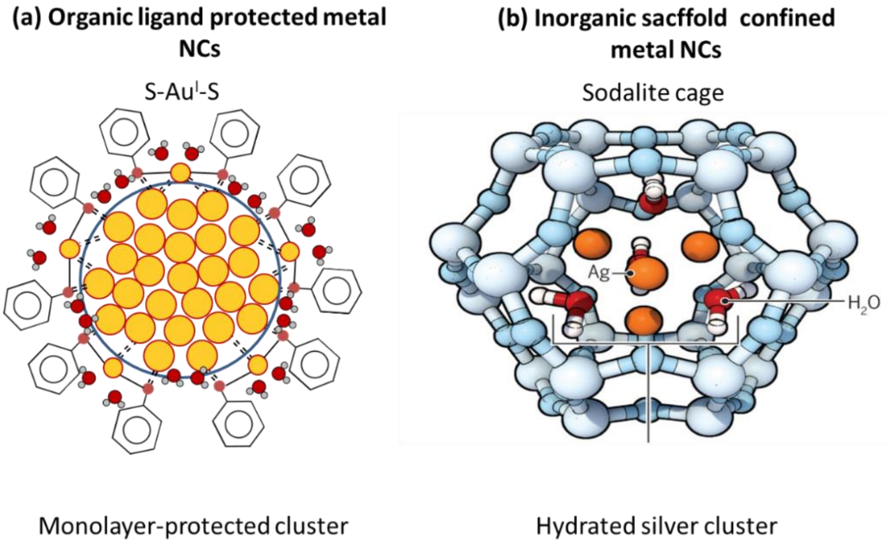

Figure 1. Two typical metal nanoclusters: surface-ligand protective Au NCs (a)[1] and solid nanocavity captured Ag NCs in LTA zeolites(b)[2].

Noble metal NCs g with a size of usually 1-3nm can be easily synthesized through chemical and physical confinement, with organic surface ligands and inorganic scaffolds serving as protective templates and matrix, respectively (Figure 1).[1-5] Due to their nano size effect, they exhibit some electronic properties similar to molecules, such as emitting tunable bright colors with quantum yield up to one unit. This is generally attributed to the quantum size effect of the metal nanocrystal core.[6-8] However, the recently observed size-independent (or ligand-coverage dependent) PL emission phenomena of noble metal NCs with identical particle size and the presence of multiple absorption bands extending from ultraviolet to near-infrared regions cannot be only explained by the metal-center quantum size effect[9, 10] indicating a new physical mechanism on PL emission of metal NCs. In fact, an increasing amount of experimental evidences suggest that water molecules adsorbed at the interface play a crucial role in regulating the PL of metal NCs,[3, 11, 12] but the true role of water and how it affects PL remains elusive, despite Ewles and Przibram proposing the possibility of adsorbed water as the emitter center nearly a century ago.[13, 14] If water really acts as a bright color emitter, considering the ubiquitous nature of water in nature, especially at nanoscale interfaces, it is necessary to re-examine the PL mechanisms of all types of low dimensional quantum dots, non-conjugated unconventional fluorescent organic molecules, AIEgens and even green fluorescence proteins (GFP).

Experimental evidences for structural water molecules (SWs) dominated P-band intermediate states as emitter centers for photoluminescence

The first direct experimental evidence for SWs as emitters is the reversible PL emission evolution of Ag NCs encapsulated in the nanocavity of LTA zeolite upon dehydration/hydration in vacuum/water vapor (Fig. 2a): under the vacuum condition, only the red emission at *ca.* 610 nm was observed; however, upon hydration (or at humid atmosphere), dual emissions at *ca.* 525 nm and *ca.* 610 nm were produced. It's very interesting that when Ag@LTA was dispersed in a mixed solvent of DMSO and water, and with an increase in the volume ratio of DMSO/water ($f_d = V_{DMSO}/V_{DMSO+water}$), the similar PL emission behavior as solid sample was observed, i.e., green emission gradually shifts to the red emission (Fig. 2b and 2c). Very surprisingly, the short excitation wavelength counterintuitively emits a long wavelength emission, exhibiting a very large Stokes shift of up to *ca.* 325 nm (Fig. 2d).

