Surface and interface design for photocatalytic water splitting

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Surface and interface structures are considered as the critical parameters which can be engineered to improve the performance of catalysts. This Frontiers article highlights our recent advances in surface and interface design toward photocatalytic water splitting.

Introduction

Exploiting sustainable energy systems is essentially important for solving the issues of an increasingly severe energy crisis and environmental pollution. Sunlight-driven water splitting provides a promising approach to transform solar energy into hydrogen fuel. Since the photocatalytic splitting of water at TiO2 electrodes was first reported by Honda and Fujishima in 1972, photocatalysis has demonstrated wide-ranging potential applications in such areas for solving the world energy crisis. However, the low overall efficiency impedes the development of industrial-scale solar-driven photocatalytic water splitting systems. Therefore, developing highly efficient photocatalysts is the vital task for the scientists of this time.

In principle, highly efficient photocatalytic systems can be fabricated through the structural engineering of photocatalysts. A top priority for structural engineering is the surface and interface design, as surface and interface structures are two critical parameters for maneuvering the performance of photocatalysts. Tailoring surface and interface structures often brings about their synergistic effects which are closely bound up with the capability for tuning light harvesting, maneuvering charge kinetics and engineering active sites (Fig. 1). These functions actually correspond to the three basic steps of a photocatalytic process. Toward tunable light harvesting, surface design enables the harvesting of broadband solar energy and thus promotes the generation of electron–hole pairs. Upon photoexcitation, charge kinetics can be manus-
ered by controlling the interface between light-harvesting centers and surface catalytic sites, with a goal to suppress adverse electron–hole recombination in photocatalysts.6 As a final step, catalytic sites – the locations for chemical reactions – should be controlled through surface engineering, which has shown important contributions for improving photocatalytic performance by means of altering surface adsorption and activation for specific reactants.7,8 For heterojunction structures, their outstanding photocatalytic performance is often enabled by the synergistic effects of surface and interface design.9,10

In recent years, the continuous clarification of photocatalytic mechanisms combined with the progress in techniques for precise synthesis and advanced characterization has paved the way for the rational surface and interface design of photocatalysts. Design strategies include the control over defects, facets, compositions, phases, areas and electronic couplings of photocatalytic materials as well as their dimensions (e.g. the distance from the interface to the surface). The development of non-oxide semiconductors (e.g. carbon nitrides, oxynitrides and oxysulfides) also brings new opportunities for surface and interface design of photocatalysts.11–14 Furthermore, a combination of experiments with simulations has played a critical role in predicting and understanding surface and interface design.15 In this Frontiers article, our recent research efforts will be summarized to shed light on how surface and interface design can optimize the three basic steps of light harvesting, charge transfer and the catalytic reactions of photocatalytic processes, thereby achieving enhanced performance in photocatalytic water splitting.

Tuning light harvesting

To efficiently utilize solar energy, harvesting visible (vis) to near-infrared (NIR) light is always the goal and challenge for photocatalysis, given that ultraviolet (UV) light only accounts for 5% of the solar spectrum. Recently, it has taken advantage of surface and interface design to extend light absorption through several strategies including impurity doping, the surface plasmon resonance (SPR) effect and Z-schemes.16–18

Doping metal cations on photocatalyst surfaces has been proven to be a fine method for extending light absorption; however, the working mechanism is rather complex and depends on material systems. We have demonstrated that metal-to-ligand charge transfer (MLCT) between Pt2+ and g-C3N4 can broaden the light absorption of g-C3N4 after incorporating Pt2+ into g-C3N4.19 As shown in Fig. 2a, except for the intrinsic band absorption of g-C3N4 at $\lambda < 460$ nm, the absorption at $\lambda > 460$ nm exhibits distinct redshift along with increasing concentrations of Pt2+. In addition to metal doping, the surface plasmon resonance (SPR) effect is another strategy for extending light absorption with metals. In brief, SPR is the

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collective oscillation of conduction band electrons in noble metal particles induced by the electromagnetic field of incident light. The surface plasmons may decay through non-radiative processes, which generates energetic electron–hole pairs (so-called “hot electrons” and “hot holes”) at the nanoparticle surface.\textsuperscript{20} We recently have designed the integration of dual plasmonic nanostructures with TiO$_2$ semiconductor nanosheets, which achieved photocatalytic hydrogen production in the visible and NIR spectral regions.\textsuperscript{25} In this design, Au nanocubes and nanocages were employed as plasmonic agents to harvest visible and near-infrared light, respectively (Fig. 2b).

