Engineering the surface charge states of nanostructures for enhanced catalytic performance

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Charge transfer typically takes place between the catalyst surface and the reaction species, accompanied by species adsorption and activation. The surface charge state of the catalyst thus becomes a major factor for tuning catalytic performance in addition to surface active sites. By tailoring the surface charge states, the reaction activity and selectivity can be tuned to optimize the performance of a specific catalytic application. In this review, we focus on the recent progress in materials design concerned with the modification of surface charge states toward enhanced catalytic performance. With the active sites categorized into metal and semiconductor surfaces, we outline the strategies for tailoring the surface charge states of metal and semiconductor catalysts, respectively, which are mainly based on interfacial electronic effects with various contact matters. The surface charge engineering approach has been implemented in a variety of model catalytic reactions including catalytic organic reactions, electrocatalysis, photocatalysis and CO oxidation reaction. The fundamental mechanisms behind each case are elucidated in this article. Finally, the major challenges and opportunities in this research field are discussed.

1. Introduction

Catalysis is the process of increasing the rate of a chemical reaction by lowering the required activation energy. The ultimate goal of catalysis is to achieve a high-efficiency and product-specific process in the reaction. The catalyst, an additional substance participating in the reaction, is the key to achieving this goal. Heterogeneous catalysis, which employs solid materials as catalysts enabling easy product separation, has been widely implemented in chemical manufacturing. It is well known that a catalytic reaction always occurs on the surface of heterogeneous catalysts. The catalytic performance is thus related to the surface state of the catalysts. In the past decade, great efforts have been made to optimize the design of catalytic materials by tailoring their shapes, sizes and structures. The central theme in this research is to engineer the surface active sites where catalytic reactions take place from the viewpoint of geometric effects. It is worth mentioning that nanomaterials have received tremendous

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Attention simply because the number of surface active sites can be dramatically boosted by shrinking particle sizes to the nanoscale.

In addition to active site engineering, electronic structure is another factor to which we should pay sufficient attention.\(^7\)\(^-\)\(^{11}\) The charge transfer between the catalyst surface and reactants is generally involved in various reaction models including photocatalysis,\(^12\)\(^-\)\(^{14}\) electrocatalysis,\(^15\),\(^16\) catalytic organic reactions and gaseous reactions.\(^17\),\(^18\) For this reason, the electronic structures of catalysts would significantly affect their interactions with reaction species particularly in the case of catalyst-reactant charge transfer. The surface charge state is one of the critical parameters to depict the electronic structures of catalysts. To this end, engineering surface charge states would endow catalytic nanostructures with unique functions in reactant adsorption and activation.

Upon identifying the importance of surface charge states to catalysis, a question naturally arises: how can the surface charge states be tailored? Interfacing the catalyst with another material has been proven as a versatile approach to engineer surface charge states. Metal nanocrystals are widely used in a variety of catalytic reactions owing to their strong interactions with the reaction species.\(^19\)\(^-\)\(^{22}\) In order to enhance their catalytic performance, various configurations for integrating different components together have been developed,\(^23\),\(^24\) which exhibit excellent performance that differs from bare metal catalysts. For instance, noble metals Pd and Pt are generally considered as active catalysts in various catalytic reactions for their high capability in molecular activation.\(^25\),\(^26\) Integrating with a semiconductor to form a Schottky junction or with another metal for interfacial charge polarization is an effective way to further improve the catalytic activity of metal catalysts, in which the static interfacial electronic effects originating from the difference of work functions can tailor the surface charge states of metal catalysts.\(^15\)\(^-\)\(^{17}\) Furthermore, light illumination may supply photoexcited electrons or plasmonic hot electrons to the metal surface, increasing surface charge density for catalytic reactions as a dynamic effect.\(^27\) In a specific case demonstrated by Park, Somorjai and Nedrygailov, nonadiabatic electronic excitation can be generated to supply a flow of energetic electrons, which are not in thermal equilibrium and are called “hot electrons”, for exothermic catalytic reactions.\(^28\)\(^-\)\(^30\) The hot electrons would be irreversibly transported across the metal–semiconductor interface toward metal catalysts for catalytic reactions, enabled by the localized Schottky barrier.

Another class of heterogeneous catalysts with lower material cost than noble metals are oxides and chalcogenides that possess semiconductor characteristics. As heterogeneous catalysis usually includes three steps – adsorption, activation and desorption – surface electron density plays a similar role in tuning the performance of semiconducting catalysts to the cases of metal catalysts.\(^31\) For ultrathin two-dimensional semiconducting nanomaterials, surface electron density can be increased to promote the adsorption and activation of reactants on account of their disordered atomic structures.\(^32\) Moreover, introducing defects into the nanomaterial surface can enhance the concentration of carriers near the defects, which in turn reduces the catalytic capability in molecular activation.\(^25\),\(^26\) Integrating with a semiconductor to form a Schottky junction or with another metal for interfacial charge polarization is an effective way to further improve the catalytic activity of metal catalysts, in which the static interfacial electronic effects originating from the difference of work functions can tailor the surface charge states of metal catalysts.\(^15\)\(^-\)\(^{17}\) Furthermore, light illumination may supply photoexcited electrons or plasmonic hot electrons to the metal surface, increasing surface charge density for catalytic reactions as a dynamic effect.\(^27\) In a specific case demonstrated by Park, Somorjai and Nedrygailov, nonadiabatic electronic excitation can be generated to supply a flow of energetic electrons, which are not in thermal equilibrium and are called “hot electrons”, for exothermic catalytic reactions.\(^28\)\(^-\)\(^30\) The hot electrons would be irreversibly transported across the metal–semiconductor interface toward metal catalysts for catalytic reactions, enabled by the localized Schottky barrier.