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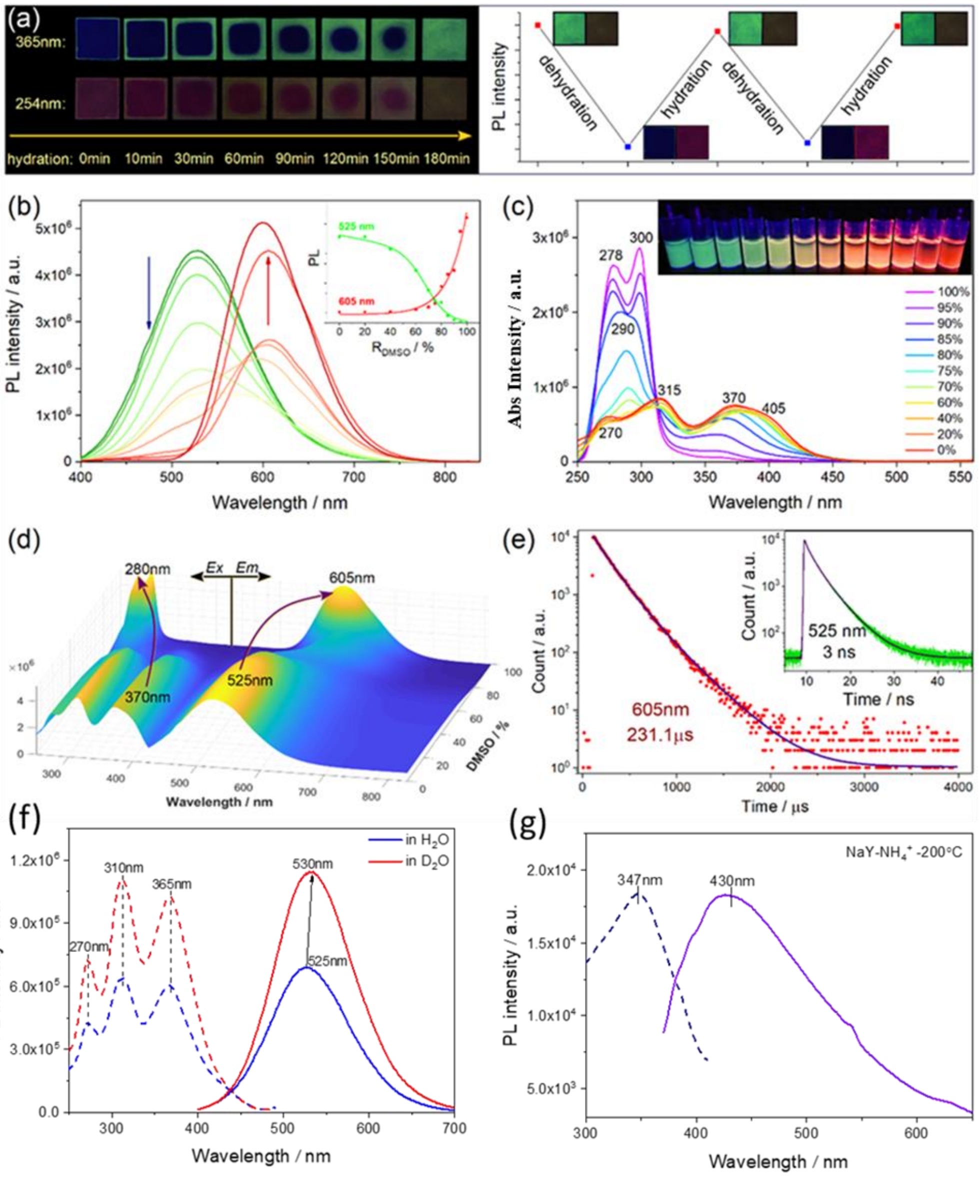

Figure 2. (a) Left, digital photos of LTA-AgNCs under UV light during the hydration process. Right, evolution of fluorescence emission intensity (at 525 nm) of Ag@LTA with alternating cycles of dehydration and hydration process and corresponding digital photos under UV light (365 nm). Photoluminescence (b) and UV–vis absorption spectra (c) of Ag@LTA in the varied volume fraction of DMSO in the mixed solvent ($f_d = V_{DMSO}/V_{DMSO+water}$). Photoluminescence was excited at 370 nm. (d) Contour representation of the excitation and emission data with varied f_d for Ag@LTA. (e) Time-resolved luminescence decay profiles of Ag@LTA in water (green) and DMSO (red) solution. (f) Effect of isotope of heavy water on PL of Ag@LTA. (g) Excitation and PL spectra of ammonia exchange NaY.[15]

The green and red emitter centers of dual-emission were assigned to physical adsorbed SWs in the confined sub-nanocavity of LTA zeolites (also called physically confined SWs, in short as PC-SWs, Type II, Fig. 1a) and chemical adsorbed SWs on metal core (also called chemically confined SWs, in short as CC-SWs, type I, Fig.1a), respectively. Here, CC-SWs mean that water molecules have strong chemical interactions with surface coordination unsaturated metal sites, while water molecules in PC-SWs are only physically confined in nano- or sub nano-spaces and have no interaction with the surface.[16] Obviously, the difference of confined state of SWs (Type I and Type II) answers the reason of the reversible PL emission stimulated by dehydration-rehydration process and solvent effect (Fig. 2a, 2b and 2c) at ca. 525 nm, and exhibits the low quantum lifetime of PC-SWs with nanosecond scale (ns) (Fig. 2e), because weakly confined PC-SWs are more mobile and can be readily removed by thermal annealing treatment and solvent extraction. This also answers why CC-SWS shows much longer lifetime in several hundreds of microseconds (μs, Fig. 2e). The attribution of SWs as emitters also explains the isotopic enhancement effect of PL emission from heavy water (Figure 2f), due to the strong hydrogen bonding effect of heavy water on the stability of the structural water emission center. Importantly note that, even in the absence of noble metals, ammonium ion exchanged NaY zeolites shows the strong blue luminescence at ca. 430 nm (Fig. 2g), indicating that metal NCs is not necessary, just playing a role of anchoring point to stabilize the SWs to strength the PL emission, but not as emitter centers.