Z-schemes are also a promising approach to realize broad-spectrum photocatalysis. Inspired by the natural photosynthesis of green plants, the so-called “Z-scheme system” is a semiconductor-based artificial photosynthetic system, composed of a H$_2$-evolving photocatalyst, an O$_2$-evolving photocatalyst and an electron mediator.\textsuperscript{22} Most narrow-bandgap semiconductors have straddling band structure alignments with TiO$_2$, constituting an obstacle to forming a Z-scheme for photocatalytic water splitting. To circumvent this situation, we have demonstrated that the energy band of narrow-bandgap Ag$_2$S interfacing with metal Ag can be upshifted. As a result, the designed ternary Ag$_2$S–Ag–TiO$_2$ heterojunction structures formed a Z-scheme between TiO$_2$ and Ag$_2$S, achieving the light harvesting of both UV and vis-NIR light.\textsuperscript{23} Recently, we have established a Z-scheme through Janus-like structures consisting of roxbyite Cu$_7$S$_4$ and γ-MnS through a cation-exchange approach. The cation-exchange synthetic scheme was beneficial to form high-quality interfaces between semiconductors at the atomic level. The roxbyite Cu$_7$S$_4$ and γ-MnS displayed a staggered alignment and absorbed NIR and UV-vis light, respectively. Moreover, the surface plasmon of Cu$_7$S$_4$ made an additional contribution to light harvesting.\textsuperscript{24}

**Maneuvering charge kinetics**

Charge kinetics is the process that links light harvesting with catalytic reactions and modulates the efficiency of the entire photocatalytic system, as it holds the key to efficient charge separation and transfer. Exploring the relationship between structure and charge kinetics is very important for the development of solar water splitting. Previous work has verified that charge transfer in periodically ordered macroporous architectures shows strong dependence on the relative size of dual porosity.\textsuperscript{25} Beyond that, constructing heterojunctions is an effective approach to promote charge separation and transfer.\textsuperscript{26,27} In a heterojunction structure, the interface between two components is the location where the charge carriers are separated and then transferred to the surface for catalytic reactions. Owing to the lack of a driving force to manipulate the migration of charge carriers from the interface to the surface, charge carriers would usually transfer via random paths in bare semiconductors, resulting in severe electron–hole recombination. Various surface and interface designs for heterojunction structures have been dedicated to the reduction of charge recombination, including Z-schemes, Schottky junctions, charge spatial distribution and plasmonic effects.\textsuperscript{28–31}

Recently, two-dimensional (2D) polymer photocatalysts have been explored as emerging materials for water splitting.\textsuperscript{32,33} In view of their ultrathin thickness as well as tunable molecular structures, we have constructed polymer-based van der Waals heterostructures as a Z-scheme system for overall water splitting by using ultrathinaza-conjugated microporous polymers (CMP) and C$_2$N nanosheets as the O$_2$- and H$_2$-evolving catalysts, respectively (Fig. 3a).\textsuperscript{34} The photogenerated electrons from the aza-conjugated microporous polymers can promptly recombine with the photogenerated holes from the C$_2$N nanosheets at the interfaces of the heterostructures. Furthermore, combined with reduced graphene oxide (rGO) as a solid electron mediator, this overlapped interface can promote the interfacial charge-transfer process.

Constructing Schottky junctions at the interface between the semiconductor and the metal is another strategy for spatially promoting the separation of electrons from holes and reducing their recombination, as the formed Schottky barriers can inhibit the backflow of electrons or holes from metal to semiconductor.\textsuperscript{35} Schottky junctions are a type of junction formed when the metal and semiconductor have appropriate work functions and are in intimate contact with each other.\textsuperscript{36} An important selection criterion for building such desirable Schottky junctions between semiconductors and metals is the work function of the semiconductor surface facets. When selecting the facets, the intrinsic charge spatial distribution has to also be considered, as the photoexcited electrons and holes will accumulate on certain semiconductor facets. By taking the Cu$_2$O-Pd heterojunction structure as a model, we have demonstrated that the surface facet of the semiconductor matters to both the establishment of a Schottky barrier and charge spatial separation.\textsuperscript{37} In a word, the synergetic use of Schottky junctions and charge spatial separation through surface and interface facet design in this system provided a new approach to maneuver charge separation and transfer.