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energy barrier.\textsuperscript{33} Another approach to surface charge engineering is the interfacial charge polarization between the metal and the semiconductor that enriches electrons on the surface of the semiconductor, which can facilitate molecular activation.\textsuperscript{18} Overall, the increased charge density on the semiconductor surface can accelerate reactant diffusion, reduce reaction activation energy and facilitate molecular activation in heterogeneous catalysis.

Taken together, tailoring surface charge states should be a versatile approach to tuning the catalytic performance of both metal and semiconductor catalysts. In this review article, we will outline the recent progress in engineering the surface charge states of catalytic nanostructures toward enhanced catalysis, together with the fundamental mechanisms behind each case. The implemented catalytic reaction systems include organic catalytic reactions, electrocatalysis, photocatalysis and CO oxidation reaction. From the working mechanisms, the readers can recognize how surface charge states can be maneuvered and in turn alter catalytic performance, and be able to design catalytic nanostructures for specific applications through electronic effects.

To elucidate the fundamental mechanisms, we categorize the catalytic materials by their electronic structures into metals and semiconductors. We first summarize the methods for tuning the surface charge states of metal catalysts mainly based on interfacial electronic effects with various contact matters – semiconductors, metals and organic ligands. Then the approaches to tunable surface charge densities in semiconductor catalysts – creating defects in ultrathin two-dimensional nanostructures, and interfacing with metals – will be outlined. In order to have a comprehensive overview on this topic, both static (i.e., interfacial charge polarization) and dynamic (e.g., Schottky junction and surface plasmon under light illumination) effects will be discussed in this article. Finally, we point out the existing challenges in terms of engineering the charge state in the current research and the opportunities open for this research field. Organized succinctly, this review article will deepen the readers’ understanding of the structure–property relationship in various catalytic systems and provide a bridge between material design and catalytic applications from the viewpoint of electronic effects, which hence puts forward a new direction in terms of optimizing catalytic properties.

\section*{2. Engineering the surface charge states of metal catalysts}

The charge state on the surface of metal nanocrystals plays a regulatory role in the state of adsorbed molecules, which in turn affects the adsorption and activation of reactants,\textsuperscript{17} thereby leading to tunable catalytic properties. Unfortunately, the charge state of a specific metal surface is largely restricted in a certain range. For this reason, one has to tailor the surface charge states by introducing electrons to the surface of metal catalysts.\textsuperscript{34} As a matter of fact, integrating with another nano-material is an effective means of regulating the surface electron densities of metals.\textsuperscript{35–38} This section mainly describes how the catalytic activity can be tuned by tailoring the surface charge states of metal catalysts.

\subsection*{2.1 Interfacing with semiconductors}

As a metal catalyst is in contact with a semiconductor, their different electronic structures will drive an electron diffusion process to build up an equilibrium state. The electronic structures of both metal and semiconductor materials can be depicted with work functions ($W$), which represent the minimum required energy to elevate an electron from the Fermi level ($E_f$) to the vacuum level ($V_{ac}$).\textsuperscript{39} For noble metals Pt and Pd, their work functions are typically larger than those of n-type semiconductors, but smaller than those of p-type semiconductors.

The Fermi level of the n-type semiconductor ($E_{fn}$), which stands near the conduction band edge ($E_c$), is higher than the Fermi level ($E_{fm}$) of the metal before their contact. Thus an equilibrium state between the $E_{fs}$ and $E_{fm}$ should be established when they are put in contact. As a result, the electrons of the semiconductor will diffuse to the metal at the lower energy level, leading to the accumulation of negative charges (Fig. 1a). This electron diffusion process will deplete the free electrons in the semiconductor near the interface, forming a space charge region. As such, the energy band of the n-type semiconductor will bend upward to establish a Schottky barrier.\textsuperscript{10} Apparently, the process of forming the Schottky barrier with the n-type semiconductor will increase the electron density of the metal.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{Fig_1.png}
\caption{Schematics illustrating the processes of forming the Schottky junction between a metal and (a) an n-type semiconductor or (b) a p-type semiconductor. Reproduced with permission from ref. 12. Copyright 2015 Royal Society of Chemistry.}
\end{figure}
component as a static effect. In the case of a p-type semiconductor, the band alignment and electron diffusion fall into a different situation (Fig. 1b). The $E_\text{g}$ of the p-type semiconductor is close to the $E_\text{F}$, and $E_\text{g}$ is lower than $E_\text{F}$. For this reason, the free electrons on the metal will flow to the semiconductor upon their contact. This process can bend the energy band of the p-type semiconductor downward to form a space charge region, and accumulate positive charges on the metal component.  