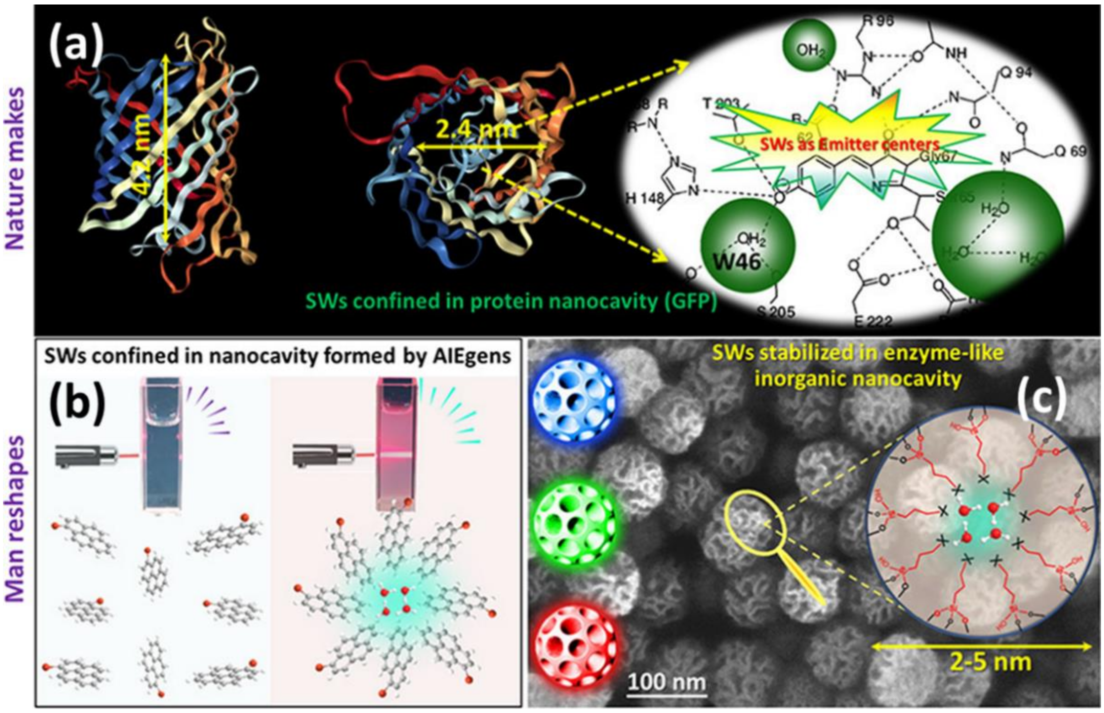

Figure 3. (a) Structural model of green fluorescence proteins (GFP); (b) Structural water molecules confined in the nanocavity formed by AIEgens; (c) Scanning electron microscopy (SEM) of as-synthesized fluorescent mesoporous silica nanoparticles (FMSNs). Inset shows the cartoon of FMSNs with different emission wavelength by surface modification under different conditions and the innersurface of mesopores was functionalized with amino- and carbonyl- groups, which mimics the enzyme-like nanocavity.[17]

Other important experimental evidences for the assignment on the SWs as emitter centers are coming from the fabrication of ideal soft and hard nanocavity for the hosting of SWs. To mimic the microenvironment of the GFP protein scaffold (Fig. 3a) at the molecule level, two groups of nanocavities were created by molecule self-assembly using aggregation-induced emission luminogens (AIEgens) (Fig. 3b) and by organic functionalization of mesoporous silica (Fig. 3c), respectively.[17] Generally, AIE enhancement was attributed to the restriction of intramolecular motions (RIM) by blocking the non-radiation decay channels of single molecules.[18] But, there is another possibility that, the water molecules coming from the impurity of solvent (in some case water is directly used as poor solvent to trigger the AIE effect) or humid atmosphere can form the SWs in the nanocavity self-assembled AIEgens as emitter center (Fig. 3b). Recently, we reported that, even without any introduction of AIEgens, just in the DMSO solution, SWs can emit the same PL emission as the tetraphenylethylene (TPE) AIEgens, showing that the SWs model as emitter center could be another explanation for AIE effect.[17]

Another proof of SWs as emitters is from the preparation of the fluorescent mesoporous silica nanospheres (FMSNs) by simple surface modification without the incorporation of organic chromophores (Fig. 3c). When different organo-silane coupling agents with amino and carboxylate groups were used or even just by control of surface hydrophobicity, FMSNs can show different color from blue to red. However, when colorful FMSNs were vacuum-treated, the fluorescence is gradually lost with time. But exposing to the humid atmosphere, the PL emission of vacuum-treated FMSNs was recovered. Thus, we confirmed that, the real emitters centers of FMSNs are SWs confined in the mesopores (*ca.* 3.0 nm) of silica matrix,[19-21] reminiscent of the size and shape of the β-can of 4.2 by 2.4 nm folded by 11 β-strands of GFP (Fig. 3a). This is also the reason we concluded that, the emitter of GFP is not single p-hydroxybenzylidene–imidazolidinone (HBDI–OH) molecule, rather hydrous anionic hydroxybenzylidene–imidazolidinone complex {(HBDI–O^{-}W46) (≡R} (in the formula, W46 means H-boned water with HBDI, and ≡R means the conserved amino acid residues in the proximity of the chromophore, Fig. 3a).[17] This also probably answers that the PL properties of GFP are extremely sensitive to the surrounding environment of chromophores, in particular, such as the architecture of the β-barrel, a delicate change of amino acid residues, and the pH value.[22]

Theoretical elucidation for P-band intermediate states with a three-dimensional electron gas model

