Integration of Multiple Plasmonic and Co-Catalyst Nanostructures on TiO$_2$ Nanosheets for Visible-Near-Infrared Photocatalytic Hydrogen Evolution

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Utilization of visible and near-infrared light has always been the pursuit of photocatalysis research. In this article, an approach is developed to integrate dual plasmonic nanostructures with TiO$_2$ semiconductor nanosheets for photocatalytic hydrogen production in visible and near-infrared spectral regions. Specifically, the Au nanocubes and nanocages used in this work can harvest visible and near-infrared light, respectively, and generate and inject hot electrons into TiO$_2$. Meanwhile, Pd nanocubes that can trap the energetic electrons from TiO$_2$ and efficiently participate in the hydrogen evolution reaction are employed as co-catalysts for improved catalytic activity. Enabled by this unique integration design, the hydrogen production rate achieved is dramatically higher than those of its counterpart structures. This work represents a step toward the rational design of semiconductor–metal hybrid structures for broad-spectrum photocatalysis.

1. Introduction

Solar photocatalysis for chemical fuel production represents a highly important approach to addressing current energy and environmental demands. Solar-to-chemical energy conversion efficiency is mainly limited by the three factors that cannot be all optimized in the existing semiconductor-based photocatalytic systems: 1) relatively narrow range of light absorption and low redox abilities of photogenerated carriers; 2) electron-hole recombination; and/or 3) lack of highly active sites for redox reactions on catalyst surface. From the viewpoint of semiconductor physics, the first factor in a semiconductor is determined by the bandgap of the semiconductor (namely, the energy range between conduction band minimum (CBM) and valence band maximum (VBM)). In terms of redox abilities, wide-bandgap semiconductors generally show superior photocatalytic performance to narrow-bandgap ones, according to the relative energy levels of CBM ($E_c$) and VBM ($E_v$) to the redox potentials of half reactions. However, the semiconductors with wide bandgaps can only absorb UV light (wavelength ($\lambda$) < 400 nm) which accounts for a very small fraction (≈5%) of solar spectrum.

Recently, the integration of plasmonic metal nanostructures with wide-bandgap semiconductors has offered a new opportunity for extending the light absorption of the photocatalysts to longer wavelengths. With the plasmonic metal (e.g., Au and Ag) in direct contact with a n-type...
semiconductor, the surface plasmon of metal can generate and inject energetic “hot” electrons into the conduction band (CB) of semiconductor (Figure S1, Supporting Information).\[12–15\] As long as the photon energy meets \( h\nu \geq E_{c0} - E_{F} \) (which has much smaller value than \( E_{c} - E_{F} \)), can the visible and NIR light be used for plasmonic photocatalysis, where \( h\nu \) is the photon energy, \( E_{c0} \) is the flat-band CB potential of the semiconductor, and \( E_{F} \) is the Fermi level of metal.\[5,14\] In this scheme, the hot electrons transferred to the semiconductor CB maintain relatively high-energy level, which is determined by the CB characteristic of wide-bandgap semiconductor. As such, this scheme enables the utilization of solar light with relatively low energy while providing sufficiently high reducing ability for surface reactions. In particular, the low-energy NIR photons thus serve as a promising light source for photocatalysis by integrating surface plasmon and NIR light be used for plasmonic photocatalysis. In this design, Au nanocubes and Au nanocages simultaneously absorb visible and NIR light and inject hot electrons into TiO\(_{2}\) nanosheets, while the Pd nanocubes trap the electrons from the TiO\(_{2}\) and provide reaction sites for the reduction of H\(_{2}\)O into H\(_{2}\). To the best of our knowledge, this is the first example for the synergistic utilization of visible and NIR light for plasmonic photocatalysts in integration with co-catalysts by employing various noble metal nanostructures.