Given this static interfacial electronic effect, it is anticipated that semiconductor supports may play a role in tailoring the surface charge states of metal catalysts. As a matter of fact, n-type semiconductors have been widely used as supports for metal catalysts in various organic reactions. Most recently, Zheng et al. developed a stable atomically dispersed Pd–TiO$_2$ catalyst (namely, Pd$_1$/TiO$_2$) in which single Pd atoms are stabilized with ethylene glycolate (EG) on ultrathin TiO$_2$ nanosheets (Fig. 2a and b). This catalyst exhibits 9 times higher catalytic activity in hydrogenation of C–C bonds than commercial Pd catalysts in terms of surface Pd atoms (Fig. 2c). It is believed that the static electronic effect plays an important role in the catalytic performance enhancement. As suggested by first-principles simulations (Fig. 2d), the Pd atoms supported on TiO$_2$ can efficiently split hydrogen into H atoms. While one H atom migrates to the EG nearby, the other H atom would form Pd–H* which can in turn transfer to C–C for efficient hydrogenation.

In general, the enhancement of catalytic activities by semiconductor supports is not very significant as the static interfacial electronic effect can only accumulate a limited number of electrons on metal catalysts. To make full use of the Schottky junction for enhanced catalysis, one can employ light illumination to excite the n-type semiconductor and transfer a large number of electrons to metal catalysts as a dynamic interfacial electronic effect. Under light illumination, the electrons in n-type semiconductors are elevated to the conduction band while the holes are left in the valence band. Once the electron-hole pairs enter the space charge region, the photogenerated electrons in the conduction band and the holes in the valence band will migrate to the bulk semiconductor and the metal under the effect of an internal electric field, respectively. Under the successive photoexcitation of the semiconductor, a large number of electrons will be accumulated in the semiconductor, making them energetic enough to transfer to the metal. The Schottky barrier will in turn prevent the electron from drifting back to the semiconductor. As such, the electron density of the metal surface can be increased. Similarly, photoexcitation can substantially reduce the electron density of the metal surface when a p-type semiconductor is used as a support.

Here we employ oxygen activation on a Pd surface as a model reaction to demonstrate the mechanisms. For most oxidation reactions, the activation of molecular oxygen is an important process determining catalytic performance. The molecular adsorption is a process that highly depends on the atomic arrangement and charge state of the catalyst surface. In 2013, we found that molecular oxygen can be better activated at the Pd{100} surface than Pd{111}. As shown in Fig. 3a and b, the molecular O$_2$ is better activated on Pd{100} according to the larger O–O bond length (1.402 Å on {100} versus 1.324 Å on {111}), which has been verified by synchrotron radiation-based near-edge X-ray absorption fine structure spectroscopy (NEXAFS). During the activation process, an electron transfer takes place from Pd to O$_2$ molecules. The transferred electrons occupy the antibonding orbital of oxygen so as to activate the molecule. In principle, the more electrons are transferred, the better oxygen is activated. The spin charge density analyses (Fig. 3c and d) revealed that about 0.7 electrons can be transferred from the Pd{100} surface to the adsorbed O$_2$, while the charge transfer in the case of Pd{111} was only ~0.4 electron charge. Thus the different amounts of electrons transferred into the anti-bonding $\pi^*$ orbital of O$_2$ should be the fundamental reason for the differentiated O$_2$ activation behavior. For this reason, the catalytic performance of Pd{100} in O$_2$ activation and oxidation reactions can be further enhanced by increasing its electron density. As displayed in Fig. 3e, higher electron density of the Pd surface enables the stretching of O–O bonds, leading to better O$_2$ activation. To increase the electron density of the Pd surface, we developed Pd–TiO$_2$ hybrid structures (Fig. 4a and b) in which TiO$_2$ can be used as the electron donor to modulate the charge state of the Pd surface under light illumination owing to the metal–semiconductor Schottky junction. We have employed 2,2,6,6-tetramethyl-4-piperidone hydrochloride (4-oxo-TMP) as a probe molecule to examine the activated oxygen species, which can produce nitroxide radicals (4-oxo-TEMPO) upon trapping the oxygen species. The electron spin resonance (ESR) spectra in Fig. 4c show that the signals for 4-oxo-TEMPO can be enhanced.

![Fig. 2](image-url) (a) TEM and (b) HAADF-STEM images of a Pd$_1$–TiO$_2$ catalyst. (c) Catalytic performance of Pd$_1$–TiO$_2$ and reference catalysts in styrene hydrogenation. (d) Energies and models of intermediates and transition states in the heterolytic H$_2$ activation process for Pd$_1$–TiO$_2$. Reproduced with permission from ref. 44. Copyright 2016 American Association for the Advancement of Science.
with the Pd–TiO₂ hybrid structures compared with bare Pd. This suggests that integrating the Pd{100} catalyst with an n-type semiconductor surely promotes the ability of Pd in activating O₂. When implemented for catalytic oxidation of glucose, the Pd–TiO₂ catalyst exhibits excellent catalytic activity in glucose oxidation under illumination, especially at the light intensity of 5.6 mW cm⁻² (Fig. 4d). Certainly a strong dependence of performance on light intensity has also been observed. The complex charge kinetics in this system has been revealed by our ultrafast absorption spectroscopy characterizations.²⁷ It indicates that too strong light illumination may induce the generation of plasmonic hot electrons on Pd although it is a metal with weak plasmonic properties.⁵³,⁵⁴ The generated plasmonic hot electrons are injected into the conduction band of TiO₂, which lowers the electron density of the Pd surface and reduces the efficacy of the Schottky junction in enhancing O₂ activation.¹²,¹⁴,²⁷ Nevertheless, this case well demonstrates that the dynamic interfacial electronic effect by the metal–semiconductor interface under light illumination can provide a powerful approach to tailor the surface charge states of metal catalysts.

