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Photocatalysis

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Designing p-Type Semiconductor–Metal Hybrid Structures for Improved Photocatalysis**

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Abstract: *A practical strategy is proposed to facilitate the migration of holes in semiconductor (the low rate of which limits photocatalytic efficiency) by taking advantage of the Schottky barrier between p-type semiconductor and metal. A high work function is found to serve as an important selection rule for building such desirable Schottky junction between semiconductor surface facets and metal. The intrinsic charge spatial distribution has to be taken into account when selecting the facets, as it results in accumulation of photoexcited electrons and holes on certain semiconductor facets. Importantly, the facets have a high work function, the same characteristic required for the formation of Schottky junction in a p-type semiconductor–metal hybrid structure. As a result, the semiconductor crystals in the hybrid design may be better enclosed by single facets with high work function, so as to synergize the two effects: Schottky barrier versus charge spatial separation.*

The low mobility of hole carriers in bare semiconductors constitutes one of the bottlenecks for their efficiency in photocatalysis.[1,2] It is thus imperative to balance the rates of photogenerated electrons and holes to reach specific reaction sites, accomplishing more efficient redox reactions. When a p-type semiconductor contacts a metal with their work functions satisfying $W_s > W_m$, a Schottky junction can be formed to expedite the migration of holes from the semiconductor to the metal.[3] On the other hand, recent progress has demonstrated that the photoexcited electrons and holes can be potentially driven to different crystal facets owing to their varied charge densities.[4–6] This effect makes it feasible to spatially separate the electron–hole pairs in a semiconductor. There is no doubt about the functions of Schottky barrier and charge spatial distribution in maneuvering the migration rates and directions of electrons and holes for photocatalysis. However, these two effects interplay with each other in a semiconductor–metal hybrid structure, and if not well harnessed, may suppress their respective efficacy. It remains an open question whether these two can jointly work for achieving better charge separation and transfer so as to facilitate the photocatalytic reactions.

The synergetic use of Schottky junction and charge spatial separation has recently been approached with n-type semiconductors.[4] The acceleration of electron migration by the Schottky barrier between n-type semiconductor and metal, however, does not help balance the migration rates of electrons and holes. When the Schottky junction is formed in a p-type semiconductor–metal hybrid structure, it has potential efficacy in expediting the migration of holes but the situation becomes much more complicated. Among others, an important factor is the dependence of surface work functions on crystal facets. It is known that whether a Schottky junction can be established heavily relies on the compatibility of the interfacial work functions of semiconductor and metal (that is, their own surfaces).[3] In fact, not all the surface facets of a semiconductor can offer appropriate work function to form the Schottky barrier with a metal, simply because different crystal facets may have varied electronic structures resulting in huge variation in their work functions. For this reason, only when the metal is deposited on specific facets of semiconductor, the desired Schottky barrier can be formed to facilitate the migration of holes. This critical factor has been somehow overlooked previously.

Herein, we demonstrate that the surface facet of semiconductor matters to both the establishment of Schottky barrier and charge spatial separation, by taking Cu_2O-Pd hybrid structure as a proof-of-concept example. The facet accumulating photoexcited electrons by spatial separation turns out to have high work function, the same characteristic required for the formation of Schottky junction in p-type semiconductor–metal hybrid structures. As long as the crystal facets of semiconductor surface are well engineered, the Schottky barrier and charge spatial separation can be synergetically utilized to improve photocatalytic efficiency.