2. Results and Discussion

The design of the quaternary hybrid structure is based on the choice of single-crystalline TiO\(_{2}\) nanosheets in large size as a semiconductor model. TiO\(_{2}\) is the most widely used and extensively investigated semiconductor in photocatalysis, which is a typical UV-excitable wide-bandgap n-type semiconductor.\[26,27\] The TiO\(_{2}\) nanosheets with an edge length above 200 nm and thickness in 5–7 nm (as displayed by transmission electron microscopy (TEM) images in Figure S2, Supporting Information) are firstly synthesized via a hydrothermal route,\[26\] whose crystal structure can be indexed to anatase phase according to their X-ray diffraction (XRD) pattern (Figure S3, Supporting Information). High-resolution TEM (HRTEM) images reveal that the top and bottom faces of TiO\(_{2}\) nanosheets are (001) facets with a percentage of over 95% on their total surface (Figure S2, Supporting Information). The nanosheets with large flat surface and high (001) coverage are thus ideal candidates to support other components with various sizes. In the meantime, the low thickness of the nanosheets not only shortens the distance of electron transfer in bulk semiconductor but also increases light transmission and attenuates shielding effect on plasmonic metals.

Another bottleneck for plasmonic photocatalysis is the low activation ability of semiconductor surfaces. Once the hot electrons are injected into the semiconductor CB, they have to be consumed by reduction reactions on the semiconductor surface. However, the semiconductor surface often does not offer highly active sites for the reduction such as the evolution of hydrogen, thereby limiting the catalytic activities of plasmonic photocatalysts. The combination of co-catalysts with a semiconductor is a solution to resolve this problem, in which the co-catalysts accept the electrons from the semiconductor and act as alternative highly active sites for reduction reactions.\[23\] For instance, noble metals with very small cross-sections for surface plasmon (e.g., Pt and Pd) have been used as reduction co-catalysts for H\(_{2}\) production reactions.\[24,25\]

In this work, we report a new design for the combina-
tive use of visible and NIR light toward improved plasmonic photocatalytic performance in H\(_{2}\) evolution. In the design, Au nanocubes and Au nanocages with visible and NIR plasmonic bands as well as Pd nanocubes as co-catalysts are co-deposited onto the surface of TiO\(_{2}\) nanosheets. In addition to the tunable plasmonic bands, the cubic profiles of metal nanostructures allow establishing facet-to-face contact with the TiO\(_{2}\), providing superior electric contact to that by metal nanospheres. In this quaternary hybrid structure, Au nanocubes and Au nanocages simultaneously absorb visible and NIR light and inject hot electrons into TiO\(_{2}\) nanosheets, while the Pd nanocubes trap the electrons from the TiO\(_{2}\) and provide reaction sites for the reduction of H\(_{2}\)O into H\(_{2}\). To the best of our knowledge, this is the first example for the synergistic utilization of visible and NIR light for plasmonic photocatalysts in integration with co-catalysts by employing various noble metal nanostructures.

2. Results and Discussion
We specifically select Au nanostructures as the plasmonic components in our design so that the Schottky junction with TiO$_2$ can be established.

In our design, Au nanocubes enclosed by six (100) facets are chosen as plasmonic nanostructures to harvest visible light. The first-principles calculations (Figure S4, Supporting Information) show that TiO$_2$(001) and Au(100) have work functions of 4.89 and 5.17 eV, respectively, confirming the establishment of the Schottky barrier from the viewpoint of work functions. The cubic profile of nanocrystals ensures the facet-to-facet contact between Au nanocrystals and TiO$_2$ nanosheets, thus facilitating the metal–semiconductor interfacial charge transfer. Figure S5 (Supporting Information) shows the TEM image of Au nanocubes used in our study.[32] The nanocubes have an edge length of $\approx 50$ nm, and exhibit a plasmonic band in the range of 500–600 nm (suspension in red color, Figure S6, Supporting Information) complementary to the UV response of TiO$_2$ nanosheets.

The Au nanocubes are further assembled on the surface of TiO$_2$ nanosheets by a ligand-exchange method.[33] With 3-mercaptopropionic acid (MPA) as an intermediate ligand, the original capping agent cetyltrimethylammonium bromide (CTAB) on the synthesized Au nanocubes can be replaced by the MPA due to the strong interaction of MPA with both Au and TiO$_2$ through its thiol and carboxylic groups, respectively. When the mixed aqueous suspension of Au nanocubes and TiO$_2$ nanosheets is sonicated with the MPA solution, the Au nanocubes can be deposited on TiO$_2$ nanosheets through the linkage of MPA, forming a hybrid structure (namely, Au cube–TiO$_2$) (Figure 1a). The MPA at the Au–TiO$_2$ interface is further removed through a vacuum evaporation and annealing treatment to enhance the interfacial contact. TEM images in Figure 1b,c clearly show that the Au nanocubes are predominately deposited on the top and bottom surfaces of TiO$_2$ nanosheets. This selective deposition should be attributed to the two structural characteristics of TiO$_2$ nanosheets: the dominant (001) surface coverage, and the thickness of 5–7 nm significantly smaller than the size of Au nanocubes ($\approx 50$ nm).