2.2 Interfacing with metals

The electron density of a metal surface can also be tailored by interfacing with another metal material. The mechanism is quite similar to the principle of a galvanic cell (also called voltaic cell) – an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. The voltaic pile, invented by Alessandro Volta in the 1800s, consists of a pile of cells with different metals (e.g., Cu and Zn). The potential difference of metals is utilized to induce electron accumulation at the metal side with a high work function, eventually generating electricity in the devices. We call this effect interfacial charge polarization. For instance, the work functions of Pd{100} and Pt{100} are 5.14 and 5.68 eV, respectively. This work function difference causes an electron to transfer from Pd to Pt so as to equilibrate the electron Fermi distribution at their interface. As indicated by the simulated differential charge density (Fig. 5), distinct interfacial polarization occurs when the Pt atoms are of 1–2 atomic layers, resulting in a substantial accumulation of negative charges on the Pt surface. However, as the Pt thickness reaches 4 atomic layers, the surface polarization effect becomes substantially weaker. In other words, the thinner the thickness, the more the charges accumulated on the Pt surface. This increased electron density on the Pt surface would facilitate a number of catalytic applications.

A typical catalytic application facilitated by the interfacial charge polarization is the electrocatalytic hydrogen evolution reaction (HER, 2H⁺ + 2e⁻ → H₂) – a highly important process for hydrogen generation constituting reversible hydrogen fuel cell technology.³³–⁶¹ Pt is the most efficient electrocatalyst for the HER due to its low overpotential and high current density; however, the usage of Pt is yet to be significantly reduced to minimize material costs. Enabled by the interfacial charge polarization, we have developed an approach to reduce Pt usage and boost HER performance at the same time. As along as the Pt layers on Pd substrates are thin enough, the interfacial charge polarization can accumulate negative charges on the Pt surface to facilitate hydrogen evolution. The developed
design is based on a Pt–Pd-reduced graphene oxide (rGO) stack structure with controllable Pt thickness ranging from 0.8 nm to 3.2 nm (Fig. 6a–c). As anticipated, the Pt–Pd–rGO I sample with the thinnest Pt shells (0.8 nm) exhibits a current density of 791 mA cm$^{-2}$ at a potential of 300 mV, dramatically larger than that of the other two samples (Fig. 6d). This suggests that the low thickness of Pt shells is more favorable for HER performance. In addition, the calculated Tafel slope of 10 mV decade$^{-1}$ for Pt—Pd–rGO I is the lowest among those reported for HER electrocatalysts (Fig. 6e). This further demonstrates that the HER performance has a strong correlation with the Pt thickness, in accordance with the proposed interfacial charge polarization mechanism. Accordingly, the requirement for ultrathin Pt shells by this working mechanism also meets our demand for reducing Pt usage.

Another example sharing a similar working mechanism is the cocatalyst design for photocatalytic water splitting – a promising approach to transform solar energy into hydrogen fuel. A typical process of photocatalysis involves three steps – light absorption, electron–hole separation, and surface reactions. To improve the efficiencies of the latter two steps, metal cocatalysts are widely used for integration with semiconductor photocatalysts. The cocatalyst not only promotes electron–hole separation via the Schottky junction, but also provides active sites for H$_2$O adsorption and activation, opening the possibility of improving the overall photocatalytic efficiency.

In this case, Pt is deposited on the Pd nanocubes, which are loaded on TiO$_2$ nanosheets to form the TiO$_2$–Pd@Pt quasi-core–shell structure with controllable Pt thickness (Fig. 7a). As illustrated in Fig. 7b, this design utilizes the Schottky junction between TiO$_2$ and Pd to trap the photoexcited electrons on Pd, and then induces the electron accumulation at the outer surface of Pt through interfacial charge polarization. As indicated by Table 1, the high electron density on the Pt surface can enhance the adsorption of H$_2$O molecules and thus facilitate the water splitting process.

The effect of interfacial charge polarization can make a significant contribution to the electron accumulation on the Pt surface only when the Pt shell thickness is less than 4 atomic layers.
The increased electron density has been proven by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using CO as a probe molecule. During the chemisorption, the CO molecules can accept electrons from the Pt surface to enter their antibonding orbitals. At higher electron density, the Pt surface would donate more electrons to the antibonding orbitals of CO molecules, which reduces the vibrational frequency of CO. Fig. 7c shows that the vibrational frequency for CO chemisorption has been lowered by the TiO$_2$–Pt/Pt$_{3L}$ with 3 atomic Pt layers. This suggests the higher electron density of the Pt surface with respect to TiO$_2$–Pt and TiO$_2$–Pt/Pt$_{3L}$. The increased electron density can also be confirmed by the reduced binding energies in X-ray photoelectron spectroscopy (XPS). As a result, the accumulated electrons on the Pt surface enable a dramatically higher hydrogen production rate by TiO$_2$–Pt/Pt$_{3L}$ (Fig. 7d).

Basically, the interfacial charge polarization is a static electronic effect. Under light illumination, the surface plasmon of noble metal nanostructures will generate plasmonic hot electrons, which may induce a dynamic effect at the metal–metal interfaces. The surface plasmon can be defined as the resonant collective oscillations of the electrons excited by incident photons at the surface of noble metal Au and Ag nanoparticles, which decays through radiative photon re-emission and non-radiative Landau damping. The non-radiative decay generates energetic electrons and holes, which are commonly referred to as hot electrons and hot holes, respectively. The majority of energetic electrons are dissipated by electron–electron scattering within about 100 femtoseconds. However, a small number of energetic electrons can be transferred to adjacent species, which may alter the catalytic process by maneuvering surface charge densities.

