Surface and interface design in cocatalysts for photocatalytic water splitting and CO₂ reduction

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Recent advances in photocatalysis highlight the important role of cocatalysts in improving the solar-to-chemical conversion efficiency for various reactions, such as water splitting and CO₂ reduction reactions. Given that cocatalysts play two important roles, in charge trapping and surface reactions, the rational material design of cocatalysts would be an effective route in pursuing their maximum contribution to the performance of photocatalysts. In this review, we aim to outline the recent progress of surface and interface design in cocatalysts for photocatalytic water splitting and CO₂ reduction. We first introduce the surface design of cocatalysts, which enables the enhancement of specific water splitting or CO₂ reduction reactions through surface parameter (e.g., the composition, facets and phases) adjustments. We then present key parameters for designing the interface between photocatalyst and cocatalyst, which offer a set of versatile options for tuning the charge transfer to the cocatalyst. Taken together, the surface and interface of cocatalysts may have synergetic effects on the photocatalytic performance, which are discussed to provide guidance for simultaneously tailoring surface and interface parameters. Finally, we summarize the challenges and opportunities for the surface and interface design of cocatalysts for the efficient production of solar fuels.

1. Introduction

Since the discovery of photocatalytic water splitting on TiO₂ electrodes by Fujishima and Honda in 1972, significant efforts have been made to develop highly efficient photocatalysts for various photocatalytic reactions, such as water splitting and CO₂ reduction, providing a promising route to alleviate steadily worsening environmental issues and an energy crisis.¹–⁵ Among various photocatalyst designs, the combination of

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a semiconductor with a cocatalyst to form a hybrid structure is a widely used approach to promote the performance of photocatalytic hybrid structures, cocatalysts themselves are not the light-harvesting components for generating photoinduced charge carriers. Instead, a cocatalyst mainly plays two positive roles in steering the charge kinetics in photocatalysis: (i) trapping charge carriers to promote electron–hole separation by forming an interface with the semiconductor; and (ii) serving as a highly active reaction site to supply the trapped charges for redox reactions on their surface. Both the improved charge separation and surface catalytic reactions contribute to the enhancement of photocatalytic activity and selectivity. In addition, the use of cocatalysts as alternative reaction sites may suppress the photocorrosion of semiconductors resulting from charge carrier accumulation and thus increase the stability of photocatalysts.

The two key roles of cocatalysts highlight the importance of designing their surface and interface to maximize the improvement in photocatalyst performance. On one hand, the surface of a cocatalyst is the location for redox reactions, which greatly determines the adsorption and activation abilities for reactant molecules and thus the activity and selectivity for photocatalytic reactions. For this reason, the design of a cocatalyst surface depends on the type of chemical reaction occurring on the surface – water splitting or CO2 reduction. On the other hand, the interface between a cocatalyst and semiconductor is the location where the charge carriers are transferred and separated, holding the key to preventing adverse electron–hole recombination in the semiconductor.

In a realistic photocatalytic system, the situation is rather complicated so as to entangle surface reactions and interfacial charge transfer, further emphasizing the significance of cocatalyst surface and interface design. Inefficient interfacial charge transfer would only bring a limited number of charge carriers to the surface of a co-catalyst, thereby restricting the efficacy of surface reactions. Inversely, slow surface reactions may lead to the accumulation of charges on the side of the cocatalyst, which in turn reduces the potential difference and prevents further interfacial charge transfer. In brief, only when the surface and interface are simultaneously well designed to promote surface catalytic reactions and interfacial charge transfer can the maximization of cocatalyst efficacy be realized. From another point of view, the surface and interface design of cocatalysts also represents a more straightforward strategy for improving photocatalysis in comparison with the surface modification of bare semiconductors. In the case of bare semiconductors, the semiconductor acts as both the light-harvesting center and surface reaction site. As such, tailoring the surface of the semiconductor would affect the light absorption of the photocatalyst in addition to tuning surface reactions, which makes it challenging to assess the contribution of surface design to photocatalytic performance.

Recently, the rational design of cocatalyst surfaces and interfaces has been widely implemented to promote the performance of photocatalytic nanomaterials. Certainly this research is greatly facilitated by the development of advanced synthetic approaches which realize design through precisely controlling surface and interface parameters of cocatalysts at the nanoscale. In this review, we focus on the design of cocatalyst surfaces and interfaces toward photocatalytic water splitting and CO2 reduction. We will first outline the forms of combination of cocatalysts with photocatalysts, as well as their basic architectural structures. Then we will discuss the surface design of cocatalysts in detail, according to the relationship between key surface parameters and photocatalysis. In the next section, the design of cocatalyst–photocatalyst interfaces will be elucidated based on a set of critical interfacial parameters. Subsequently, we will further highlight the simultaneous control of surfaces and interfaces associated with cocatalysts for enhanced photocatalytic performance. Finally, the remaining challenges and future prospects for surface and interface design in cocatalysts for photocatalytic applications will be provided.

2. Architectural structures of cocatalysts in photocatalysis

According to the trapped charge carriers that in turn determine the type of surface reaction, cocatalysts can be classified as having two functions: reduction cocatalysts trapping electrons for reduction half reactions, and oxidation cocatalysts trapping holes for oxidation half reactions. In general, noble metals (e.g., Pt, Pd, Rh and Au), non-noble transition metals (e.g., Cu, Co and Ni), metal sulfides (e.g., MoS2, NiS and WS2), metal oxides (e.g., NiO and CuO), phosphides (e.g., Co2P, NiP and MoP), carbon materials (e.g., graphene and carbon nanotubes) can serve as reduction cocatalysts for the hydrogen evolution reaction. In parallel, noble metals (e.g., Pt, Pd and Ag), metal oxides (e.g., CuO, NiO and RuO2), and cobaltates (e.g., ZnCo2O4 and MnCo2O4) have been reported as reduction cocatalysts for CO2 reduction. As for oxidation cocatalysts, transitional metal oxides (e.g., IrO2, MnO3, RuO2 and CoO3) and phosphates (e.g., CoP) have been widely used for water oxidation.

Cocatalysts can be integrated into photocatalysis in many different forms. In a hybrid photocatalyst, reduction or oxidation cocatalysts can be loaded alone on a light-harvesting semiconductor, in which the photogenerated electrons in the conduction band (CB) or holes in the valence band (VB) of the semiconductor are transferred to the cocatalyst for a reduction or oxidation reaction (Fig. 1a and b). In other cases, reduction and oxidation cocatalysts can be co-loaded on the same semiconductor for reduction and oxidation reactions (Fig. 1c). It is worth pointing out that the semiconductor for loading cocatalysts is not necessarily photoexcited. Alternatively, plasmonic metals or photosensitizers are integrated with a semiconductor so that the photoexcited metals or sensitizers can inject hot electrons or holes into the CB or VB of the semiconductor, respectively. As such, the injected electrons or holes are further transferred to the reduction or oxidation cocatalyst for surface reactions (Fig. 1d). Certainly in rare circumstances, cocatalysts may directly interface with plasmonic metals or photosensitizers to

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form hybrid photocatalysts in the absence of a semiconductor (Fig. 1e). The hot charge carriers generated in the plasmonic metal or photosensitizer are directly injected to the cocatalyst for redox reactions without the bridge of a semiconductor.