As indicated by HRTEM image (Figure 1d), the Au nanocubes are enclosed by (100) facets, and as a result, an Au(100)–TiO$_2$(001) interface is formed. Such facet-to-facet contact at the Au–TiO$_2$ interface is better resolved by a cross-section TEM image (Figure S7, Supporting Information). Fourier transform infrared spectra (Figure S8, Supporting Information) show that both the CTAB and MPA ligands have been removed from the hybrid structure through our postsynthesis treatment. As such, the efficiency of interfacial electron transfer can be ensured. With Au nanocubes added onto TiO$_2$ nanosheets, the color of sample turns into red (Figure 2a). UV–vis–NIR diffuse reflectance spectra (Figure 2b) show that the addition of Au nanocubes does not alter the bandgap of TiO$_2$ nanosheets. The additional peak in the visible region is ascribed to the surface plasmon band of Au nanocubes. Thus, this Au cube–TiO$_2$ hybrid structure can harvest visible light in addition to the UV light absorption of TiO$_2$.

However, the plasmonic band of Au nanocubes can only cover part of the visible spectral range. In the case of the TiO$_2$–Au Schottky junction, the barrier is $E_{c0} - E_f = (W_m - W_s) + (E_c - E_f) \approx 1.2$ eV (Figure S1a, Supporting Information). As long as the light meets
the $\lambda < 1000$ nm, can the plasmonic hot electrons on Au jump over the Au–TiO$_2$ Schottky barrier and be injected into the CB of TiO$_2$. To further utilize the light at longer wavelengths, Au nanocages are used as another plasmonic component in our design. Similarly to Au nanocubes, the Au nanocages have a cubic profile and the size of ≈50 nm, and are enclosed by (100) facets despite their porous hollow structure (Figure S5b, Supporting Information). Owing to their hollow structure, the Au nanocages exhibit a plasmonic band in the range of 600–1000 nm (suspension in blue color, Figure S6, Supporting Information), which is complementary to the light absorption region of plasmonic Au nanocubes. By implementing the same ligand exchange and postsynthesis treatment, the Au nanocages can be loaded on the TiO$_2$ nanosheets to form a hybrid structure (namely, Au cube/cage–TiO$_2$, Figure 3a). As shown in Figure 3b–d and Figures S7b and S8 (Supporting Information), Au nanocages are uniformly dispersed on the surface of TiO$_2$ nanosheets through facet-to-facet contact, with ligands removed from their Au(100)–TiO$_2$(001) interface. The addition of Au nanocages turns the color of TiO$_2$ into blue, enabling the light absorption at 600–1000 nm (Figure 2).

The two successful cases that TiO$_2$ is assembled with Au nanocubes and nanocages, respectively, demonstrate the possibility of simultaneously utilizing the light absorption bands of two different plasmonic agents. Integrated with the Au nanocubes and nanocages, the TiO$_2$ nanosheets exhibit purple color (the combination of red and blue colors) in their suspension (see Figure 2a). The resulted hybrid structure (namely, Au cube/cage–TiO$_2$, Figure 4a) possesses the capability of harvesting light at 500–1000 nm in addition to the light absorption of TiO$_2$ as indicated by the UV–vis spectra (Figure 2b), covering the most spectral region of visible and NIR light. As shown in Figure 4b,c, cubic Au nanocrystals in both solid and hollow structures are distributed on the TiO$_2$ nanosheets through facet-to-facet contact. The combination of Au nanocrystals with TiO$_2$ nanosheets is further confirmed by XRD pattern (Figure S3, Supporting Information). Such a synthetic approach sets up a generic platform for the further integration with Pd co-catalysts in efforts to enhance catalytic activity (Figure 4d–f), which will be demonstrated at the end of this work.