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In our study, we first take into account the intrinsic charge spatial distribution in the Cu_2O, as it may result in accumulation of photoexcited electrons and holes on certain Cu_2O facets. The charge spatial distribution of $Cu_2O(100)$ and $Cu_2O(111)$ facets is analyzed by first-principles simulations.[7] Taking a glance at the crystal structures (Figure 1 a, b), one can see that more oxygen atoms are exposed on the top layer of $Cu_2O(100)$ surface, indicating the high probability of photoexcited electrons migrated to (100) surface. Further potential analysis (Figure 1 c) shows that the work function of $Cu_2O(100)$ (ca. 7.2 eV) is much higher than that of bulk Cu_2O (ca. 4.8 eV),[8] also suggesting that the electrons prefer to transfer from bulk phase to (100) surface. In contrast, the work functions of $Cu_2O(111)$ and bulk Cu_2O are very comparable (see Figure 1 d), implying no selectivity of (111) surface in electron–hole separation. Given the preference of electrons accumulated on (100), the photoexcited electrons and holes will most likely migrate to (100) and (111) surface, respectively, as illustrated in Figure 1 e. Such charge spatial separation has been verified by photocurrent measurements (Figure 1 f). The photocurrents by the photoelectrodes made of Cu_2O cuboctahedrons are roughly three times those by cubes and octahedrons. The Cu_2O cubes and octahedrons are enclosed by {100} and {111} facets, respectively, while the cuboctahedrons have both {100} and {111} facets on their surface (see the Supporting Information, Figure S1 for their morphologies). To further confirm the charge spatial separation, we have performed visible-light illumination on the Cu_2O cuboctahedrons in the presence of $K_2[PdCl_4]$. It turns out that $K_2[PdCl_4]$ is more preferentially reduced to Pd nanoparticles on the {100} facets (Supporting Information, Figure S2), indicating that the electrons are mostly accumulated on the {100} surface when the Cu_2O is photoexcited.

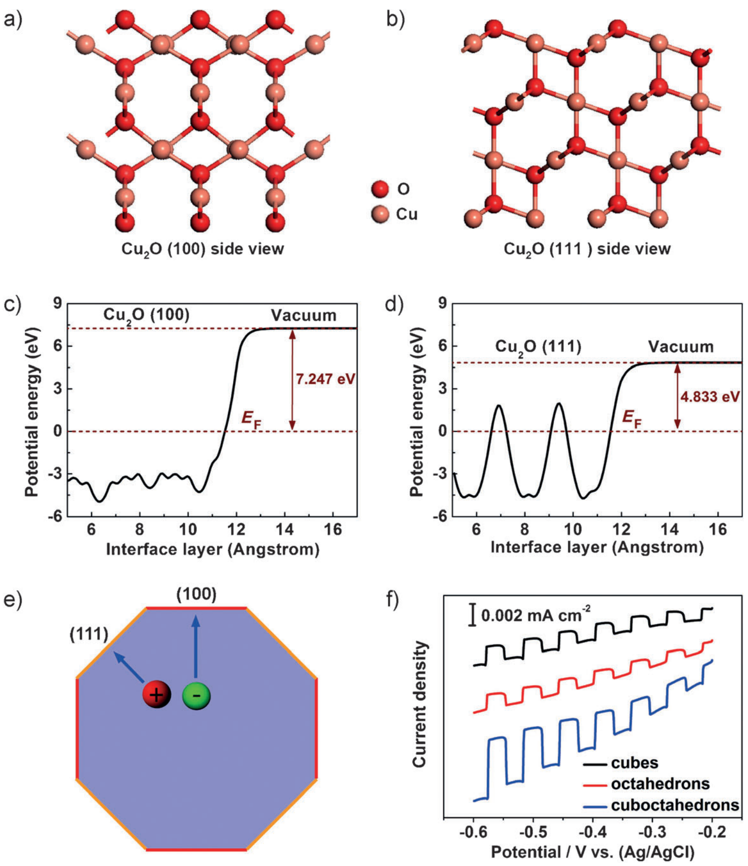

Figure 1. Representations of the atomic arrangement for the a) $Cu_2O(100)$ and b) $Cu_2O(111)$ surface. Potential diagrams of c) $Cu_2O(100)$ and d) $Cu_2O(111)$ surface obtained from first-principles simulations. E_F denotes the Fermi level. e) Illustration of the charge spatial distribution between the $Cu_2O(100)$ and $Cu_2O(111)$ surface. f) Photocurrent versus potential responses of photoelectrodes made of Cu_2O cuboctahedrons, cubes, and octahedrons at the same Cu_2O loading weight, measured in a 0.5 M Na_2SO_4 electrolyte under chopped visible-light ($\lambda > 400$ nm) irradiation.