Obviously, due to the strong electrostatic repulsion between O atoms with lone electron pairs, free water molecules cannot form π-electron delocalization. However, if the water molecules are physically or chemically confined in subnano- or nano-systems, the overlaps of atomic orbitals could happen by space interactions.[23] To evaluate the reliability of PBIS model in theory, we propose a three-dimensional free electron model in which the valence electrons of the conjugate water chain formed though the overlaps of *p* orbitals of O atoms are assumed to move freely in a cylinder with a length of d and a radius of a (Fig. 4a). By solving the Schrödinger equation (equation 1, Fig. 4a), the wave function (Ψ, equation 2, Fig. 4a) and transition energy (E_r and E_z, equation 3 and 4, Fig. 4a) of the confined electrons can be calculated using a cylindrical free electron gas model.[24]

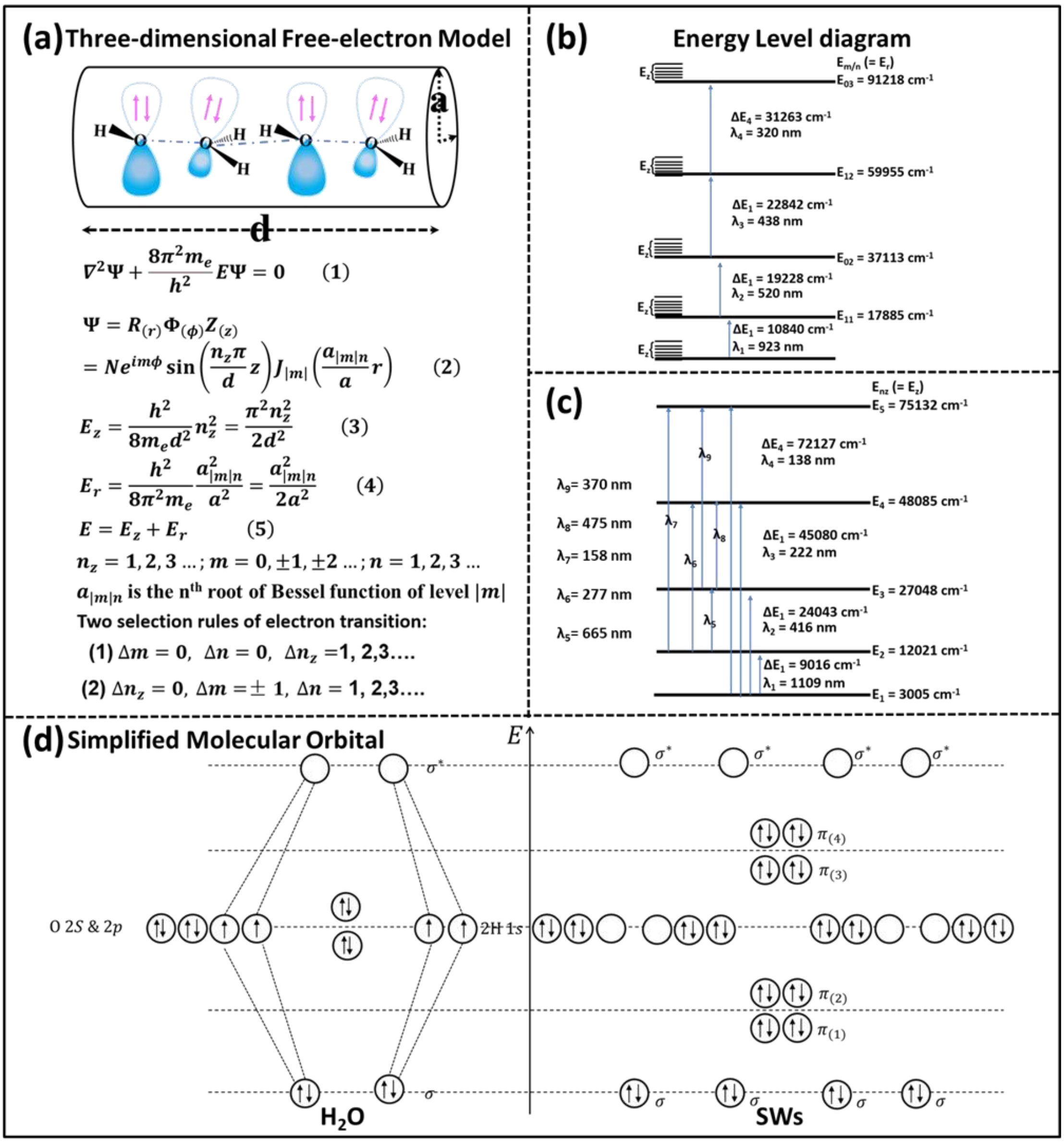

Figure 4. The nature of chemical bonding of structure water molecules (SWs). (a) The wave function (Ψ) and energy level (E_r and E_z) of electrons confined in 3-dimensional potential box and its selection law of electron transitions by solving the Schrödinger equation; (b) and (c) Energy level diagrams calculated with 3-dimensional electron gas model with a = 5.0 Å (b) and d= 10 Å (c); (d) simplified energy level diagrams of molecular orbitals for single water molecule (Left) and structural water molecules (SWs) composed of water dimmer (Right). Detailed solution process of Schrödinger equation see ref. 24.