The plasmonic effect of Au nanocubes and nanocages on the TiO$_2$ nanosheets has been revealed by photocurrent measurements under light irradiation with $\lambda > 400$ nm and light power density of 100 mW cm$^{-2}$. The performance of Au cage/cube–TiO$_2$ hybrid structure is evaluated against bare TiO$_2$ as well as binary Au cube–TiO$_2$ and Au cage–TiO$_2$ hybrid structures (Figure 5a). TiO$_2$ nanosheets generate negligible photocurrent, as they do not absorb light in the visible and NIR spectral regions (see Figure 2b). In comparison, distinctive photocurrents have been observed for both Au cube–TiO$_2$ and Au cage–TiO$_2$ hybrid structures, implying that plasmonic hot electrons generated from Au nanocubes and nanocages can be injected into TiO$_2$ nanosheets, respectively. Furthermore, when Au nanocubes and nanocages are both integrated with TiO$_2$ nanosheets, the photocurrent of hybrid structure is further enhanced, indicating that both plasmonic agents simultaneously contribute to the hot electron injection.

It is worth mentioning that no photocurrent enhancement can be observed for Ag cube–TiO$_2$ hybrid structure against bare TiO$_2$ (i.e., the replacement of Au nanostructures by Ag nanocubes), although the Ag nanocubes show a similar plasmonic band in the visible region (see Figure S9, Supporting Information). This result highlights the importance of Schottky junction to hot electron injection. The work function of Ag(100) is 4.28 eV as determined by the first-principles calculations, relatively lower than that of TiO$_2$(100) (Figure S4, Supporting Information). Thus, no Schottky barrier can be established at the Ag(100)–TiO$_2$(100) interface to suppress the backflow of plasmonic hot electrons (i.e., the case in Figure S1b, Supporting Information). Note that TiO$_2$ nanosheets are not photoexcited by the light of $\lambda > 400$ nm, so the other two possible mechanisms for plasmonic effect in literature (i.e., local electromagnetic field enhancement and resonant photon scattering) cannot work in our system.[8, 19]

The contribution of NIR light in the hot electron injection is further examined by switching the light irradiation to $\lambda > 780$ nm but maintaining the distance from sample to light source (Figure 5b). It turns out that the photocurrents of bare TiO$_2$ and Au cube–TiO$_2$ hybrid structure become negligible, while the photocurrents of Au cage–TiO$_2$ and Au cube/cage–TiO$_2$ are still distinct, confirming the NIR light excitation of
Au nanocages contribute to the photocatalytic process and inject hot electrons into TiO$_2$. Note that the power density of $\lambda > 780$ nm light (18 mW cm$^{-2}$) is significantly lower than that of $\lambda > 400$ nm (100 mW cm$^{-2}$), which is the typical characteristic of NIR light in Xe lamp source.

Upon acquiring the function of plasmonic effect in Au–TiO$_2$ hybrid structures, we are in a position to further implement the TiO$_2$-based materials in photocatalysis, using photocatalytic hydrogen evolution from water as a model reaction. The hydrogen evolution is an absolute electron-participating reaction, which can exactly reflect the behavior of electrons in the photocatalytic process. As shown in Figure 6a, bare TiO$_2$ nanosheets show no photocatalytic activity under $\lambda > 400$ nm simply because TiO$_2$ nanosheets do not absorb visible and NIR light. In sharp contrast to the bare TiO$_2$, both Au cube–TiO$_2$ and Au cage–TiO$_2$ hybrid
structures exhibit apparent photocatalytic activities, identifying the role of plasmonic hot electrons in the photocatalysis. Furthermore, the ternary Au cube/cage–TiO$_2$ hybrid structure shows an enhanced hydrogen production rate against the binary Au–TiO$_2$ hybrid structures, demonstrating the synergetic effect of Au nanocubes and nanocages on photocatalytic performance enhancement.

Intuitively the Au nanorods with two plasmonic bands in visible and near-infrared regions corresponding to transverse and longitude modes, respectively, can also be used as plasmonic nanostructures.\cite{34} We have loaded the Au nanorods on TiO$_2$ nanosheets for performance comparison (Figure S10a–e, Supporting Information). The obtained Au rod–TiO$_2$ sample exhibits notably lower photocatalytic H$_2$ production activity under light irradiation with a) $\lambda > 400$ nm and b) $\lambda > 780$ nm at a bias potential of 0.6 V versus Ag/AgCl. The power densities of light are measured to be 100 and 18 mW cm$^{-2}$ for $\lambda > 400$ nm and $\lambda > 780$ nm, respectively. The photocurrents are reflected by the difference of current densities between light on and light off.