As the viewpoint is further narrowed down to a single reduction or oxidation cocatalyst, the integration of a cocatalyst with a semiconductor can still involve a variety of basic architectural structures, particularly in the case of reduction cocatalysts. This situation involves many different surface and interface structures in the cocatalyst design. To simplify the case, here we mainly take reduction cocatalysts as examples. When the cocatalyst is a mono-component structure (namely, a semiconductor–reduction cocatalyst I structure), the cocatalyst surface and semiconductor–cocatalyst I interface are quite simple (Fig. 2a). As the reduction cocatalyst has two or more components involved, the models for integrating the components become more diversified. In one case, two reduction cocatalysts (namely, cocatalyst I and cocatalyst II) in mutual contact are loaded on the same semiconductor. In this so-called “semiconductor–catalyst I/II structure”, two semiconductor–catalyst interfaces (i.e., the interfaces of semiconductor–catalyst I and semiconductor–catalyst II) as well as a catalyst I–catalyst II interface are simultaneously formed for electron transfer, and meanwhile, the surfaces of the two cocatalysts are both exposed for reduction reactions (Fig. 2b).

In another case, a quasi-core–shell structure is formed between cocatalyst I and cocatalyst II, fabricated by selectively coating the semiconductor-supported cocatalyst I core with a shell of cocatalyst II (i.e., a semiconductor–catalyst I@II core–shell structure) (Fig. 2c). In this structure, the interfaces of semiconductor–catalyst I and cocatalyst I–catalyst II are formed for tandem electron transfer, leaving only the cocatalyst II surface exposed for reduction reactions. Similarly, the semiconductor–catalyst I–II structure, in which cocatalyst II is selectively loaded on cocatalyst I to form a supported structure (Fig. 2d), has both the interfaces of semiconductor–catalyst I and cocatalyst I–catalyst II designed for electron transfer. In this case, however, both the surfaces of cocatalyst I and cocatalyst II are exposed for reduction reactions.

Certainly it is not necessary to have the cocatalyst in direct contact with the semiconductor. Alternatively, a conductive component (e.g., graphene or carbon quantum dots) can also serve as a charge bridge between the cocatalyst and semiconductor to form a semiconductor–conductor–catalyst structure (Fig. 2e). As the conductor surface barely possesses catalytic activity, a tandem electron transfer through the interfaces of semiconductor–conductive layer and conductive layer–catalyst will designate the cocatalyst surface as the reduction reaction site. In the literature, there have been reported more complicated architectural structures for cocatalysts (e.g., ternary cocatalysts), and they still derive from one of the aforementioned structures or the combination of multiple structures. From the discussion above, it can be recognized that the mutual interfaces of the cocatalyst–catalyst or cocatalyst–conductor are also of great importance to the charge transfer in photocatalysis when multiple components are involved in the cocatalyst design.
and activation behavior of reactants. To date, the surface design of cocatalysts through composition optimization has been widely used to enhance the performance of photocatalysts for various reactions. As the adsorption and activation behaviors are the keys to this performance tuning, the selection of cocatalyst compositions certainly depends on the type of reaction – water splitting or CO2 reduction. For instance, metallic Pt is the most widely used reduction cocatalyst in water splitting mainly due to its low activation energy for H2 evolution.4 However, the back reaction of hydrogen oxidation may also be catalyzed by the metallic Pt cocatalyst, thus limiting the solar energy conversion efficiency. To solve this problem, Li et al. loaded Pt in an oxidized state (PtO) on anatase TiO2 nanosheets (Fig. 3a), using a similar chemical reduction method to metallic Pt, except for the addition of a poly(methacrylic acid) ligand.24 Fig. 3b summarizes the photocatalytic performance of the two samples in pure water splitting, with the pre-injection of stoichiometric H2 and O2 into the closed test system. The TiO2–Pt photocatalyst exhibited a remarkable decrease in H2 and O2 amounts with extended periods of light irradiation, mainly resulting from the undesirable hydrogen oxidation reaction (HOR) on the Pt cocatalyst. In sharp contrast, the TiO2–PtO offered the capability for stoichiometric H2 and O2 to evolve steadily as the reaction proceeded. The cocatalyst PtO not only acts as efficient H2 evolution sites, but also exhibits the remarkable ability of suppressing the HOR as it can hardly activate and dissociate H2 molecules (Fig. 3c).

In photocatalytic water splitting, another effective strategy for suppressing the back reaction of hydrogen oxidation on noble metals is to develop core–shell cocatalysts. In a typical case, to prevent the HOR on a metal cocatalyst, Cr2O3 was selectively coated on the noble metal (e.g., Rh) to form an M@Cr2O3 core–shell cocatalyst. The Cr2O3 surface provided alternative H2 evolution sites and prevented the back reaction, while the metal facilitated electron migration toward the Cr2O3 surface (Fig. 3d and e).21 In a further study, a selective permeation mechanism was proposed for the core–shell cocatalyst, in which the Cr2O3 layer (i.e., microporous CrO3(1.5–m)(OH)2m·nH2O in aqueous solution) does not interfere with proton reduction at the Cr2O3–Pt interface and the diffusion of H2, but suppresses the permeation of oxygen atoms and molecules (Fig. 3f).22 Later on, metal@Cr2O3 core–shell cocatalysts have been widely used in photocatalysis and further extended to metal oxide@Cr2O3 core–shell cocatalysts.27–29 With a similar mechanism, the Ni@NiO core–shell structure is another important cocatalyst with the capability of inhibiting the back reaction in water splitting.28–31 In the structure, the NiO shell allows the diffusion of protons to reach Ni sites for reduction reactions as well as the diffusion and escape of the produced H2, but it can act as a valid barrier for O diffusion.