For instance, Pd is a widely used catalyst for organic hydrogenation reactions – a large group of addition reactions of hydrogen at unsaturated bonds, which are among the simplest transformations in organic chemistry and are extensively involved in various chemical processes. The hydrogenation reactions usually take place through the dissociation of molecular H$_2$ and desorption of H atoms from the surface. As molecular H$_2$ can be easily dissociated at the Pd surface, the desorption of H$_2$ atoms from the Pd surface becomes the rate-limiting step in the process of hydrogenation reactions. Our simulation (Table 2) indicates that the binding of dissociated H atoms to the Pd surface is enhanced by the addition of one electron, regardless of the locations of H atoms on Pd nanocrystals. Thus the high electron densities on the Pd surface (e.g., through plasmonic hot-electron injection) would disfavor hydrogenation reactions.

One of our recent works proved this hypothesis, in which ultrathin layers of catalytic metal Pd are grown on plasmonic gold nanorods (Fig. 8a and b). The Pd thickness can be controlled from 2 atomic layers to tens of atomic layers. Once the plasmonic hot electrons are generated in Au, they have to travel through the Pd layers before reaching the reaction species (Fig. 8c). As such, the lifetime of hot electrons can be modulated through Pd layer thickness. We have acquired the time constant of hot electrons using ultrafast absorption spectroscopy, which can be well correlated with catalytic performance (Fig. 8d). The longer the lifetime the plasmonic hot electrons exhibit, the lower the conversion yield the catalytic reaction achieves. This suggests that plasmonic hot electrons indeed make a negative contribution to hydrogenation reactions.

The correlation of hot electron lifetime with the Pd thickness (Fig. 8d) reveals that the plasmonic hot electrons tend to interact more thoroughly with the Pd lattice by increasing Pd shell thickness. This interaction will reduce the number of hot electrons reaching the Pd surface. Nevertheless, if the Pd shells are too thick, hot electrons would be generated by the Pd shells on their own, which brings more electrons to the Pd surface. Thus the charge densities of the Pd surface can be tailored by...
controlling the Pd thickness over plasmonic nanostructures. Although plasmonic hot electrons suppress the hydrogenation reactions, this working mechanism should be implemented to promote the reactions that require high surface electron densities (e.g., oxygen activation and oxidation reactions). It is anticipated that future works will validate this assumption.

2.3 Interfacing with organic ligands

Organic ligands are key components in homogeneous catalysis which can induce significant steric and electronic effects for catalytically active metal sites to tune catalytic selectivity. In terms of heterogeneous catalysis, the organic ligands are mainly employed as the agents for improving catalytic selectivity through steric effects or the stabilizers for loading atomically dispersed metal atoms. In principle, the organic ligands should be capable of creating electronic effects on catalytic sites when the catalytic materials are shrunk to the atomic level. In recent years, it has been demonstrated that such electronic effects can indeed tune catalytic activities.

Most recently, Zheng et al. reported that electronic effects can serve as a knob for tuning the selectivity of catalytic reactions in the partial hydrogenation of nitroaromatics to N-hydroxylaniline derivatives (an important class of intermediates for many high-value products). The demonstration is based on the ethylenediamine (EDA)-chelated ultrathin Pt nanowires. The nanowires have an ultralow diameter of 1.1 nm (Fig. 9a), which allows the significant electronic effects of EDA on Pt nanowires. As indicated by Bader charge analysis (Fig. 9b), the EDA ligands can donate electrons to Pt nanowires and make the Pt surface highly electron rich. Such an increase in the electron density on the Pt surface favors the adsorption of electron-deficient reactants (i.e., nitroaromatics) and the desorption of electron-rich substrates (i.e., N-hydroxylaniline derivatives) (see Fig. 9c). As a result, full hydrogenation can be effectively prevented to achieve high selectivity in the production of N-hydroxylanilines by EDA-chelated Pt nanowires. As a matter of fact, the electronic effects by EDA ligands can be readily implemented in various Pt catalysts. For instance, when commercial Pt black is treated with Pt(EDA)2(acac)2, the Pt-EDA chelating units can be deposited on the surface. As a result, the EDA-modified Pt black catalyst exhibits a dramatically enhanced selectivity to N-hydroxylaniline derivatives (Fig. 9d and e), which are applicable to nitroaromatics with various substitutions.

As the electronic effects of organic ligands have been extensively investigated in homogeneous catalysis – the main branch in organic chemistry studied for centuries – we would envision that many concepts and findings can be borrowed from traditional organic chemistry in the future. Moreover, despite rare attempts in dynamic electronic effects, it is anticipated that some photosensitizers can be employed as ligands to integrate with heterogeneous catalysts for light-enhanced catalysis.

3. Engineering the surface charge states of semiconductor catalysts

In addition to noble metals, metal oxides and chalcogenides are a class of catalysts at lower material costs. For instance, metal oxides have been widely employed as catalysts for CO oxidation – a typical reaction well studied in heterogeneous catalysis. Many metal oxides and chalcogenides possess semiconductor characteristics, which provides an opportunity for tuning their catalytic performance through electronic effects.

3.1 Creating defects in ultrathin two-dimensional nanostructures

As the surface charge density of catalysts plays a key role in catalysis, ultrathin two-dimensional nanosheets that offer high charge density provide an opportunity for achieving high catalytic performance. Taking CO oxidation as an example, the high charge density can promote the activation of oxygen and accelerate CO diffusion, facilitating the CO oxidation process.