Taking Ag NCs@LTA as a typical example (Fig. 2c and 2d), we made a simple theoretical calculation since we have verified that two types of SWs with red color (CC-SWs, Type I) and green-yellow (PC-SWs, Type II) are confined in the β cages (the radius in size range of 2.5 ~3.3 Å) and α cages (the radius in size range of 5.0 ~5.5 Å), respectively. If we simply consider α cage as a three-dimensional cylindrical box with length of 10 Å and the radius of 5.0 Å, the energy level diagram can be drawn based on the quantum calculation (Fig. 4b and 4d). Using the same method, the absorption spectra of SWs in the β cage (CC-SWs, Type I) can also be calculated, and all the sorption bands are listed in Table 1. These are consistent with the experimental results observed in absorption spectra (Fig. 2c), which typically have multiple absorption bands in a broad range from UV-visible to even near-infrared region for the SWs in the confined system (Table 1).[10] This calculation also answers why the noble metal NCs often shows the large wavelength near-infrared PL emission and very large Stokes shift (Fig. 2d), because the presence of multiple adsorption bands provides more alternative transfer or decay channels of excited state electrons. In fact, three-dimensional electron gas model was not only used to calculate the interfacial delocalized state or three-dimensional surface state of SWs in the confined systems, but also previously was used to successfully calculate the adsorption spectra of the amylose-iodine complex.[24] The calculated results can also be understood from the viewpoint of molecular orbital (MO): the σ bond of O-H bond in SWs could be weakened due to the formation of multi-atom π bonds in the water chain where the electrons of fully occupied π* antibonding orbital can fill into the σ* antibonding orbital of O-H Bonds (Fig. 4d). This probably answers the extremely low dielectric constant of water confined in the 2D cavity in graphite with a nominal height of ~6.7 Å,[25, 26] and also the origin of spontaneous generation of hydrogen peroxide on the bubble interfaces from aqueous microdroplets.[27-29]

Table 1. Comparison of calculated adsorption bands with experimental observed values using Ag@LTA zeolites as an example with the β cages (the radius in size range of 2.5 ~3.3 Å) and α cages (the radius in size range of 5.0 ~5.5 Å).

Item	a/d (Å)	λ_1 (nm)	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	λ_8	λ_9
Calculation	a = 3.0 Å	332	187	158	115					
	a = 3.3 Å	402	227	191	139					
	a = 4.0 Å	590	333	280	205					
	a = 5.0 Å	923	520	438	320					
	a = 5.5 Å	1116	629	530	387					
Calculation	d = 5 Å	277	104							
	d = 10 Å	1109	416	222	138	665	277	158	475	370
	d = 20 Å	4436	1663	873	554	380	277	211		
	d = 30 Å	4990	3743	1996	1247	855	623	475	374	302
Experimental (Ag NCs@LTA zeolite)	**α cage (5.0~5.5 Å)**	**270**	**315**	**370**	**405**	**430**				
	β cage (2.5~3.3 Å)	**278**	**300**							

The proposal of structural water molecules dominated P-band intermediate state model forces us to rethink the physical essence of nanoconfinement and nanoconfinement catalysis. In a broad sense, nanoconfinement is just a size effect, which locates at the boundary between micro and macro scales. The quantum calculation with three-dimensional cylindrical free electron model indicates that as long as electrons are confined in nano or subnano spaces in any directions, they will exhibit the quantum characteristics, like molecules having a definite electron motion trajectory and energy levels. Therefore, the physical and chemical essence of confinement is a microscopic motion state of electrons, which can be considered as a 'supermolecule', where the confined electrons have a fixed movement state and energy level. In fact, confinement refers to a strong interaction between host and guest molecules at mesoscale, here host could be any nanomaterials. This answers why the performance of nano catalysts is strongly dependent on the structural feature, such as the particle size, crystal facet effect, morphology, composition etc. But, they overlooked the contribution of surface adsorbate molecules and orbital interactions between adsorbate molecules to the catalytic active centers (Fig. 5a).