As a matter of fact, Cr2O3 has been extensively employed as a second cocatalyst component in UV-excitable photocatalysis with wide-bandgap semiconductors. Recently, novel surface modification methods have offered alternative materials to replace the Cr2O3 shell to achieve overall water splitting.32–34 A layer of amorphous transition-metal oxynitride or oxyhydroxide covered the entire surface of the semiconductor and cocatalyst,

3. Surface design of cocatalysts in photocatalysis

The analysis above clearly reveals that the cocatalyst surface is the location where activation reactions take place during the photocatalytic process. For this reason, surface design holds promise for tuning photocatalytic reactions through tailoring some surface parameters of cocatalysts. Firstly, surface parameters can be designed not only to realize high adsorption and activation ability for specific reactant molecules, but also to prevent side or back reactions. This would enhance the activity in the main photocatalytic reaction as well as improve the selectivity between competing reactions. Secondly, surface parameters are critical for the accumulation of electrons or holes on the reactive surface for reduction or oxidation reactions, respectively. Thirdly, the chemical stability of photocatalysts during the catalytic process can be improved by modifying the surface parameters. In this section, the surface design of cocatalysts for photocatalytic H2 evolution and CO2 reduction is discussed according to some important surface parameters such as surface composition, facets, phases and defects.

3.1 Surface composition

The surface composition greatly determines the atomic or ionic arrangements on a cocatalyst surface and thus the adsorption
and functioned as a molecular sieve to selectively filter reactant and product molecules. For instance, to prevent the backward oxygen reduction reaction (ORR) reaction on the surface of a SrTiO$_3$-supported Rh$_2$O$_3$ cocatalyst, oxyhydroxide layers of Ta$^{5+}$ (referred to as Ta$_2$O$_5$ for simplicity) were formed to fully cover the photocatalyst to form SrTiO$_3$:Sc–Rh$_2$O$_3$/Ta$_2$O$_5$ core–shell structures (Fig. 3g).

In the absence of a Ta$_2$O$_5$ coating, the photocatalytic H$_2$ and O$_2$ evolution on SrTiO$_3$:Sc–Rh$_2$O$_3$ was largely limited by the rapid backward reaction (Fig. 3h). In comparison, SrTiO$_3$:Sc–Rh$_2$O$_3$/Ta$_2$O$_5$ behaved very differently. Upon irradiation, a considerable amount of O$_2$ evolved during the initial 3–4 h due to contaminants from the catalyst synthesis. After evacuating the reaction system, H$_2$ and O$_2$ were produced at constant rates and at the stoichiometric ratio of water splitting. It was demonstrated that the ORR back reaction was successfully prevented by the Ta$_2$O$_5$ coating. In this design, the amorphous Ta$_2$O$_5$ layer allows H$^+$ ions and H$_2$O molecules to reach the surface of Rh$_2$O$_3$ and SrTiO$_3$ for H$_2$ and O$_2$ evolution, respectively. Although the produced O$_2$ can be released from the coating layer through penetration, O$_2$ permeation in the opposite direction is unlikely to occur as the partial O$_2$ pressure in the outer phase is lower than in the coating layer. Such one-way permeation of O$_2$ effectively prevents the back reaction without compromising the forward reaction (Fig. 3i).

In addition to water splitting, the surface composition also plays an important role in the photocatalytic reduction of CO$_2$ with H$_2$O. For instance, a Pt@Cu$_2$O core–shell cocatalyst was designed to enhance photocatalytic selectivity in the reduction of CO$_2$ to CO and CH$_4$. Given the high ability of the Pt cocatalyst for H$_2$O activation, H$_2$ would be the major product when a TiO$_2$–Pt hybrid structure is used as a photocatalyst, reducing the selectivity of CO$_2$ conversion. To improve the selectivity, Cu$_3$O$_3$ coating with high CO$_2$ activation ability, was selectively coated on the Pt to modify the surface composition (Fig. 4a). As shown in Fig. 4b, the Cu$_3$O$_3$ coating significantly suppressed the
formation of H₂ and promoted the production of CH₄ and CO, remarkably increasing the selectivity for CO₂ reduction. In this structure, the Pt core transferred the photogenerated electrons from TiO₂ to the Cu₂O shell, and the Cu₂O shell served as the reaction sites for producing CH₄ and CO (Fig. 4c).

In addition to surface coating or decoration, surface composition control can also be achieved through incorporating new atoms into a cocatalyst surface. Metal cocatalysts can be tailored by forming alloys with different metal atoms.⁸⁵,⁸⁶ For instance, H₂ evolution using TiO₂ nanosheets with a Pt cocatalyst could be enhanced by incorporating Pd into the Pt lattice to form a PdPt alloy cocatalyst with both cases of Pt/Pd{100} and {111} surface facets at various typical Pd/Pt ratios (Fig. 4d–f).⁸⁶ In this system, the difference in the work functions of Pd and Pt induced electron accumulation at Pt sites. The increase in electron density in turn enhanced the H₂O adsorption and activation on the Pt sites for H₂ production (Fig. 4g). In another case, an Au@(AuPd alloy) core–shell cocatalyst has been developed for efficient H₂ production with CdSe@CdS as the photoactive charge generation unit (Fig. 4h).⁸⁷ The CdSe@CdS rods with Au@alloy core–shell tips exhibited a significant enhancement in photocatalytic activity in comparison with Pd, Au and Au@Pd core–shell tips, benefiting from both the alteration in electronic structure by the Au core and the atomic rearrangement of the Pd surface (Fig. 4i). In the AuPd alloy, Pd reaction sites are separated with Au, which reduces the H adsorption strength to release H₂ as well as eliminating the so-called self-poisoning effect. Furthermore, the Au on the surface enhances the photocatalytic stability by suppressing cation exchange reactions between Cd and Pd (Fig. 4j and k).

![Fig. 4](image-url)
3.2 Surface facets

With the same surface composition, tailoring the facets exposed on a cocatalyst surface can also lead to a variation in atomic arrangements. Similarly, this would maneuver the adsorption and activation of reactive molecules, and tune the photocatalytic activity and selectivity. During the process of photocatalytic conversion of CO$_2$ and H$_2$O into carbon fuels, water splitting often competes with CO$_2$ reduction by consuming photoexcited electrons. In a typical case, the selectivity between CO$_2$ reduction and water splitting can be tuned through adjusting the exposed facets of Pd reduction cocatalysts supported on g-C$_3$N$_4$ nanosheets.\[^{14}\] In this example, Pd nanocubes enclosed with \{100\} facets and Pd nanotetrahedrons with \{111\} facets were grown in situ on C$_3$N$_4$ nanosheets to form C$_3$N$_4$–Pd\{100\} and C$_3$N$_4$–Pd\{111\} photocatalysts, respectively (Fig. 5a and b). With the same Pd loading (ca. 6 wt\%), C$_3$N$_4$–Pd\{100\} preferred to reduce H$_2$O to H$_2$, while C$_3$N$_4$–Pd\{111\} mainly supported CO$_2$ reduction to carbon products (i.e., CO, CH$_4$ and C$_2$H$_5$OH). As a result, the selectivity for CO$_2$ reduction turned out to be 20.7% for Pd\{100\} versus 78.1% for Pd\{111\} (Fig. 5c). Behind the observations, theoretical simulations revealed that the Pd\{111\} facets offered higher CO$_2$ adsorption energy and a lower CO$_2$ activation barrier, while the Pd\{100\} facets possessed much higher H$_2$O adsorption energy. Despite comparable electron transfer efficiencies, the electrons trapped on various facets of the Pd cocatalyst would be mainly utilized for different reduction reactions (Fig. 5d). Besides Pd, the exposed facets of Pt cocatalysts have also been reported to play an important role in determining the photocatalytic performance for H$_2$ production.\[^{88,89}\]