![Fig. 3](https://example.com/f3.png) (a) Illustration of the electronic band structures of aza-CMP and C$_2$N nanosheets, resulting in a Z-scheme structure. Reproduced with permission from ref. 34, Copyright 2018 Wiley-VCH Verlag GmbH & Co. (b) Schematic illustrating the band alignments and charge flow at two metal–semiconductor interfaces. Reproduced with permission from ref. 38, Copyright 2015 Wiley-VCH Verlag GmbH & Co.
Another new design by our research group is the synergy of the plasmonic effect with the Schottky junction (Fig. 3b). The design rule is to separate the Schottky junction from the plasmonic hot carrier injection by building two metal–semiconductor interfaces based on the selection of semiconductor facets and metals. Given the facet-dependent spatial charge separation, the (001) and (110) facets of a p-type BiOCl semiconductor were selected as the surface to contact with the plasmonic metal and non-plasmonic metal, respectively. Bridged by the facet-dependent spatial charge separation of the semiconductor, the injection of plasmonic hot holes can be synergized with the hole trapping by the Schottky junction. As such, both plasmonic hot holes and semiconductor-photogenerated holes can be trapped on the non-plasmonic metal, thus realizing a highly-efficient charge separation.

The strategy of metal nanoparticles decorated on a semiconductor for reduced electron–hole recombination generally faces two obstacles: (i) the emergence of defects through the formation of an interface in the heterojunction structures, where the electron–hole recombination tends to occur; and (ii) the formed interface reduces the exposed surfaces for reaction molecules to pick up the photogenerated charges for redox reactions on the surface. To overcome these two obstacles, we have presented novel Cu2O-Pd-rGO stack structures to promote charge transfer and electron–hole separation for photocatalytic hydrogen production through interface design. In this design, the single-crystal Cu2O was selected to form the Schottky barrier with single-crystal Pd nanoparticles, which could reduce the number of interface defects in the stack structure. Furthermore, rGO nanosheets were introduced to establish an intimate interface with Pd for transferring holes to graphene, whereas electrons were driven to flow from Pd to Cu2O by the Schottky barrier. Taken together, the harmful electron–hole recombination has been greatly suppressed by the fast charge transfer processes in our designed ternary stack structure.

Engineering active sites

In general, the surface of a pristine semiconductor does not possess highly active sites both for the reduction reaction (H2 evolution) and the oxidation reaction (O2 evolution). The combination of a semiconductor with a cocatalyst is a widely used approach to promote the performance of photocatalytic water splitting by offering active sites. In this case, surface design of the cocatalyst through tailoring certain surface parameters holds the key to tuning photocatalytic performance. The performance of active sites is strongly correlated with some important surface parameters such as composition, facets, phases and defects, which allows the control of the cocatalyst. Moreover, interface design can be implemented in the cocatalyst through interfacial charge polarization, which tailors the electron density of active sites and thus influences the water splitting process at the sites. In this section, our endeavors in engineering active sites of cocatalysts through surface/interface design for photocatalytic H2 evolution and O2 evolution are discussed, including control over surface composition, facets, phases and interfacial charge polarization.