Upon acquiring the charge spatial distribution, we are in a position to investigate whether the effects of facet-dependent charge spatial separation and Schottky function (between p-type semiconductor Cu_2O and Pd) can be combined to allow the electrons and holes separately collected on the {100} and {111} facets of a cuboctahedron, respectively, at more balanced rates (Figure 2 a). It turns out to be not feasible to achieve this goal in consideration of work functions. According to their potential lineup (Figure 2 b), the Schottky barrier cannot be formed at the $Cu_2O(111)$-Pd interface to accelerate the migration of holes from $Cu_2O(111)$ to Pd, simply because of the low work function of $Cu_2O(111)$. Instead, an anti-blocking layer (for hole carriers) will be formed at the interface due to the preferential accumulation of holes at the $Cu_2O(111)$ surface,[3] thereby giving rise to the electron–hole recombination. Nevertheless, to explore this possibility we have selectively deposited Pd on the {111} facets of Cu_2O cuboctahedrons (Figure 2 c). As expected, the photocurrents of Cu_2O cuboctahedrons are suppressed by the addition of Pd (Figure 2 d). The incompatibility of $Cu_2O(111)$-Pd to forming the Schottky barrier has been also demonstrated in the system of Cu_2O octahedrons deposited by Pd at various concentrations (Supporting Information, Figures S3, S4).

In consideration of the work function, the {100} facets should be a better choice to establish the Schottky barrier with Pd in favor of the migration of holes (Figure 3 a). We have simulated the potential lineups of Pd interfacing with $Cu_2O(100)$ facets. As shown in Figure 3 b, the potential of Pd is about 1.7 eV higher than that of $Cu_2O(100)$, suggesting the electron flow from Pd to Cu_2O at their interface. This is indicative of the formation of the Schottky junction in a p-type semiconductor–metal hybrid structure.[3] As a result, the migration of holes can be expedited by the addition of Pd only at the $Cu_2O(100)$-Pd interface. To verify this feature, we have synthesized the Cu_2O cubes deposited with Pd (Figure 3 c; Supporting Information, Figure S5). The photocurrent measurements clearly depict the charge behavior altered by the $Cu_2O(100)$-Pd interface. As displayed in