3.3 Surface phase

When we design the surface of a cocatalyst, the surface phase is another important parameter that has to be taken into account. For instance, it turned out that different photocatalytic H$_2$ production rates could be achieved when metallic (1T, octahedral phase) and semiconducting (2H, trigonal prismatic phase) MoS$_2$ were used as reduction cocatalysts with light-harvesting TiO$_2$.\[^{90}\] In this case, comparable TiO$_2$ nanocrystals were loaded on the MoS$_2$ nanosheets in 1T and 2H phases to form TiO$_2$–MoS$_2$(1T) and TiO$_2$–MoS$_2$(2H) hybrid structures (Fig. 6a). As shown in Fig. 6b, TiO$_2$–MoS$_2$(1T) exhibited a dramatically higher photocatalytic H$_2$ production rate in comparison to TiO$_2$–MoS$_2$(2H). The advantages of the 1T phase in cocatalysts originated from two aspects: (i) the active sites for H$_2$ evolution were only located at the edges of the 2H MoS$_2$ nanosheets, while the 1T MoS$_2$ nanosheets had abundant active sites at both the edges and basal planes; and (ii) the 1T MoS$_2$ nanosheets offered significantly higher mobility for electron transfer in comparison with the 2H MoS$_2$ nanosheets. As such, the higher diffusion rate and shorter diffusion distance ensure more photogenerated electrons from TiO$_2$ arrive at the reaction sites of the 1T MoS$_2$ cocatalyst and participate in photocatalytic reactions (Fig. 6c). Owing to these advantages, transition metal oxides and

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**Fig. 5** (a and b) TEM and HRTEM images of (a) C$_3$N$_4$–Pd nanocubes with exposed Pd\{100\} facets and (b) C$_3$N$_4$–Pd nanotetrahedrons with Pd\{111\} facets; (c) production rates of H$_2$ and carbon products using C$_3$N$_4$–Pd photocatalysts with ca. 6 wt\% Pd loading; and (d) schematic illustration of C$_3$N$_4$–Pd\{100\} and C$_3$N$_4$–Pd\{111\} samples in photocatalytic CO$_2$ reduction in the presence of H$_2$O (adapted with permission from ref. 14, Copyright 2014 Royal Society of Chemistry).
phosphides (e.g., MoO2 and MoP) with surface metallic phases have also been developed as highly efficient noble-metal-free cocatalysts for photocatalytic hydrogen production from water.32,60

3.4 Surface defects

In terms of surface photocatalytic reactions, the adsorption and activation of reactants often take place at surface defects or vacancies where dangling bonds are prone to capture both charge carriers and reactants. Thus the activity and selectivity in photocatalysis can be improved by controlling the number of surface defects or altering the type of surface defects. For instance, CdS nanocrystals were anchored on defect-free and defect-rich MoS2 ultrathin nanoplates, respectively, to act as H2 evolution cocatalysts.91 The CdS–MoS2 (defect-rich) structure exhibited dramatically higher H2 evolution activity compared to CdS–MoS2 (defect-free), mainly owing to the role of defects as reactive sites (Fig. 6d). It should be noted that here we do not bother to consider the side effects of surface defects on charge recombination, as only electrons or holes are trapped on the surface of cocatalysts.

4. Interface design of cocatalysts for photocatalysis

Differently from surface design, interface design is mainly performed via parameter adjustments and optimization of the contact interfaces between cocatalysts and other components. The interface has to be tightly controlled simply because it is the location through which the photogenerated charge carriers are transferred. As a matter of fact, interface design enables an improvement in photocatalytic performance from several different angles. Firstly, interface parameters can be designed to realize highly efficient charge transfer. The efficiency of charge transfer determines the number of charge carriers for redox reactions at the cocatalyst surface. Secondly, spatial charge separation can be enabled through interface control to prevent detrimental electron–hole recombinations in the semiconductor. Thirdly, the interface quality actually represents the bonding between the cocatalyst and other components, so the stability of the photocatalyst is largely relevant to the interface. In this section, we will discuss interface design according to key interface parameters, including interfacial composition, location and facets.

4.1 Interfacial composition

Similarly to surface composition, the composition of the interface, where the cocatalyst contacts with the adjacent component, is a key parameter for affecting the efficiency of charge transfer across the interface. For instance, the similar composition of the two sides of an interface would favor their intimate contact and strong coupling for highly efficient charge transfer. In typical cases, transition metal sulfides (e.g., MoS2, WS2 and NiS) were often used as H2 evolution cocatalysts for CdS-based photocatalysts,26–28,91 because their analogous compositions (i.e., containing S2− anions) favored the formation of a covalent junction with a low defect density at the interface to facilitate electron transfer.

Recently, interfacial composition adjustment on the cocatalyst has been reported to improve the performance of photocatalysts. For instance, the interface between a CoOx oxidation co-catalyst and a Ta2N5 semiconductor has been tailored toward
improved water oxidation. As intimate contact could hardly be made between the hydrophobic Ta₃N₅ and hydrophilic CoOₓ for efficient interfacial charge transfer, a magnesia nanolayer was used to turn the Ta₃N₅ surface from hydrophobic to hydrophilic through in situ or ex situ surface coating prior to CoOₓ deposition, forming Ta₃N₅-(in)MgO/CoOₓ and Ta₃N₅-(ex)MgO/CoOₓ, respectively (Fig. 7a). The magnesia coating not only improved the interfacial contact between CoOₓ and Ta₃N₅, but also reduced the defect density of Ta₃N₅ through a passivation effect (Fig. 7b). As a result, Ta₃N₅-(in)MgO/CoOₓ and Ta₃N₅-(ex)MgO/CoOₓ exhibit substantially higher oxygen evolution rates than Ta₃N₅–CoOₓ (Fig. 7c). The transient absorption spectra revealed that the MgO layer effectively suppressed the recombination of photoinduced carriers and prolonged their lifetimes (Fig. 7d).