In comparison, the curved surface of Au nanorods forms small interfacial area with the TiO$_2$ nanosheets (Figure S10c,d, Supporting Information), lowering the efficiency of interfacial charge transfer. Second, the light-absorption coverage from visible to near-infrared regions can be facilely optimized by controlling the loading amounts of Au nanocubes and nanocages, fully utilizing solar photons for photocatalysis. As shown in Table S1 (Supporting Information), different loading amounts of Au nanocubes and nanocages in Au cube/cage–TiO$_2$ lead to varied photocatalytic H$_2$ production rates owing to tunable light absorption. In the case of Au nanorods, it is quite difficult to make the transverse mode have a large optical cross-section, although the modes can be tuned by tailoring the aspect ratios of nanorods. As a result, the light absorption by Au nanorods particularly in the visible region is not comparable to our design.

As the light source is switched to $\lambda > 780$ nm, both the Au cage–TiO$_2$ and Au cube/cage–TiO$_2$ hybrid structures exhibit photocatalytic hydrogen evolution activities whereas bare TiO$_2$ and Au cube–TiO$_2$ cannot (see Figure 6b). It further confirms that the plasmonic hot electrons generated by NIR light irradiation can participate in the hydrogen evolution reaction indeed. Certainly, as Au nanocubes cannot be excited by NIR light, there is no performance difference
between Au cage–TiO$_2$ and Au cube/cage–TiO$_2$ in the rates of hydrogen production. Overall, the visible and NIR light is fully utilized for photocatalysis by the Au cube/cage–TiO$_2$ hybrid structure.

To further enhance the photocatalytic performance of the Au–TiO$_2$ hybrid structures, the Pd nanocubes are deposited on TiO$_2$ nanosheets as co-catalysts and provide active sites for the enhanced surface reaction. In our previous work, it has been demonstrated that Pd nanocubes enclosed by Pd(100) facets are ideal co-catalysts for hydrogen production due to the strong adsorption of H$_2$O molecules to Pd(100) surface.$^{[25]}$ The work function of Pd(100) is calculated to be 5.11 eV (Figure S4, Supporting Information), so it can form a Schottky junction with the TiO$_2$(001) having smaller work function to readily trap electrons on Pd.$^{[5,23,26]}$ In our study, we synthesize Pd nanocubes with sizes in range of 8–12 nm (Figure S5c, Supporting Information),$^{[35]}$ and further assemble them on the surface of TiO$_2$ nanosheets to form a TiO$_2$–Pd cube hybrid structure (Figure S11, Supporting Information). Similarly to the case of Au–TiO$_2$, TiO$_2$(001)–Pd(100) interface is formed through facet-tofacet contact between TiO$_2$ and Pd in the hybrid structure (Figures S7c and S11, Supporting Information). The Pd nanocubes barely possess plasmonic absorption in visible and NIR light region (Figure S6, Supporting Information), so no plasmonic effect should be considered for the addition of Pd component.$^{[36]}$

This argument is further supported by the UV–vis–NIR diffuse reflectance spectrum of TiO$_2$–Pd cube structure (Figure 2). Note that this weak "broad band" should be attributed to the interband electronic transition as well as the high scattering of Pd nanocubes closely packed on 2D materials.$^{[37]}$ It is worth pointing out that the TiO$_2$–Pd sample does not produce H$_2$ under irradiation of either $\lambda > 400$ nm or $\lambda > 780$ nm. This result confirms that no hot electron has been injected from Pd to TiO$_2$. Thus, the Pd only plays the role as a co-catalyst for enhancing the photocatalytic activity of Au cube/cage–TiO$_2$–Pd cube in the visible and near-infrared light region.

Toward the combinative use of plasmonic agents and co-catalysts, we have designed an Au cube/cage–TiO$_2$–Pd cube hybrid structure through the deposition of Pd nanocubes on Au cube/cage–TiO$_2$ hybrid structure with optimal loading amounts of Au nanocubes and nanocages (Figure 4d). As shown in Figure 4e,f, small Pd nanocubes together with large Au nanocubes and nanocages are uniformly distributed on the TiO$_2$ nanosheets in this hybrid structure. The structure and composition of the final sample are characterized by the XRD pattern (Figure S3, Supporting Information) and X-ray photoelectron spectroscopy (XPS, Figure S12, Supporting Information), respectively. Note that no distinct N1s and S2p peak can be found in the XPS spectrum, suggesting that the CTAB, MPA, and poly(vinyl pyrrolidone) (PVP, another capping agent used for metal nanocrystal synthesis) have been removed from the hybrid structure through postsynthesis treatments.