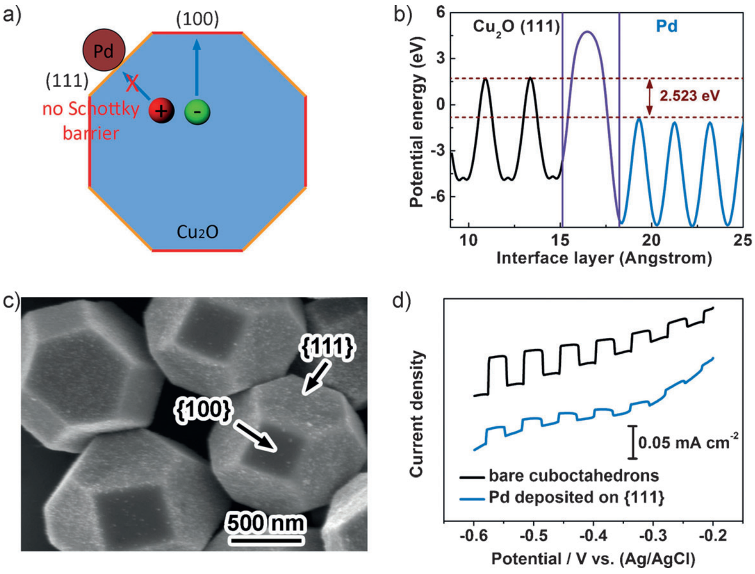

Figure 2. a) Illustration for the charge transfer in the Cu_2O cuboctahedrons with Pd deposited on {111} facets. b) Potential lineup diagram of Cu_2O(111)-Pd interfaces obtained from first-principles simulations. c) SEM image of Cu_2O cuboctahedrons for which the {111} surface was selectively deposited with Pd through PVP capping {100} facets. d) Photocurrent versus potential responses of photoelectrodes made of bare Cu_2O cuboctahedrons and those with {111} surface selectively deposited with Pd, respectively, at the same Cu_2O loading weight, measured in a 0.5 M Na_2SO_4 electrolyte under chopped visible-light ($\lambda > 400$ nm) irradiation.

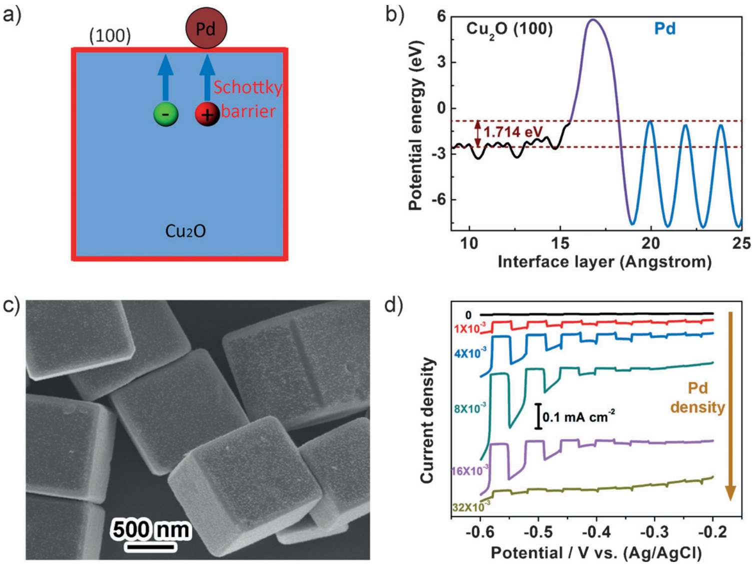

Figure 3. a) Illustration of the charge transfer at the Cu_2O(100)-Pd interface in the Pd-decorated Cu_2O cubes. b) Potential lineup diagram of Cu_2O(100)-Pd interfaces obtained from first-principles simulations. c) SEM image of Cu_2O cubes that were deposited with Pd (molar ratio of Pd/Cu_2O at 8×10^{-3}). d) Photocurrent versus potential responses of photoelectrodes made of Cu_2O cubes that were deposited with different amounts of Pd at the same Cu_2O loading weight, measured in a 0.5 M Na_2SO_4 electrolyte under chopped visible-light ($\lambda > 400$ nm) irradiation. The shown concentrations are molar ratios of Pd to Cu_2O.

Figure 3d, the photocurrents of Cu_2O cubes can be significantly enhanced by the addition of Pd nanoparticles on their {100} surface. The photocurrent measurements reflecting the efficiency of charge separation suggest that the electron–hole pairs can be better separated at the Cu_2O(100)-Pd interface, validating the function of Cu_2O(100)-Pd Schottky junction in facilitating the migration of holes. This result reveals that the facet selection rule for the Schottky barrier formation is in line with the need of electron migration along the charge spatial separation (that is, Cu_2O(100)). Thus the Cu_2O cubes having high work function represent an ideal geometry to compromise the Schottky barrier with the charge spatial separation for their synergetic utilizations.