4.2 Interfacial location

The location for forming the interface is critical to the efficiency of interfacial charge transfer, especially when electrons and holes are accumulated on different components in a heterostructure. To ensure high charge-transfer efficiency, reduction or oxidation cocatalysts should be deposited on locations where electrons or holes are accumulated, respectively. For instance, Park et al. reported that the configuration of loading Pt cocatalysts onto Cds/TiO₂ hybrid catalysts greatly determined the overall H₂ production efficiency. The Pt cocatalyst could be deposited on the surface of either Cds (i.e., TiO₂/Cds–Pt) or TiO₂ (i.e., Cds/TiO₂–Pt) or on both surfaces, to form different interface configurations (Fig. 8a). Under visible light, the Cds/TiO₂–Pt structures exhibited remarkably higher H₂ production rates in comparison with (Cds/TiO₂)–Pt and TiO₂/Cds–Pt (Fig. 8b and c), as the decoration of Pt cocatalyst on the TiO₂ side enabled successive electron transfer along Cds → TiO₂ → Pt and maximized the electron transfer efficiency. In a different way, the multi-directional electron transfer throughout (Cds/TiO₂)–Pt and TiO₂/Cds–Pt inevitably lowered the efficiency (Fig. 8a).

When dual cocatalysts are involved in a photocatalytic system for reduction and oxidation reactions, the relative locations of the cocatalysts can also affect the photocatalytic performance. The spatial separation of a reduction cocatalyst from an oxidation one can not only reduce charge recombination owing to the different transfer directions of electrons and holes, but also prevent the back reaction between products given their long-distance separation. As just mentioned, the key to this system is to deposit the corresponding cocatalysts at appropriate locations on the semiconductor where electrons or holes are accumulated. Mubeen et al. designed and fabricated an autonomous plasmonic solar water splitter based on Au nanorod arrays. In the system, the TiO₂ at the tips of the Au nanorods was decorated with Pt nanoparticles, as a H₂ evolution cocatalyst, while Co-OEC material, as an O₂ evolution cocatalyst, was deposited on the lower portion of the nanorods (Fig. 8d and e). The different interfacial locations of the Pt and Co-OEC cocatalysts along the Au nanorods effectively lowered the possibility of recombining plasmonic hot electrons with the remaining positive charges (i.e., hot holes) on the nanorods.

Apparently nanorods provide an anisotropic platform for separating electrons from holes, designating the locations for reduction and oxidation cocatalysts. However, the anisotropy of semiconductor nanostructures is not indispensable for cocatalyst separation. For example, Wang et al. reported a SiO₂/Ta₃N₅ core–shell photocatalyst with reduction cocatalyst Pt nanoparticles loaded on a Ta₃N₅ inner shell surface, and with an oxidation cocatalyst, IrO₂ or CoOₓ, on the outer shell surface (i.e., Pt(in)–Ta₃N₅–MOₓ(out), M = Ir or Co) (Fig. 8f). The separated locations of the cocatalysts facilitated the migration of photoexcited electrons and holes toward the inner and outer surfaces, respectively. This design not only reduced charge recombination, but also prevented the back reaction between the newly produced H₂ and O₂ to form H₂O. As a result, Pt(in)–Ta₃N₅–IrOₓ(out) exhibited higher H₂ evolution rates than a SiO₂/
Ta$_3$N$_5$ core–shell structure with both Pt and IrO$_x$ on the outer surface (Pt(out)–Ta$_3$N$_5$–IrO$_x$(out)) (Fig. 8g). Similarly, the separated loading of the Pt and CoO$_x$ cocatalysts on the inner and outer surfaces of SiO$_2$/Ta$_3$N$_5$, respectively, could also improve the O$_2$ evolution rate (Fig. 8h).

Recently, new insight into the interfacial locations of cocatalysts has been proposed by Ma et al.\textsuperscript{95} They found that intimate contact between the reduction (Pd) and oxidation (IrO$_x$) cocatalysts on TiO$_2$ (i.e., TiO$_2$–Pd/IrO$_x$) could surprisingly lead to a significant enhancement in the photocatalytic activity for H$_2$ production via methanol reforming compared with separated Pd and IrO$_x$ cocatalysts on TiO$_2$ (i.e., Pd–TiO$_2$–IrO$_x$). As shown in Fig. 8i, with Pd–TiO$_2$–IrO$_x$ with separated cocatalysts the H$_2$ production can be increased by 32% with respect to TiO$_2$ with a single Pd cocatalyst deposited with the same photodeposition method (i.e., TiO$_2$–Pd(PD)). In comparison, the TiO$_2$–Pd(IrO$_x$/Pd(IM)) achieved an 81% enhancement in H$_2$ production in reference to TiO$_2$–Pd(IM) prepared with the same impregnation method. In addition, the Pd–IrO$_x$/TiO$_2$ design also achieved improved performance toward the CO/H$_2$ ratio (Fig. 8j). They proposed that the electrons and holes could be readily separated at the interface between IrO$_x$ and Pd in this special case. Moreover, the photogenerated charges in the surface skin region would have a shorter transportation length to the surface where the reduction and oxidation cocatalysts were closely located. On the other hand, differently from water splitting, the backward reaction with the methanol reforming products (CO$_2$ + H$_2$) could hardly take place when the cocatalysts were in intimate contact.
contact. A similar design has also been reported for other cocatalysts. For instance, the NiOx cocatalyst has been widely used for water splitting, and most recently, it was found that this material was actually composed of Ni and NiO which could play the role of H2 and O2 evolution cocatalyst, respectively.96,97

4.3 Interfacial facets

The efficiency of charge transfer is also dependent on the facets of components used in forming the interface. First of all, the interfacial facets, which are characterized with atomic arrangements, determine the bonding situation and lattice consistency between components as well as the coupling of their electronic structures. Secondly, the energy bands of material surfaces have a strong correlation with their surface facets, resulting in a certain alignment on the interface between the electronic band structures. Taken together, the interfacial structures can be tailored either through adjusting the facet of the cocatalyst or by controlling the facet of the semiconductor for the deposition of the cocatalyst.

For instance, Pt nanoparticles with different exposed facets were loaded on graphene (rGO) nanosheets to form rGO–Pt{100} and rGO–Pt{111} cocatalysts, respectively.58 With Eosin Y (EY) as a photosensitizer and rGO as a conductive component, the photoinduced electrons were transferred to the Pt cocatalyst through the rGO–Pt interface for H2 evolution. Enabled through different Pt facets at the interface, the H2 evolution activity using rGO–Pt{100} was substantially higher than that with rGO–Pt{111} (Fig. 9a). With the same tunable facets, however, bare Pt {111} as a cocatalyst exhibited a higher H2 evolution activity than bare Pt{100}, manifesting the higher catalytic activity of Pt {111}. The performance of Pt(100) can be boosted via integration with rGO because it has stronger interactions with rGO than Pt{111} enabling faster interfacial charge transfer (Fig. 9b).