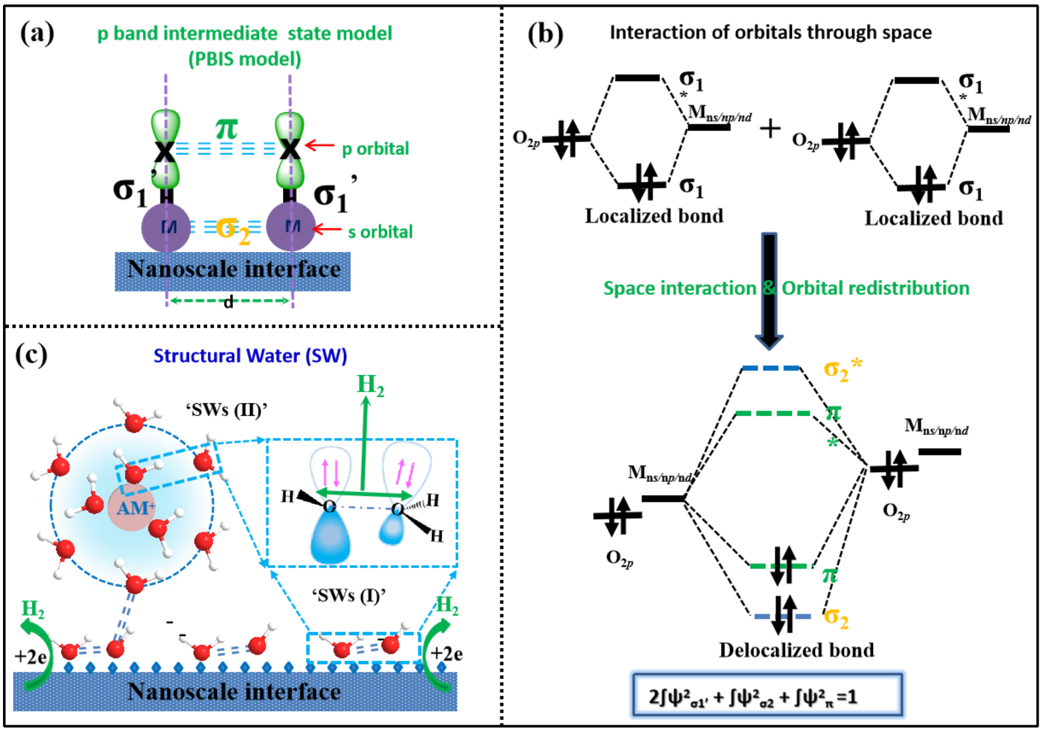

Figure 5. Physical nature of nanoconfined catalysis. (a) The construction of P-band intermediate states (PBIS) at nanoscale interface where a pair of chemical adsorption bonds (σ_1) can split into four chemical bonds of two σ_1' bonds, one σ_2 bond and one π bond, and we call the energy level of π bond as P-band intermediate state, where the old bond (σ_1) is not completely broken, and the new bond (σ_2 and π bond) is not completely formed, which is very similar to the transition state (TS) of chemical reaction, and according to quantum conservation, the sum of four orbitals ($\mathbf{2\int\psi^2_{\sigma1'} + \int\psi^2_{\sigma2} + \int\psi^2_{\pi} = 1}$) is equal to 1 (b), suggesting that the redistribution of four molecular orbitals is competitive; (b) Understanding the formation of PBIS from the perspective of Molecular orbital, we call it a new surface or interface delocalization, differing from conventional coujugated π bonds. Obviously, the PBIS provides more alternative channels for surface electron transfer. (C) Structural water molecules (SWs) at confined nanoscale interface could act as a bridge to accelerate the electron transfer though interface delocalization, thus enhancing the reaction kinetics of HER as a typical example.[30]

Application of P-band intermediate state theory in confined nanocatalysis

In both experiment and theory, we validated the rationality of the concept of structural water as a chromophore (or emitter) and answered the century long debate on whether water molecules emit color and how it is colorful.[13, 14] The proposal of the concept of SWs actually implies that water not only has hydrogen bonding interactions, but also there is multiple atomic π bond interactions in the confined system, where due to spatial interactions, O atoms in SWs can form multiple atom π bonds, we called it P bands, a new type of interface delocalization. The formation of PBIS means that there are more transfer paths for surface electrons at nanoscale interfaces (Fig. 5a and 5b). Form the viewpoint of reaction kinetics, the reaction can be carried out through pathways with lower activation energy. By coupling the quantum conservation and the molecular orbital theory, we propose a simple mathematical equation ($\mathbf{2\int\psi^2{}_{\sigma1'} + \int\psi^2{}_{\sigma2} + \int\psi^2{}_{\pi} = 1}$) to describe the interaction between valence electron orbitals of molecules or atoms adsorbed on the nano interface (Fig. 5b), and the core feature of this equation is that there is competition between the interactions of these delocalized orbitals. For example, if considering σ_1 is chemical adsorption bond (perpendicular to interface), PBIS (parallel to interface) can regulate the strength of chemical adsorption bonds, i.e., the stronger π bonds, the weaker σ_1' (Fig. 5a and 5b).[15] It suggests that PBIS as catalytic active site can regulate the adsorption strength of reactant and hence change the reaction kinetics as the classical Sabatier principle described. In addition, according to the symmetry matching principle of molecular orbital, the preferential interaction between PBIS and reaction substrates with the same symmetry orbital can improve the selectivity of the catalytic reaction. Below, several typical redox reactions are listed to demonstrate how the PBIS theory affects the three key evaluation parameters of catalysts, including activity (conversion rate), selectivity, and lifetime (stability) (Fig. 6).

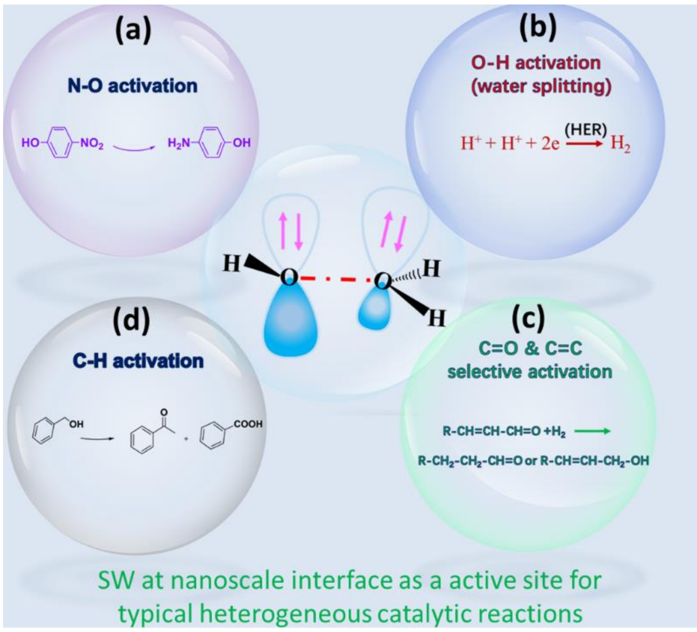

Figure 6. Typical oxidation and reduction reactions mediated by P-band intermediate state.