Pt is the most widely used cocatalyst exhibiting the best performance in photocatalytic hydrogen evolution, as Pt possesses the lowest activation energy for hydrogen evolution in comparison with other noble metals. However, the high material cost of Pt greatly impedes its practical application. For this reason, reducing Pt usage or developing Pt-based alloy cocatalysts through surface design is an effective method for lowering costs. Toward this goal, we have reported atomically controlled Pd@Pt core–shell cocatalysts in combination with anatase TiO2 for photocatalytic water splitting. The well-designed structures enabled the higher electron density on the Pt surface through interfacial charge polarization. Together with the increased lattice strain, the high density of electrons significantly enhanced the adsorption of reactive H2O molecules onto the Pt surface for efficient water splitting. A cocatalyst with a similar composition but different surface design was implemented in another work by our research group (Fig. 4a). By incorporating Pd into Pt cocatalysts, PdPt alloy cocatalysts enclosed by (100) and (111) facets were grown in situ on TiO2 nanosheets, respectively. Similar to other reports, the performance of hydrogen production turned out to be related to the surface facets of the cocatalysts. In both cases, caused by the interatomic charge polarization between Pd and Pt, the composition of the cocatalysts could tune the adsorption of molecular water as well as the activation on Pt reaction sites, resulting in a composition dependence.

Fig. 4 (a) Illustration of the reduction reactions at PdPt alloy nanoparticles with different facets. Reproduced with permission from ref. 42, Copyright 2016 Wiley-VCH Verlag GmbH & Co. (b) Schematic illustrating the charge-transfer behavior and H2-evolution active sites of MoS2 with different phases. Reproduced with permission from ref. 46, Copyright 2015 Springer.
In order to reduce material costs, numerous low-cost non-noble metal cocatalysts such as metal sulfides, transition metals and 2D metal carbides (MXenes) have been exploited.\textsuperscript{34–46} As shown in Fig. 4b, we established heterojunction structures where TiO\textsubscript{2} nanocrystals were supported on 1T (octahedral phase)-MoS\textsubscript{2} and 2H (trigonal prismatic phase)-MoS\textsubscript{2}, respectively.\textsuperscript{46} In sharp contrast to 2H-MoS\textsubscript{2}, 1T-MoS\textsubscript{2} not only acted as electron delivery channels with higher mobility, but also offered additional reaction sites for H\textsubscript{2} production on their basal plane. As a result, the developed TiO\textsubscript{2}-MoS\textsubscript{2}(1T) heterojunction structure exhibited excellent performance for photocatalytic hydrogen production.

Conclusions and outlook

After years of active research, the unremitting efforts dedicated to marvellous heterogeneous photocatalysts have led to a rich database and knowledge for rational surface and interface design. The powerful roles of surface and interface design in bringing remarkably improved and appealing performance for photocatalytic water splitting have been undoubtedly illustrated in this Frontiers article. Our recent research efforts have elaborated the design rules for tuning light harvesting, maneuvering charge kinetics and engineering active sites, which can promote the three basic steps holding the key to photocatalysis. Meanwhile, surface and interface designs have been further synergized according to their interplay relationships to maximize the performance improvement.

Although great achievements have been made in the surface and interface design of photocatalysts, it still remains a grand challenge to fully exert the functions for photocatalytic water splitting. Especially when more parameters are involved in a photocatalytic system, the complicated structures of photocatalysts and the interplay effects of these parameters would bring bigger challenges for material design and synthesis. One of the challenges is that the synthetic techniques have lagged behind our demands for precisely controlling the surface and interface parameters. Furthermore, thus far the characterization techniques can barely give a clear picture of the variations in some surface and interface parameters. The limitations of the synthetic and characterization techniques make the real mechanisms behind the structure–property relationships remain elusive, formulating an obstacle for further optimization of material design. For this reason, the further development of surface and interface design should be performed at the intersection of precisely controlled synthesis, advanced characterization and theoretical simulations.

Firstly, novel synthetic methods are required to tailor the surface and interface parameters with atomic precision. Secondly, \textit{in situ} advanced characterization techniques at high spatial, spectral and temporal resolutions are highly desirable for monitoring the processes of surface reactions and interfacial charge transfer at the electron and molecular level. Thirdly, theoretical simulations are needed as a complement to the syntheses and characterization. The simulations not only provide information for guiding surface and interface design, but also make up for the limitations of current characterization techniques. With these developments, the relationship between surface/interface parameters and catalytic performance will be elucidated more accurately, and the more rational and systematic surface and interface design would serve as a strong driving force toward the fabrication of highly efficient catalysts for photocatalytic water splitting.

Conflicts of interest

There are no conflicts to declare.

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Notes and references