In addition to the interfacial coupling, facet control also allows the tuning of the interfacial band alignments. For instance, the EY-sensitized TiO2–Pt samples with different exposed Pt facets including {100}, {100/111} and {111} were employed as photocatalysts toward H2 evolution.98 EY–TiO2–Pt{111} presented the highest H2 generation rate among the EY–TiO2–Pt samples (Fig. 9c), owing to its unique energy band alignment. The Fermi level of Pt{111} is lower than that of Pt{100}, so as to enlarge the difference between the Fermi level and the conduction band minimum (CBM) of TiO2. As a result, Pt{111} should be capable of trapping electrons from the CB of TiO2 more effectively (Fig. 9d).

It is worth noting that the variation in cocatalyst facets not only alters the interfacial structure, but also designates different exposed facets for surface reactions. This feature makes it difficult to analyze the contribution of interfacial facet design to facet-dependent photocatalytic performance. To exclude the

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**Fig. 9** (a) H2 evolution from EY-photosensitized systems catalyzed using RGO, Pt(100), Pt(111), RGO–Pt(100), and RGO–Pt(111) as cocatalysts; (b) the proposed photocatalytic mechanism for hydrogen evolution over RGO–Pt(100) and RGO–Pt(111) cocatalysts under visible-light irradiation (adapted with permission from ref. 58, Copyright 2015 American Chemical Society); (c) photocatalytic H2 evolution rates from a TEOA aqueous solution on EY–TiO2–Pt(100), EY–TiO2–Pt(100/111), and EY–TiO2–Pt(111) under visible-light irradiation; and (d) schematic diagram of the different energy levels in the Pt(100) (dotted curve) and Pt(111) facets (solid curve) (adapted with permission from ref. 98, Copyright 2013 American Chemical Society).
effect from surface facets, a more straightforward method has been developed to tune interfacial facets, in which cocatalysts are selectively deposited on the different facets of a semiconductor. When semiconductor crystals are enclosed with more than one type of facet, the varied energy band structures of the surface facets may lead to spatial charge separation, so as to accumulate electrons and holes on different facets. In this case, the selective deposition of a reduction cocatalyst on the facet which has accumulated electrons and/or an oxidation cocatalyst on the one with holes can readily realize highly efficient interfacial charge transfer. This further promotes spatial charge separation between the facets.

For instance, Li et al. reported the selective photodeposition of metals (e.g., Pt) as reduction cocatalysts on the {010} facets of BiVO_4 crystals, and metal oxides (e.g., MnO_x) as oxidation cocatalysts on the {110} facets, respectively (Fig. 10a). This selective photodeposition is indeed enabled by spatial charge separation accumulating photogenerated electrons and holes on the {010} and {110} facets, respectively (Fig. 10b). In the photocatalytic water oxidation reaction, the Pt-{010}BiVO_4{110}-MnO_x structure exhibited remarkably higher activity in comparison with bare BiVO_4 as well as BiVO_4{010}–Pt and BiVO_4{110}–MnO_x with a single cocatalyst, manifesting the synergistic function of dual-cocatalysts (Fig. 10c). Furthermore, this study demonstrates well that interfacial facets are critical in the efficacy of cocatalysts, as a random distribution of Pt and MnO_x on BiVO_4 cannot offer comparable efficiency for photocatalysis.

Nowadays, many photocatalysts have been reported through photodeposition suitable reduction (e.g., Au) and/or oxidation (e.g., Co_3O_4 and MnO_x) cocatalysts on electron- and/or hole-accumulating facets, respectively. In addition to the spatial charge separation between different facets, photogenerated electrons and holes may also diffuse in opposite directions through spontaneous polarization, driven by an built-in dipole field in semiconductor crystals with polar facets or by a ferroelectric field in ferroelectric oxide semiconductors. This mechanism can accumulate electrons and holes at the two ends of the facets perpendicular to the field direction. This case calls for the necessity of selectively depositing an appropriate cocatalyst on a specific location of a facet. For instance, the asymmetric selective photodeposition of Pt and MnO_x cocatalysts on the positively and negatively charged {001} facets of PbTiO_3, a ferroelectric oxide semiconductor, has been demonstrated by Zhen et al. The resulting product showed greatly improved photocatalytic activity over those with random deposition.

When a semiconductor nanocrystal is enclosed with different facets, the traveling length of charge carriers toward the facets may depend on the nanocrystal geometry. In this case, the selective deposition of cocatalysts on the facet with a short charge transfer length may reduce electron–hole recombination and enhance the photocatalytic performance. For instance, Pt and PtO as reduction cocatalysts were dispersed on TiO_2 nanosheets and octahedra dominated with {001} and {101} facets, respectively (namely, TiO_2/001 and TiO_2/101). The synthesis indicated that the metallic Pt cocatalyst was more favorably deposited on the {101} facet, while the PtO could be stabilized on both the {001} and {101} facets (Fig. 10d–g). For photocatalytic H_2 evolution, TiO_2/101-Pt exhibited higher activity than TiO_2/001-Pt, and the activity of TiO_2/001-PtO exceeded that of TiO_2/101-PtO (Fig. 10h). This performance difference may originate from the reduction of charge recombination from short traveling lengths. The average electron migration length (i.e., the distance from the center of the photocatalyst to the co-catalyst) was measured to be 2 nm in TiO_2/001-PtO, 25 nm in TiO_2/001-Pt, and 12 nm in both TiO_2/101-PtO and TiO_2/101-Pt. As a result, the TiO_2/101-Pt and TiO_2/001-PtO greatly shortened the migration path of photogenerated electrons as compared to TiO_2/001-Pt and TiO_2/101-PtO (Fig. 10i), reducing the probability of charge recombination.

As the energy band structure of the semiconductor surface depends on the facets, face control would also alter interfacial band alignments, altering the charge transfer efficiency at the interface. In a typical example, for Cu_3W_8S_4 (CWS) decahedra, the CBM and valance band maximum (VBM) of the {101} facets are 80 meV and 60 meV higher than those of the {001} facets, respectively, thus resulting in spatial charge separation between the facets. Using a photodeposition method, a Pt cocatalyst was preferentially formed on the {001} facets owing to the accumulation of photogenerated electrons; the photo-free chemical deposition resulted in Pt nucleation at both the {001} and {101} facets (Fig. 10j and k). As illustrated in Fig. 10l, the spatial charge separation in CWS{001}–Pt drove the photogenerated electrons to move toward the Pt cocatalyst for H^+ reduction, while the holes transferred toward the uncovered {101} facets to oxidize the Na_2S/Na_2SO_3 sacrificial reagent. In comparison, CWS{001}/{101}-Pt contained one additional CWS {101}–Pt interface (Fig. 10m). As the {101} facet was rich with holes, it is not expected to be an ideal facet for loading Pt cocatalysts. In the practical photocatalytic measurements, however, CWS{001}/{101}-Pt exhibited notably higher H_2 evolution activity than CWS{001}–Pt (Fig. 10n), and this activity was further promoted by increasing the {101}/001 ratio from CWS-S to CWS-L. This indicates that the catalytic activity of Pt cocatalysts on the {101} facet should be higher than on the {001} facet (Fig. 10n). As revealed from energy band analysis, the elevated CB level of the CWS{101} facet in comparison with the {001} facet offered a larger potential difference, so that the excited electrons would more easily jump from the CWS{101} facets to the Pt cocatalysts. This feature enabled faster interfacial electron transfer toward improved photocatalysis (Fig. 10m).