With the most widely used catalytic hydride reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as a model reaction (Fig. 6a), we demonstrate that structural water molecules (SWs) adsorbed on noble metal NPs in the form of $\{OH^{-}\cdot H_2O@\text{Metal NPs}\}$ is the real catalytically active site (not metal NPs alone).[31, 32] The isotope labeling and kinetic isotope effect (KIE) experiments of heavy water and $NaBD_4$ proved that the reduction of 4-NP does not follow the classical Langmuir–Hinshelwood (L–H) bimolecular mechanism, but an interfacial SWs dominated electron and proton transfer mechanism.[33, 34] The proposed mechanism explains why the dissociation of the O–H bond of water is the rate-determining step (RDS) of 4-NP reduction, and, counter-intuitively, the solvent water is the hydrogen source of final product 4-AP, instead of sodium borohydride ($NaBH_4$) reducer.[35, 36]

Another interesting example with SWs as catalytic active sites is the hydrogen evolution reaction (HER) at basic conditions ($pH > 7.0$). With Co-C-N as an prototype electrocatalyst, we clearly demonstrates that the reaction dynamics of HER does not follow the classical two-step process of Volmer step and Heyrovsky step (or Tafel step), while working the P-band mediated electron transfer process for the direct activation of O-H bonds of water.[37] We unambiguously identified that the structural water molecules (SWs) in the form of hydrous hydroxyl complexes absorbed on metal centers $\{OH_{ad}\cdot H_2O@M^{+}\}$ were catalytic active sites for the enhanced HER, where M^{+} could be transition or alkaline metal cations (Fig. 5c). When the ratio of the OH^{-}/H_2O is close to 1:1, the Co/NC nanocatalyst shows the best reaction performance under the condition of high-pH electrolytes, e.g., an overpotential of only 232 mV at a current density of 10 mA cm^{-2} in the 1 M KOH electrolyte. In addition, we first show another possible pathway for water activation under alkaline conditions ($pH > 7.0$) where it does not pass the M-H step, but rather a direct metal-non-contact activation pathway (Fig. 5c): SWs adsorbed on metal cations can directly interact with the water reactants, owing to the space interaction of p orbitals of O atoms in SWs and water reactants, the energy level of the formed p band anti-bonding level (π^*) is even higher than that of the σ anti-bonding (σ^*) of O-H bonds in water, thus the electron can be directly fill with σ^* energy level, resulting in the O-H bond activation and subsequent hydrogen evolution reaction (Fig. 4d and Fig. 5c).[6, 37] Thus, we concluded that, the catalytic active sites of 4-NP reduction and HER are not just the metal itself, but also the complex of metal and SWs, where SWs act as a bridge to accelerate surface electron transfer through interface delocalization of PBIS, thus enhancing reaction kinetics via the inner-coordination sphere electron transfer route.

PBIS can not only accelerate the reaction rate by promoting electron transfer, but also improve the selectivity of chemical reactions. The selective hydrogenation of cinnamyl aldehyde (CAL) to cinnamyl alcohol (COL) and hydrocinnamaldehyde (HCAL) is a perfect example due to the close bond energy between the conjugated C═O and C═C double bonds (Fig. 6c). Recently, just by simply tuning the interfacial microenvironment of catalytic active site of Pt@P25 catalysts with the selective adsorption of organic additives, the selective transformation of C═C and C═O groups of cinnamaldehyde (CAL) was achieved.[38] We demonstrate that the catalytic performance of selective hydrogenation of CAL is strongly dependent on the nature of interface states, rather than the crystal structure of titania (TiO_2). The parent Pt@P25 and sodium formate (HCOONa) covered Pt@P25 catalysts exhibit the preferred hydrogenation of C═C double bonds, i.e., the production of HCAL, because of the blocking of Pt active sites by the spontaneously formed interfacial carbonate species and formate anions, which suppresses the adsorption of C═O groups of CAL. In the basic solution (CH_3ONa and NaOH), due to the competitive binding of hydroxide groups (OH^-) with carbonate or organic species at Pt NPs, a new surface state in the form of hydrated hydroxide complex, i.e., PBIS, is formed though space overlapping of *p* orbitals of O atoms, which promotes the favorite interaction of C═O groups of CAL, preferentially resulting in the production of COL. The key to the favored hydrogenation of C=O functions is the spatial overlapping of *p* orbitals of O atoms in SWs and carbonyl groups due to the orbital symmetry matching, which weakens the energy of C=O double bonds, leading to COL as the main product. To further test the generality of PBIS theory, we recently demonstrated that, the selective hydrogenation of CO_2 to the products of C_1 and/or C_1^+ can also be achieved by following the interfacial SWs dominated reaction route.[39]

The core of redox chemistry is how to manipulate the electron transfer at heterogeneous nanoscale interfaces. With the high-temperature gas-phase selective oxidation of alcohols to aldehydes, especially benzyl alcohol-to-benzaldehyde as a model oxidation reaction (Fig. 6d), we show that how regulates the interface state of Au NPs catalyst to achieve its high activity and high selectivity with long lifetimes. At present, the only way to control catalyst lifetime is to optimize the adsorption strength of reactants, intermediate species or products on the catalyst surface, which usually follows the classic Sabatier principle. One of the biggest advantages of P-band theory is that it can regulate the adsorption intensity of adsorbates and metal active centers at the molecular level through the spatial overlap of *p* orbitals. Due to the chemical adsorption bonds (σ_1) competing with π bonds formed by PBIS in the equation (Fig. 5a and 5b), constructing targeted P-band centers on metal core can optimize the adsorption intensity of surface adsorbed species at nanoscale interfaces. With this idea, we deigned the thiol group covered Au NPs catalysts.[40] Strikingly, the Au/DMSNs-4.4%SH catalyst with low loading weight of Au (~2%) and thiol ligand (~4.4%) achieved high conversion of benzyl alcohol (*Conv.* 91%) and selectivity for benzaldehyde (*Sel.* 98%) and unprecedented long lifetime up to 820 h at 250 °C, which surpassed all the reported Au based nanocatalysts.[41, 42] We clearly showed that, the new PBIS state formed by the overlapping *p* orbitals of S and O atoms in thiol, silanol, and hydroxyl groups (adsorbed on Au NPs) regulates the adsorption strength of benzyl alkoxide intermediates, promotes the diffusion of reactants, avoids the formation of carbon deposition, and thus accelerates the reaction kinetics.