The high catalytic performance of ultrathin two-dimensional nanosheets is related to their large surface area, abundant active sites and high carrier concentration. For instance, SnO2 nanosheets with 5 atomic layers at the thickness of about 0.66 nm can be obtained by EDA-assisted synthesis. The unique electronic structures of the 0.66 nm SnO2 nanosheets enable their excellent activities in CO oxidation, with lower conversion temperature and lower activation energy, as compared with 1.9 nm SnO2 nanosheets, SnO2 nanoparticles and bulk SnO2. As metal oxides such as SnO2 serve as catalysts, CO oxidation generally follows the Mars van Krevelen mechanism. In this case, CO diffusion is one of the important factors that affect the catalytic activities. The density of states (DOS) and charge density contour plots show the increased charge density at the valence band of ultrathin SnO2 nanosheets (Fig. 10c–f). This feature...
would result in fast electron transport to facilitate CO diffusion so that CO can more efficiently react with the activated O atom, improving the overall performance of CO oxidation.

The atomically thin nanosheets set up a platform for further engineering the subtle features toward tunable charge densities. The surface defect is such a structural feature in ultrathin nanosheets that can further boost CO oxidation activity. Taking ultrathin CeO$_2$ nanosheets with surface pits as an example, two different kinds of coordinated Ce atoms are generated on account of plentiful surface pits: the 4-coordinated Ce atom at which CO is more likely to adsorb, and the 5-coordinated Ce atom at which O$_2$ prefers to adsorb and activate (Fig. 11a). During the formation of CO$_2$, CO should overcome a diffusion barrier to react with the adjacent O atom. The pit-surrounding Ce sites help to increase the hole carrier density by increasing the DOS near the Fermi level (Fig. 11b), thereby lowering the CO diffusion barrier. In this case, the CO adsorbed at the 4-coordinated Ce site can easily diffuse to the O atom absorbed at the neighboring 5-coordinated Ce site to produce CO$_2$. Although O$_2$ activation is the rate-determining step in CO oxidation, the reduced CO diffusion barrier caused by the increased carrier density also contributes to lowering the overall activation energy. As a result, the ultrathin CeO$_2$ nanosheets with surface pits can efficiently improve the CO oxidation rate and lower the activation energy (Fig. 11c and d). It is anticipated that lattice engineering on ultrathin two-dimensional nanostructures with semiconductor characteristics can create more efficient catalysts for other catalytic applications from the angle of electronic effects.

However, it is worth mentioning that the defects are often the centers for charge recombination particularly in the case of light illumination (i.e., dynamic charge systems). As ultra-thin two-dimensional nanostructures are further interfaced with other materials (e.g., metals), charge recombination would become more severe at the defects existing at the interfaces (i.e., interfacial defects). Thus creating defects toward tunable charge states requires systematic study in which the material models and their interlinked effects should be carefully analyzed.

### 3.2 Interfacing with metals

Similarly to the case of metal catalysts, the surface charge states of semiconductor catalysts can also be tailored through interfacial electronic effects. Here we first name an example using CO oxidation as a model reaction. Cu$_2$O/CuO is a catalyst that has been intensively investigated for CO oxidation owing to its relatively high catalytic activity. Recently we have revealed that interfacial charge polarization can enhance the catalytic activity of Cu$_2$O/CuO through integration with Ag. In the synthesis, Cu$_2$O is grown on Ag nanoplates in the solution phase, in which the coverage of Cu$_2$O on Ag can be well controlled to form tunable interfacial lengths. As a result, three Ag–Cu$_2$O samples with various partial coverage and full coverage can be obtained, while Cu$_2$O frames are prepared by removing Ag as a reference sample (Fig. 12a–e). Prior to the

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**Fig. 10**  (a) Catalytic activity for CO oxidation vs. reaction temperature for 0.66 nm SnO$_2$ nanosheets, 1.9 nm SnO$_2$ nanosheets, SnO$_2$ nanoparticles and bulk SnO$_2$ (from left to right). (b) The corresponding Arrhenius plots. Calculated density of state (DOS) for (c) 0.66 nm SnO$_2$ nanosheets and (d) bulk SnO$_2$. Charge density contour plots projected along the (100) plane for the valance band maximum of (e) 0.66 nm SnO$_2$ nanosheets and (f) bulk SnO$_2$. Reproduced with permission from ref. 32. Copyright 2013 John Wiley.

**Fig. 11**  (a) Top-view structural schematic for CeO$_2$ nanosheets with 3 atomic layers and with numerous pits on the surface. CO molecules prefer to adsorb at the P$_2$ site, while O$_2$ molecules tend to adsorb and dissociate at the adjacent P$_1$ sites. (b) Calculated densities of states (DOS) for the ultrathin CeO$_2$ nanosheets with numerous pits, ultrathin CeO$_2$ nanosheets and bulk CeO$_2$. (c) Catalytic activities for CO oxidation vs. reaction temperature and (d) the corresponding Arrhenius plots for the three catalysts. Reproduced with permission from ref. 33. Copyright 2013 Nature publishing Group.
catalytic assessment, all the samples have been treated in a cycle of CO oxidation to form a stable CuO surface. Our catalytic assessment (Table 3) indicates that the apparent activation energies can be dramatically reduced to 36.7–42.7 kJ mol\(^{-1}\) with partial coverage, which should be ascribed to the exposed Ag–CuO interfaces. Moreover, the CO conversion rates turn out to be dependent on the interfacial lengths (Fig. 12f), suggesting that the interfacial lines are the locations of active sites.