Similarly to cocatalysts, altering the facets of semiconductors also brings about variations in interfacial coupling with the cocatalyst, which will influence the charge transfer efficiency across the interface. For instance, a Ni@NiO core–shell cocatalyst could be selectively loaded on the {002} and {101} facets of K_2La_2Ti_5O_10 photocatalysts for water splitting. The interfacial electronic structures between Ni[111] and the different facets of K_2La_2Ti_5O_10 were investigated using two-dimensional surface model density functional theory (DFT) calculations (Fig. 10o). As indicated from the electron density contour maps for K_2La_2Ti_5O_10 CBM (Fig. 10p), the Ni3d + Ti3d hybrid orbitals...
Fig. 10 (a) SEM image and geometric models of Pt-{010}BiVO₄{110}-MnOₓ; (b) schematic diagram illustrating the selective deposition of reduction and oxidation cocatalysts on the (010) and (110) facets of BiVO₄ based on the charge separation between different facets; (c) the photocatalytic water oxidation performance of BiVO₄-based photocatalysts (adapted with permission from ref. 99 and 100, Copyright 2013 Nature Publishing Group and 2014 Royal Society of Chemistry); (d–g) STEM images and geometric models of the following samples: (d) TiO₂/001-Pt, (e) TiO₂/101-Pt, (f) TiO₂/001-PtO and (g) TiO₂/101-PtO; (h) H₂ evolution rates for bare TiO₂ and photocatalysts loaded with PtO clusters and metallic Pt co-catalysts, respectively; (i) schematic diagram illustrating the migration of photogenerated electrons in photocatalysts (adapted with permission from ref. 104, Copyright 2015 Elsevier); (j and k) SEM images of Pt loaded CWS-S photocatalysts through (j) photodeposition and (k) chemical deposition methods; (l and m) charge kinetics of (l) CWS(001)–Pt and (m) CWS(001)(101)–Pt photocatalysts for H₂ evolution; (n) rates of photocatalytic hydrogen production over Pt deposited CWS photocatalysts (adapted with permission from ref. 105, Copyright 2015 Wiley-VCH); (o) Ni(111)/K₂La₂Ti₃O₁₀{002} surface unit cell model; and (p) electron density contour maps for the bottom of the CB of K₂La₂Ti₃O₁₀ at the Ni(111)–K₂La₂Ti₃O₁₀(101) and Ni(111)–K₂La₂Ti₃O₁₀(002) interfaces (adapted with permission from ref. 107, Copyright 2007 The Chemical Society of Japan).
spread from the interface region to the Ni bulk region in the K$_2$La$_2$Ti$_3$O$_{10}$[101]–Ni[111] interface, whereas the K$_2$La$_2$Ti$_3$O$_{10}$[002]–Ni[111] interface localizes electron density within K$_2$La$_2$Ti$_3$O$_{10}$. This suggests that electron transfer at the K$_2$La$_2$Ti$_3$O$_{10}$[101]–Ni[111] interface can work more smoothly.

5. Simultaneous control over the cocatalyst surface and interface for photocatalysis

In Sections 3. and 4., surface and interface design in cocatalysts have been discussed, respectively. As briefly mentioned above, interfacial charge transfer and surface activation reactions have substantial interplay and thus are entangled together, which highlights the necessity of simultaneously controlling surface and interface parameters. If achieved, this design will allow the improvement of both charge trapping and surface activation in a single system, which would be a promising approach for high-performance photocatalysts. Certainly the parameters to be controlled in the co-design of surface and interface are quite similar to those mentioned in Sections 3. and 4. However, given the entangled relationships between surface and interface parameters, we have to more systematically consider their interplay as well as find out new approaches. For instance, it was reported that, in comparison with Pt[100], Pt[111] cannot only trap electrons from TiO$_2$ more effectively, but also provide more reaction sites for water reduction. In practical application, however, the corresponding design has not shown its strong advantages, as a high-quality interface may not be formed based on the selected cocatalyst surface. For this reason, it is imperative to develop new methods, theories and mechanisms to circumvent undesired situations.

Recently, Su et al. realized the co-design of surface and interface by optimizing the electronic properties of metal cocatalysts through compositional and structural fine-tuning. In a semiconductor (TiO$_2$)–metal cocatalyst system, the interfacial charge transfer from the metal to the electron acceptor (A)
is a very slow process as compared to from TiO$_2$ to the metal. For this reason, the electrons accumulated in the metal may get trapped via reverse transportation to the trap states ($E_t$) of the semiconductor (Fig. 11a). Thus a fast reduction reaction (high $k_{\text{red}}$) on the surface and a slow reverse transfer process (low $k_{\text{rev}}$) for the trapped photogenerated electrons at the interface are both required for optimal performance. Au nanoparticles that were deposited on TiO$_2$ could offer a large $k_{\text{red}}$ and $k_{\text{rev}}$, whereas Pd on TiO$_2$ showed the opposite. To optimize both the $k_{\text{red}}$ and $k_{\text{rev}}$, Au- and Pd-based nanoparticles in a range of specific random alloy and core–shell configurations, such as Au$_x$Pd$_{1-x}$ random alloy (Fig. 11b), Au$_{\text{shell}}$–Pd$_{\text{core}}$ (Au$_{\text{Pdc}}$, Fig. 11c) and Pd$_{\text{shell}}$–Au$_{\text{core}}$ (Pd$_{\text{Au},c}$, Fig. 11d) nanoparticles, were formed and supported on TiO$_2$ as cocatalysts. By probing the kinetics under constant irradiation, it was revealed that an increase in Pd content in the alloy nanoparticles resulted in a ~33–50% reduction in $k_{\text{red}}$ as well as an exponential decrease in $k_{\text{rev}}$ (Fig. 11c). Conversely, Pd$_{\text{Au},c}$ maintained a relatively high $k_{\text{red}}$ but a very low $k_{\text{rev}}$ relative to Au$_{\text{Pdc}}$. As a result, the TiO$_2$–Pd$_{\text{Au},c}$ exhibited higher H$_2$ evolution rates in comparison with the TiO$_2$–AuPd$_{\text{c}}$ alloy and TiO$_2$–Au$_{\text{Pdc}}$ (Fig. 11f).