Moving forward

The concept of structural water molecules (SWs) as bright color emitters makes us to redefine the interactions between water molecules, especially under confinement conditions, in addition to traditional hydrogen bonding, there is also another type of interaction, i.e., multiple atomic π bonding interaction owing to the spatial overlapping of *p* orbitals of the oxygen atoms in SWs, we called it P-band intermediate state (PBIS).[15, 17] The calculation of three dimensional free electron gas model shows the rationality of PBIS theory, and it showed that P-band theory is not just limited to water molecules, but also includes any other heteroatoms or molecules containing *p* orbitals.[43]

In particular, the proposal of SWs dominated PBIS theory provides nobel insights into the physical origin of photoluminescence emission of low-dimensional quantum nanodots and the physical nature of nanoconfinement and nanoconfined catalysis. For example, we give a clear definition on the nanoconfinement for the first time: the confinement is a state of electronic motion between the host and guest molecules (or atoms) on the mesoscopic scale at the boundary of the micro and macro levels, with determined orbitals and energy levels. In other words, the host and guest can only be viewed as a whole, and it can be called the 'supermolecule', or in the heterogeneous catalysis, often called the 'nanoreactor'. Thus, in zeolite chemistry, the 'hydrocarbon pool' often mentioned for the methanol-to-olefins (MTO) conversion can be directly understood as a nanoreactor, where the catalytic active center of solid acid catalysts not only includes the zeolite host, but also includes the adsorbed guest molecule, i.e., hydrocarbon intermediate species. This answers why the topological structure of the zeolites, the size and shape of the pores, the type, distribution and strength of the acid center, and the type of the doping heteroatoms in the frameworks of zeolites synergistically determine the final reaction pathway, i.e., via the olefin or aromatic conversion path.[44-47] From the molecule vista vision,[30] upon the formation of 'hydrocarbon pool', the route of the electron and hydrogen transfer during the reaction process is determined.

Inspired by structure water molecule model dominated by PBIS model, in our opinions, two research domains should be concerned: (1) Considering the ubiquitous existence of water in nature, especially preferred adsorbed at nano interfaces, the physical origin of PL of all the low-dimensional quantum dots (including carbon nanodots, semiconductor quantum dots and Perovskite quantum dots etc.) and nontraditional chromophores without conjugated structures has to be reexamined; (2) The design of novel heterogeneous nanocatalysts should not only focuses on the optimization of catalytic active center or support, but also the construction of surface or interface state at nanoscale interface. Finally, we finish this Perspective article with one word as such 'confined spaces, no limits', in Chinese, which means 'Xian Yu Kong Jian, Tian Di Wu Xian'.

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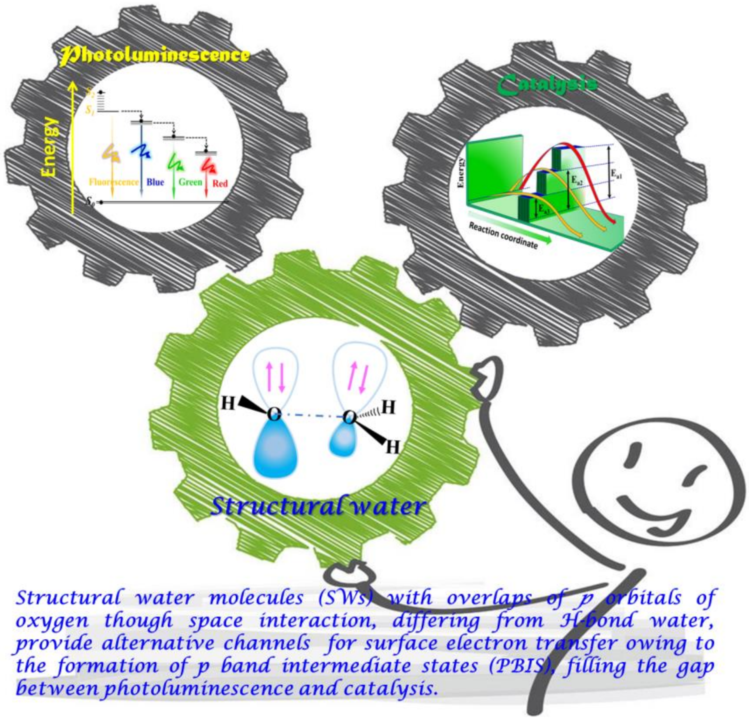
TOC



Structural water molecules (SWs) with overlaps of p orbitals of oxygen though space interaction, differing from H-bond water, provide alternative channels for surface electron transfer owing to the formation of p band intermediate states (PBIS), filling the gap between photoluminescence and catalysis.