Given the weak plasmonic feature of Pd nanocubes, the addition of Pd nanocubes to Au cube/cage–TiO$_2$ hybrid structure does not much alter light absorption as indicated by Figure 2. Although the photocurrents under light irradiation of both $\lambda > 400$ nm and $\lambda > 780$ nm are not changed by forming the quarternary hybrid structure (Figure 5), the photocatalytic performance in hydrogen production is greatly enhanced by the addition of Pd nanocubes. As shown in Figure 6a, the H$_2$ production rate of Au cube/cage–TiO$_2$–Pd cube exceeds those of other counterparts under light illumination with $\lambda > 400$ nm. This rate is about 3.3 times higher than that of Au cube/cage–TiO$_2$, well demonstrating the important role of Pd co-catalyst in facilitating the reduction reaction by providing active sites. In the Au cube/cage–TiO$_2$–Pd cube structure, the hot electrons injected from Au nanostructures to TiO$_2$ can be trapped by TiO$_2$–Pd Schottky junction, and then the trapped electrons on Pd will be supplied for H$_2$ evolution reaction, designating Pd as the reaction sites. As the Pd co-catalyst provides more effective proton reduction sites in comparison with TiO$_2$, the H$_2$ evolution reaction can be dramatically enhanced. When the spectral range of incident light is narrowed to $\lambda > 780$ nm, the Au cube/cage–TiO$_2$–Pd cube still exhibits a higher hydrogen production rate as compared with the Au cube/cage–TiO$_2$ (Figure 6b). It further highlights the positive role of Pd nanocubes in improving the solar-to-chemical energy conversion efficiency under both visible and NIR light irradiation. The Au cube/cage–TiO$_2$–Pd cube hybrid structure exhibits stable photocatalytic activity in H$_2$ evolution with time (Figure S13, Supporting Information). After the photocatalytic reaction, Au and Pd nanostructures are well retained on the TiO$_2$ nanosheets (Figure S14, Supporting Information), showing the strong binding of cubic metal nanocrystals to TiO$_2$ nanosheets. As a result, the Au cube/cage–TiO$_2$–Pd cube sample maintains excellent photocatalytic stability during the successive cycles (Figure S15, Supporting Information).

It is worth pointing out that the loading amounts of Au nanocubes/nanocages or Pd nanocubes can influence the hydrogen evolution activity of catalysts as indicated by Table S1 (Supporting Information). First, the loading amounts of Au nanocubes/nanocages determine the light absorption ability of Au cube/cage–TiO$_2$, leading to different photocatalytic H$_2$ production rates. Second, similarly to previous reports,$^{[38,39]}$ the photocatalytic H$_2$ production activity has a volcano relationship with the loading amount of Pd co-catalyst, maneuvered by the balance between the number of active sites/Schottky junctions and the optical shielding effect of Pd. By tailoring the loading amounts, an optimal photocatalytic activity can be achieved for the Au cube/cage–TiO$_2$–Pd cube hybrid structure.

3. Conclusion

In summary, we have designed a hybrid structure based on the semiconductor model of TiO$_2$ nanosheets, which achieves broad-spectrum light utilization in plasmon-mediated photocatalytic hydrogen production. In this design, Au nanocubes and nanocages are employed as plasmonic agents to harvest visible and NIR light, respectively. Meanwhile, Pd nanocubes are used as co-catalysts to provide highly active sites for the reaction. The hydrogen production rate of the well-designed quarternary hybrid structure is dramatically higher than
those by its component structures, demonstrating the unique functions of multiple components. This work represents a step toward the rational design of hybrid structures for full-spectrum photocatalysis.