The high catalytic activity enabled by the exposed Ag–CuO interfaces has been well elucidated by our first-principles simulations. Ag and CuO possess different work functions (4.45 eV vs. 5.97 eV) to induce an interfacial charge polarization effect (Fig. 12g and h), which increases the electron density of the CuO surface near the Ag–CuO interface and dramatically decays with the distance to the interface. Consequently, the increased electron density on the CuO surface can lower the transition energy barrier from 0.60 to 0.24 eV in CO activation as indicated by our simulations. This feature designates the exposed Ag–CuO interface as the location of active sites so that the number of active sites can be readily tailored by controlling the interfacial lengths.

The interfacial charge polarization is also applicable to other materials and reaction systems. For example, MoS\(_2\) is a material with a layered structure to replace expensive Pt for electrocatalytic HER application.\(^{98–101}\) As compared with metallic 1T-MoS\(_2\), semi-conducting 2H-MoS\(_2\) is more chemically stable but exhibits relatively low HER activity. The limitation of the 2H-MoS\(_2\) catalyst originates from the limited number of active sites – the unsaturated sulfur atoms located along the edges of the MoS\(_2\) layers and the low mobility for charge transport.\(^{98,100}\) To overcome this limitation, we have developed a hybrid structure of 2H-MoS\(_2\) and Pd nanowires (Fig. 13a).\(^{102}\) As a result, the hybrid structure exhibits a current density of 122 mA cm\(^{-2}\) at \(-300\) mV versus RHE and a Tafel slope of 44 mV decade\(^{-1}\) with excellent durability (Fig. 13b and c), which well exceeds the performance of bare 2H-MoS\(_2\) and 1T-MoS\(_2\).

![Fig. 12 SEM images of (a) partial coverage I, (b) partial coverage II, (c) partial coverage III and (d) full coverage Ag–Cu\(_2\)O hybrid structures, and (e) Cu\(_2\)O frames. (f) Catalytic performance of Ag–Cu\(_2\)O/Cu\(_2\)O partial coverage I, II and III samples in Cycle 2 of CO oxidation. (g) Schematic illustration for Ag–Cu\(_2\)O/Cu\(_2\)O hybrid structures with interfacial charge polarization for CO oxidation (side view for the cross-section). (h) Differential charge density by first-principles simulations illustrating the increase (olive color) and decrease (cyan color) of electron distributions in the atomic model for the Ag(111) substrate interfacing with the extension part of the side CuO layer. Reproduced with permission from ref. 18. Copyright 2014 American Chemical Society.](image)

![Fig. 13 (a) Schematic illustration for the synthesis of a Pd NWs@2H-MoS\(_2\) hybrid structure. (b) Polarization curves and (c) the corresponding Tafel plots for the Pd NWs@2H-MoS\(_2\) hybrid structure in reference to bare 2H-MoS\(_2\), Pd NWs and Pt/C. (d) Raman spectra and (d) S L3–3-edge NEXAFS spectra of the Pd NWs@2H-MoS\(_2\) hybrid structure and bare 2H-MoS\(_2\). (f) Schematic illustrating the working mechanisms involved in the Pd NWs@2H-MoS\(_2\) HER electrocatalyst. Reproduced with permission from ref. 97. Copyright 2016 Springer.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Partial cover. I</th>
<th>Partial cover. II</th>
<th>Partial cover. III</th>
<th>Full cover. Frames</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>42.7 ± 1.3</td>
<td>37.0 ± 1.8</td>
<td>36.7 ± 1.3</td>
<td>62.8 ± 2.1</td>
</tr>
</tbody>
</table>

Table 3 Apparent activation energies \(E_a\) of CO oxidation catalyzed by various CuO/Cu\(_2\)O-based samples calculated from the Arrhenius plots employing the steady-state CO conversion data measured in the second cycle of catalytic CO oxidation. Reproduced with permission from ref. 18. Copyright 2014 American Chemical Society.
In addition to the improved charge transport by Pd nanowires, the interfacial charge polarization between 2H-MoS2 and Pd is believed to play a key role in the performance enhancement. The difference in their work functions (5.12 eV for Pd vs. 6.53 eV for MoS2) induces the accumulation of negative charges on MoS2 through charge polarization at the Pd–MoS2 interface. XPS characterization indicates that the increased negative charges are donated to the S sites of 2H-MoS2. This argument has been further supported by Raman spectroscopy and NEXAFS spectroscopy. The increased electron density stiffens the out-of-plane vibration of the S atom, which has been resolved by the blue-shifted Raman peak (Fig. 13d). Moreover, the partial occupancy of upper energy levels in S by the donated electrons reduces the probability of the transitions of S 2p electrons to the S s-like state (peak A) and to the empty S 3d state (peak B), which is reflected in the reduced NEXAFS peak intensities (Fig. 13e). As such, the polarized electrons on the S sites can promote the Heyrovsky step—a key step in the HER—enhancing the HER performance. Overall, interfacial electronic effects can serve as a versatile tool for tailoring the electron densities of active sites and maneuvering the catalytic activities in various reaction systems.