Interestingly, the efficacy of this synergetic strategy heavily relies on the density of Schottky junctions. The observed photocurrent enhancement turns out to strongly correlate with the density of Pd nanoparticles on the Cu_2O surface (see the Supporting Information, Figure S5 for their morphologies). From Figure 3d it can be seen that the photocurrents are initially enhanced with increasing the Pd density, followed by photocurrent suppression beyond a certain point (that is, Pd/$Cu_2O = 8\times10^{-3}$ mol ratio). To help decode the mechanism behind this, we have employed ultrafast transient absorption spectroscopy to track in real time the electron dynamics.[9] Using a femtosecond visible pump/white-light-continuum probe, the involved transient electron behavior dependent on the Pd density was examined (Figure 4). The positively valued transients probed between 625–675 nm (in red) can be assigned to excited-state absorption (ESA) that reflects the lifetime of photoexcited electrons in the semiconductor. Apparently, the Pd density has a significant impact on the electron lifetime, which follows the same trend as in the photocurrent measurements. It is understandable that the increase in the Pd density can aid the migration of holes from the Cu_2O to the Pd, prolonging the electron lifetime; however, it seems puzzling why excessive Pd plays a contrary role. Given that both the electrons and holes have to reach the same surface in the configuration, the holes migrated to the Pd can be predicted to bear a high chance to recombine with the electrons in the case of dense Pd, most likely reducing the lifetime of carriers. To verify this prediction, we have measured the photoluminescence (PL) emission spectra of samples which may provide insight into the electron–hole recombination. As shown in the Supporting Information, Figure S6, the PL peaks gradually blue-shift with increasing the Pd density, indicating the enhanced recombination of photoexcited electrons with the holes closer to the Cu_2O-Pd interface. These results reveal the importance of finding an appropriate balance between the collection of holes by Pd and the accumulation of electrons on Cu_2O at their interface, to minimize the recombination of photo-generated carriers. It turns out that the density of metal has to be kept moderate for

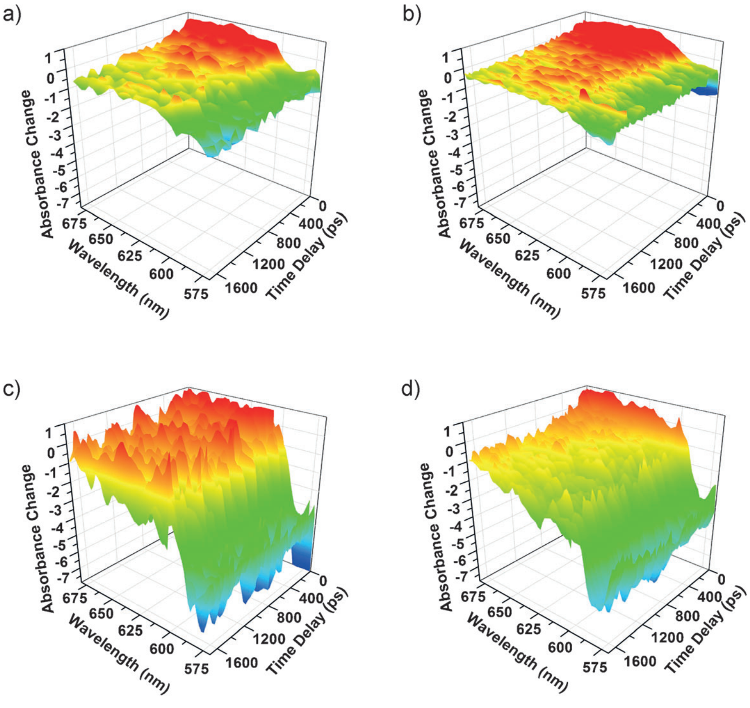

Figure 4. 480 nm pump-induced, temporally and spectrally resolved absorbance changes (normalized) as functions of time delay and probe wavelength for a) bare Cu_2O cubes, and Cu_2O cubes deposited with different amounts of Pd: b) 1×10^{-3} Pd/Cu_2O (mol), c) 8×10^{-3} Pd/Cu_2O (mol), and d) 32×10^{-3} Pd/Cu_2O (mol).

efficient electron–hole separation in the case of single-faceted semiconductors.