4. Experimental Section

**Synthesis of Au Cube–TiO₂ Hybrid Structure:** The Au cube–TiO₂ hybrid structure was obtained by depositing Au nanocubes on TiO₂ nanosheets. The deposition was achieved through a ligand-exchange method, in which the CTAB on Au nanocubes was replaced by the intermediate ligand 3-MPA. In brief, 20 mg of TiO₂ nanosheets were dispersed in 50 mL of an aqueous solution containing 50 µL of NH₄H₂O (28%) and 50 µL of MPA by sonication. Then 5 mL aqueous suspension (0.6 mg mL⁻¹) of Au nanocubes was added under sonication for 10 min. The as-obtained mixture was kept static for precipitation, centrifuged and washed with water for several times, dried at 60 °C in vacuum to remove the MPA, and further annealed at 100 °C for 2 h to increase the contact between Au nanocubes and TiO₂ nanosheets.

**Synthesis of Au Cage–TiO₂ Hybrid Structure:** The Au cage–TiO₂ hybrid structure was obtained through a similar procedure to that for Au cube–TiO₂ hybrid structure, except the use of 5-mL aqueous suspension (0.4 mg mL⁻¹) of Au nanocages instead of Au nanocubes. In this case, the original PVP on Au nanocages was replaced by the MPA.

**Synthesis of TiO₂–Pd Cube Hybrid Structure:** The TiO₂–Pd cube hybrid structure was obtained by directly depositing Pd nanocubes on TiO₂ nanosheets. In brief, 20 mg of TiO₂ nanosheets were dispersed in 50 mL of an aqueous solution containing 50 µL of NH₄H₂O (28%) and 50 µL of MPA by sonication. Then 10 mL aqueous suspension (10 mg mL⁻¹) of Pd nanocubes was added into the dispersion, which was further sonicated for 10 min. The as-obtained mixture was kept static for precipitation, centrifuged, and washed with water for several times, dried at 60 °C in vacuum, and further annealed at 100 °C for 2 h to increase the contact between Pd nanocubes and TiO₂ nanosheets.

**Synthesis of Au Cube/Cage–TiO₂ and Au Cube/Cage–TiO₂–Pd Cube Hybrid Structures:** The Au cube/cage–TiO₂ hybrid structure was obtained through a similar procedure to that for Au cube–TiO₂ hybrid structure, except the use of 5 mL aqueous suspension (0.4 mg mL⁻¹) of Au nanocages together with 5 mL aqueous suspension (0.6 mg mL⁻¹) of Au nanocubes. In the fabrication of Au cube/cage–TiO₂–Pd cube hybrid structures, Pd nanocubes were directly deposited on the as-prepared Au cube/cage–TiO₂ hybrid structure. The procedure is similar to that for TiO₂–Pd cube hybrid structure, except the use of Au cube/cage–TiO₂ hybrid structure (after vacuum evaporation) instead of TiO₂ nanosheets. Au cube/cage–TiO₂ and Au cube/cage–TiO₂–Pd cube hybrid structures with different loading amounts of Au nanocubes/nanocages or Pd nanocubes were obtained by changing the adding amounts of metal precursors.

**Photocatalytic Hydrogen Production Measurements:** To investigate the photocatalytic activities of TiO₂-based catalysts for hydrogen generation, methanol was used to sacrifice the holes. 15 mg of photocatalysts were added to 20 mL methanol/H₂O (25 vol%) methanol). The samples were sonicated to form uniform suspension, followed by saturation with Ar to eliminate air. The light-irradiation experiment was performed by using a 300 W Xe lamp with a 400 nm long-wave-pass cutoff filter (i.e., λ > 400 nm) or a 780 nm long-wave-pass cutoff filter (i.e., λ > 780 nm). The power densities of light were measured to be 100 and 18 mW cm⁻² for λ > 400 nm and λ > 780 nm, respectively. The photocatalytic reaction was typically performed for 4 h. The amount of H₂ evolved was determined using gas chromatography (GC, 7890B, TCD, Agilent). Three replicates were collected for each sample with relative error <10%.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the 973 Program (No. 2014CB848900), NSFC (No. 21471141), Recruitment Program of Global Experts, CAS Hundred Talent Program, Hefei Science Center CAS (2015HSC-UP009), and Fundamental Research Funds for the Central Universities (No. WK2060190025, WK2310000035), and Open Research Fund of Top Key Discipline of Chemistry in Zhejiang Provincial Colleges and Key Laboratory of the Ministry of Education for Advanced Catalysis Materials (Zhejiang Normal University) (ZJHX201507). S.B. was supported by the Zhejiang Provincial Natural Science Foundation (No. LQ16B010001).


Received: November 22, 2015
Revised: December 18, 2015
Published online: February 2, 2016