4. Summary and outlook

The regulation of surface charge states for catalytic nanostructures exerts an important and far-reaching influence on various catalytic reaction systems. In this article, we summarize the efforts made by our research group and other researchers to tailor the compositions and structures of catalysts through lattice and interface engineering. Interfacial electronic effects have been proven as a powerful tool for tailoring the surface charge states of catalytic materials. Beyond the cases that have been discussed in this article, there would be a number of directions worth exploring in this research field.

(1) We mainly focus on the interfaces between metals and/or semiconductors in this review; however, the interfacial electronic effects can generally work for various material types. For instance, the integration of metal catalysts with a ferroelectric substrate also provides an opportunity for tuning catalytic performance with electronic effects. The catalytic activity of Ni in ethylene hydrogenation can be maneuvered by altering the substrates (Fig. 14).

When supported on γ-Al2O3, the conversion yield is raised along with the increase of temperature. Nevertheless, as the Ni supported on ferroelectric materials catalyzes the hydrogenation of ethylene, the reaction exhibits parabola-like rules around the substrate’s Curie temperature (e.g., the Curie temperature of BaTiO3 is 120–130 °C). It is well known that the chemical structures and charge densities of ferroelectric materials will dramatically change at the Curie temperature owing to internal electronic polarization. As a consequence, the polarization of ferroelectric materials promotes electronic perturbation especially at the Curie temperature. This promotion in turn changes the chemical structure and charge density of the metal catalyst, and hence influences the catalytic activity. This case highlights that future efforts should be made for substrate engineering toward catalytic performance tuning. As a matter of fact, substrate engineering has been widely investigated in organic synthesis; however, more attention should be paid to electronic effects in future studies.

(2) The utilization of interfacial electronic effects with organic ligands is another direction in this field, which has been briefly discussed in Section 2.3. Organic ligands have been widely used in homogeneous catalysis, so many concepts of traditional organic chemistry can be borrowed to maneuver the surface charge states of heterogeneous catalysts. Furthermore, this strategy should be able to extend to other soft matters such as polymers with coordination atoms. Our recent work indicates that polymeric materials can play a similar role to organic ligands in tuning electronic structures.

(3) In addition to the material design alone, external field is another possible approach to tune catalytic performance through electronic effects. In solid-state electrochemistry, the activity and selectivity of metal catalysts can be modified by the non-Faradaic electrochemical modification of catalytic activity (NEMCA) effect. However, only when the interface of the metal and solid–electrolyte is fully polarized can the NEMCA effect happen. Fig. 15a shows the principle of NEMCA in a solid–electrolyte cell composed of gaseous reactants, metal catalyst [ZrO2–Y2O3]M and O2. The concentration of O2− at the polarized metal–electrolyte interface can be changed by applying an external voltage, which induces a variation in work function and thus adjusts the catalytic reaction rate. As the polarization-induced NEMCA effect is used in Pt-catalyzed ethylene oxidation reaction, the catalytic reaction rate and activation energy exhibit exponential and linear relationships with the work function, respectively (Fig. 15b). Consequently, the polarization can serve as an effective electron regulatory tool for varying the ion concentration and work function, further optimizing the catalytic properties. Thus the use of an external magnetic or electric field would become a promising strategy for tuning catalytic performance complementarily to material design.

(4) As discussed in Sections 2.1 and 2.2, light illumination on reaction systems would induce dynamic interfacial electronic...
effects, which opens up the possibility of harvesting solar energy to drive catalytic reactions. The dynamic process is rather complex but offers a broader range for modulating surface charge states as compared with static electronic effects. This research would be performed at the intersection with photocatalysis and plasmonics.\textsuperscript{12}

In this case, charge separation is a key process for the enhancement of catalytic performance.\textsuperscript{12}

Plenty of opportunities are usually accompanied with grand challenges. In spite of the considerable progress, research into novel hybrid catalytic systems designed to regulate surface charge states still has a long way to go. The challenges mainly come from two aspects. (1) This research calls for future efforts on lattice and interface engineering at atomic precision for catalyst design, in efforts to rationally control surface charge states. Large-scale production techniques for catalysts have to be developed before moving forward to the next application stage. (2) The fundamental understanding in this research field has yet to be deepened, and more information should be collected to bridge the catalyst structures, surface charge states and catalytic performance. In this case, we have to develop characterization techniques for surface and interface structures at atomic resolution, surface charge states at high spatial resolution, dynamic charge transfer processes at high temporal resolution, and in situ chemical reactions. Synchrotron radiation-based spectroscopy and ultrafast spectroscopy are the currently used techniques with relatively high spatial and temporal resolutions. In particular, it is imperative to develop operando surface characterization techniques for directly probing the surface charge states. For instance, Salmeron et al. has employed ambient-pressure XPS (APXPS) to measure the charge state of Au nanoparticles supported on TiO\textsubscript{2} under O\textsubscript{2} pressure, which provides valuable information for decoding the mechanism for high catalytic activities in various reactions such as CO oxidation.\textsuperscript{105}

Overall, it is anticipated that further research on the catalyst design from the angle of surface charge states will definitely strengthen our capability of controlling catalytic activity and selectivity. Moreover, the modification on surface charge states will provide a new train of thought for industrial production of advanced materials to realize the efficient utilization of energy and the maximization of atom economy. Apart from the surface charge states, other factors such as reaction dynamics may make contributions to the enhanced catalytic performance. Taken together, the factors tightly controlled in a well-designed system would boost the overall catalytic performance.

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**Notes and references**