The information of charge behavior gleaned above has demonstrated the importance of facet design to charge separation. Further, we implement our designed materials in photocatalysis. As a proof-of-concept demonstration, we use photocatalytic hydrogen production from pure water as a model system,[10,11] systematically correlating the efficiency of charge separation with that of photocatalysis. The holes collected by the Pd and the electrons reaching the Cu_2O surface can be provided for oxidation and reduction in photocatalysis, respectively. Cu_2O is a p-type semiconductor with a direct bandgap of about 2 eV, the conduction band levels of which should be qualified for water reduction to produce hydrogen.[12–14] Thus Cu_2O is supposed to have photocatalytic activities in a broad visible spectral region;[12] however, the low migration rate of holes remains a bottleneck to its efficiency. In the current case, with the hole carriers well-harnessed, the Pd-decorated Cu_2O cubes at the moderate Pd density show a hydrogen production of 2.20 $\mu mol\,g^{-1}$ over 4 h, which is significantly higher than those by other Cu_2O counterparts (Figure 5). This observation clearly demonstrates the niche of our photocatalyst design in charge separation and transfer.

In summary, both the Schottky barrier and charge spatial distribution are critical elements to the electron–hole separation and charge accumulation at surface, and highly dependent on semiconductor facets in a semiconductor–metal configuration. As demonstrated in our Cu_2O-Pd model system, these two effects can be reconciled in a single-faceted configuration by taking advantage of high work function of semiconductor surface. To achieve better efficiency, the establishment of the Schottky barrier has to be prioritized by selecting an appropriate surface facet for metal deposition and charge migration sites, and meanwhile the photoexcited electrons should be allowed to migrate out from this facet by virtue of the charge spatial distribution. Moreover, the density of metal deposition definitely holds the key to suppressing potential electron–hole recombination, as both the electrons and holes are accumulated on the same surface. With this design optimized, the charge migration rates can be better harnessed. Given that the mobility of holes limits to a large extent the efficiency of various photocatalytic reactions, it is anticipated that this work casts new light on photocatalysts design in consideration of facet effect.

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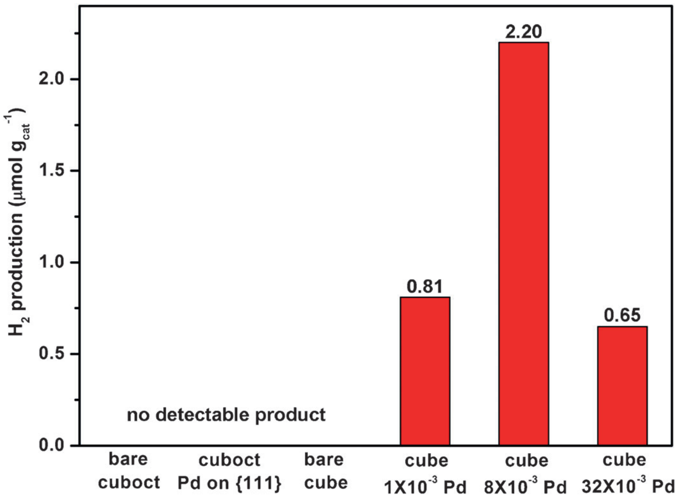

Figure 5. Photocatalytic hydrogen production from pure water under visible-light ($\lambda > 400$ nm) irradiation for 4 h using different photocatalysts at the same Cu_2O loading weight. The variations of production rates are within 10% when the loading weight is varied from 20 to 200 mg. The hydrogen was detected by a gas chromatography (GC) thermal conductivity detector (TCD). The evolution of oxygen was also observed by the TCD during the photocatalytic reactions. “Cuboct” denotes cuboctahedron, and the shown concentrations are molar ratios of Pd to Cu_2O.

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