Fig. 11g shows the electronic density of states (DOS) profiles of 147-atom icosahedral clusters of Au, Pd, Au$_x$Pd$_{1-x}$, and Pd$_{\text{Au},c}$, respectively. It depicts that Pd clusters possess more unoccupied states just above the Fermi level ($E_F$) than Au, favorable for electron trapping. In the case of the core–shell structure, the number of unoccupied surface states just above $E_F$ increases with the Pd concentration on the surface. Compared to <8% for Au$_{\text{Pdc}}$, Pd$_{\text{Au},c}$ shows that >60% of all states just above $E_F$ are surface-localized d-orbitals, which are highly beneficial for extending the lifetime of the photoexcited states transferred from the CB of TiO$_2$. Furthermore, charge localization on the surface of the icosahedral clusters shows that net electron accumulation predominantly occurs throughout the shell, whereas for Pd$_{\text{Au},c}$, a net accumulation of charge takes place primarily on the vertex sites (Fig. 11h). On the other hand, charge depletion is prominent for the core regions of all the cocatalysts except Pd$_{\text{Au},c}$ owing to the electronegative and capacitive properties of the Au core. It was proposed that the reduced surface accumulation of electrons in Pd$_{\text{Au},c}$ facilitated the storage and release of photoexcited electrons toward surface catalysis.

In another case, we achieved the co-design of a cocatalyst surface and interface by employing a different mechanism – interfacial charge polarization. To implement the mechanism, atomically controlled Pd$_{\text{n}}$Pt$_{\text{m}}$ core–shell cocatalysts were fabricated on TiO$_2$ nanosheets.$^{65}$ Specifically, we used Pd nanocubes supported on TiO$_2$ nanosheets (TiO$_2$–Pd) as precursors, and Pt shells with a controllable thickness could be selectively coated on the Pd cubes to form TiO$_2$–Pd$_{\text{n}}$Pt$_{\text{m}}$ photocatalysts. As shown in Fig. 12a and b, TiO$_2$–Pd$_{\text{n}}$Pt$_{\text{m}}$ photocatalysts with three (TiO$_2$–Pd$_3$Pt$_{10}$) and ten (TiO$_2$–Pd$_2$Pt$_{10}$) Pt atomic layers on average were synthesized by altering the TiO$_2$–Pd$_{\text{n}}$Pt$_{\text{m}}$ precursor ratios. As such, the surface of the cocatalysts changed from Pd{100} to Pt {100} with higher H$_2$ evolution activity. Furthermore, the Pt nanocubes with the same Pt{100} exposed were also loaded on TiO$_2$ nanosheets to provide a reference sample (TiO$_2$–Pt). From the photocurrent versus time (I–t) curves in Fig. 12c, the
photocurrents turn out to be in the order of TiO$_2$–Pd < TiO$_2$–Pt < TiO$_2$–Pd@Pt$_{10L}$ < TiO$_2$–Pd@Pt$_{3L}$, suggesting more efficient electron–hole separation by the Pd@Pt cocatalyst. The same order was also recognized for hydrogen production rates, but the improvement in hydrogen production from the cocatalyst design appears to be more significant than the photocurrent (Fig. 12d).

The enhancement of photocatalytic performance with the Pd@Pt cocatalyst resulted from charge polarization at the Pd–Pt interface. Owing to the different work functions of Pd and Pt, electron migration across the interface from Pd to Pt will equilibrate their electron Fermi distributions. When TiO$_2$ was photoexcited, interfacing charge transfer would occur from TiO$_2$ to Pd driven by a TiO$_2$–Pd Schottky junction. Meanwhile, the interfacing polarization would serve as a new driving force for the migration of photogenerated electrons from the Pd to Pt surface, improving the charge separation in the entire system. Furthermore, the interfacing polarization also led to the accumulation of electrons on the Pt surface. Both the electron accumulation and lattice strain at the Pd–Pt interface facilitated H$_2$O adsorption. As a result, the charge polarization does not only improve the charge separation, but it also enhances the H$_2$O adsorption. It should be noted that the interfacing polarization effect decays with an increase in Pt shell thickness (Fig. 12e). For this reason, the shell thickness has to be kept within a few atomic layers. This delicate design enables a boosting of the photocatalytic performance and a reduction in the amount of expensive Pt used.

6. Summary and outlook

The surface and interfacing design of cocatalysts would be a promising route to fabricate high-performance photocatalysts through maximizing the efficacy of cocatalysts. In this review, we have highlighted the emerging horizons of cocatalyst design based on surface and interfacing adjustment. On one hand, surface parameters such as the composition, facets, phases and defects have been tailored to enhance catalytic reactions on cocatalyst surfaces. On the other hand, interface parameters including interfacing composition, location and facets have been optimized to improve the charge transfer across the interface of cocatalysts with semiconductors. With novel methods, theories, and mechanisms (e.g., the interfacing polarization effect) implemented in cocatalyst design, surface and interfacing control has enabled the enhancement of surface reactions and interfacing charge transfer simultaneously. This set of designs not only deepens our understanding of fundamental aspects, but also provides technical approaches to significantly enhance the activity and selectivity in water splitting and CO$_2$ reduction.

Although great achievement and remarkable progress have been made in the surface and interfacing design of cocatalysts, there is a long way to go toward the practical use of photocatalysis in industry and our lives. Firstly, most of the previous reports on cocatalyst design were to tailor only one surface or interfacing parameter. It remains a grand challenge to design cocatalysts taking more parameters into account. The bottlenecks include the interplaying effects of the parameters and the limited synthetic methods for realizing complicated designs. Secondly, some experimental results achieved in the designs still remain elusive. In many cases, existing observations seem contradictory between different reports. For instance, it has been reported that spatially separating reduction and oxidation cocatalysts and having them in intimate contact can both enhance charge separation;\textsuperscript{6,7} and that surface reactions on reduction cocatalysts can be facilitated by both reducing electron density or accumulating electrons on the surface.\textsuperscript{8,9} Thirdly, advanced characterization techniques are lacking to monitor the processes of surface reactions and interfacing charge transfer at high spatial and temporal resolution. Dynamic evolution at electron and molecular levels will provide important information for establishing the relationship between surface/interface parameters and catalytic performance. The above bottlenecks call for research at the intersection of precisely controlled synthesis, theoretical simulations and advanced spectroscopic characterization.\textsuperscript{a} Multidisciplinary collaborations at the intersection of these will offer the research community the capabilities to tailor cocatalyst structures with atomic precision and to understand the underlying mechanisms at the electron and molecular level. As soon as these existing bottlenecks are overcome, the more rational and systematic design of cocatalyst surfaces and interfaces would serve as a strong driving force toward the fabrication of highly efficient photocatalysts for solar fuel production.

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Notes and references