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Steering plasmonic hot electrons to realize enhanced full-spectrum photocatalytic hydrogen evolution

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ABSTRACT

Integration of surface plasmons into photocatalysis is an intriguing approach to extend the light absorption range over the full solar spectrum. However, the low migration rates and uncertain diffusion directions of plasmonic hot electrons make their photocatalytic efficiency fail to meet expectations. It remains a challenging task to steer the migration of hot electrons and take full advantage of the plasmonic effect to achieve the desired high photocatalytic efficiency. Herein, we have developed an efficient strategy to steer the migration of plasmonic hot electrons through a well-designed hybrid structure that synergizes a "surface heterojunction" with a Schottky junction. The hybrid structure was synthesized by modifying titanium dioxide (TiO₂) nanosheets (NSs) with gold (Au) nanoparticles (NPs) as a plasmonic metal and platinum (Pt) NPs as a co-catalyst. The "surface heterojunction" formed between two different crystal facets in the TiO₂ NSs can induce the injection of plasmonic hot electrons from Au NPs excited by visible light to TiO₂. Meanwhile, the Schottky junction formed between the Pt NPs and TiO₂ NSs can force the migration of electrons from TiO₂ to Pt NPs instead of flowing to Au NPs, attaining the efficient unidirectional transfer of carriers in the Au–TiO₂ system. Plasmonic photocatalysts with this design achieved dramatically enhanced activity in full-spectrum photocatalytic hydrogen production. This work opens a new window to rationally design hybrid structures for full-spectrum photocatalysis.

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1. Introduction

Photocatalytic hydrogen evolution is a promising approach to address current energy and environmental demands. Ideal

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solar-to-fuel photocatalysts should harvest the broad spectrum of solar light to maximize the formation of photoinduced electron-hole pairs. It remains an important challenge to develop photocatalysts that can harvest the full solar spectrum to achieve efficient solar energy conversion. Titanium dioxide (TiO_2) has attracted much attention because of its great potential in photocatalysis and solar cells [1–5]. However, because TiO_2 has a wide bandgap (~ 3.2 eV), it can only absorb ultraviolet (UV) light, which accounts for just ca. 5% of the solar spectrum [6]. Given this situation, great effort has been made to extend the light absorption of TiO_2 to the visible spectral region, typically by combining it with narrow-bandgap semiconductors [7–9] or dye molecules [10,11]. In particular, plasmon-mediated photocatalysis has attracted considerable attention from researchers interested in semiconductor photocatalyst systems [12–16]. Recently, the development of plasmonic gold (Au) [17,18] and silver (Ag) [19,20] has offered TiO_2 a new opportunity to achieve visible-light photoactivity via the plasmonic effect.

Taking plasmonic Au as a model system, it demonstrates plasmon-enhanced photoactivity when directly contacting a semiconductor. When irradiated by visible light, the electrons in the d -band of Au nanoparticles (NPs) can be excited to empty bands above the Fermi level (E_F) to form “hot electrons”, leaving equilibrated d -band “hot holes” below E_F [21]. These hot electrons can inject into the conduction band (CB) of n -type semiconductors and initiate reduction reactions [22]. Recently, several Au– TiO_2 hybrid systems that display plasmon-enhanced photoactivity in the visible-light region because of the plasmonic absorption of Au NPs have been reported [23–25]. However, the plasmon-enhanced photoactivity of these Au– TiO_2 hybrid systems has been primarily restricted to the visible region. In these cases, TiO_2 cannot be excited by visible light, and only plays roles in separating and transferring the injected electrons from Au NPs. When irradiated under the full solar light spectrum, TiO_2 and plasmonic Au NPs are simultaneously excited. In this case, the injection of plasmonic hot electrons from Au NPs to TiO_2 is counteracted by the opposite flow of photogenerated electrons from TiO_2 to Au NPs determined by the Schottky junction, weakening the plasmonic effect. To make full use of plasmonic hot electrons and achieve full-spectrum photocatalysis, it is necessary to steer the migration of plasmonic hot electrons from Au NPs and photogenerated electrons from TiO_2 in the desired directions.

Herein, we develop a hybrid structure to steer the migration of electrons in the desired direction, which enables the full use of plasmonic hot electrons to realize full-spectrum photocatalysis. In this design, a “surface heterojunction” is synergized with a Schottky junction. The “surface heterojunction” consists of a semiconductor with two or more different exposed crystal facets, in which electrons can be transferred from the facet with higher E_F to the facet with lower E_F by the internal electric field because of their different electronic states [26,27]. When plasmonic Au NPs are deposited onto the facet with higher E_F , hot electrons can be efficiently steered towards the facet with lower E_F . Meanwhile, a Schottky junction can be formed through the intimate contact between the noble metal NPs and n -type

semiconductor when the work function of the noble metal is higher than that of the n -type semiconductor [22]. Driven by the Schottky junction, the photogenerated carriers on the semiconductor can be separated more efficiently, thereby enhancing the photocatalytic activity of the structure [28–31]. Platinum (Pt) is a widely used co-catalyst that possesses a high work function to form the Schottky junction and thus can efficiently separate the photogenerated electrons from the semiconductor [32].

In this work, we use TiO_2 nanosheets (NSs) covered with {001} and {101} facets as a model “surface heterojunction”. Au NPs as the plasmonic metal are anchored on the {001} surface of TiO_2 by the intermediate ligand 3-mercaptopropionic acid (MPA). This structure can achieve facile injection of hot electrons because of the internal electric field of the “surface heterojunction” in the TiO_2 NSs. To prevent the backflow of electrons from TiO_2 NSs to Au NPs under full-spectrum irradiation, we integrate co-catalyst Pt NPs with the designed Au– TiO_2 {001} sample to form a Schottky junction. This Schottky junction can force the migration of electrons from TiO_2 to Pt NPs instead of flowing back to Au NPs to realize the efficient unidirectional transfer of electrons in the Au– TiO_2 system. This hybrid structure is a highly efficient catalyst for full-spectrum photocatalytic hydrogen production. This work provides fresh insights into the rational design of photocatalyst structures that steer plasmonic hot electrons, representing a step towards full-spectrum photocatalysis.

2. Experimental

2.1. Synthesis

TiO_2 NSs were synthesized by the solvothermal method as reported previously [33]. Typically, hydrofluoric acid (HF) aqueous solution (4.5 mL, 40 wt%) was added to tetrabutyl titanate (25 mL) and stirred for 30 min. Subsequently, the mixture was transferred into a 50-mL Teflon-lined autoclave and kept at 180 °C for 24 h. After the solvothermal reaction, the obtained white precipitate was collected, washed with deionized water and ethanol several times, and then calcined at 550 °C for 2 h in a furnace to remove surface fluoride ions.

In a standard process, sodium citrate dihydrate (107.04 mg) and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (4.79 mL, 0.1 mol/L) were mixed in deionized water (93 mL). The stirred mixture was heated at 80 °C for 2 h in a 250-mL round-bottom flask. The as-synthesized Au NPs were dispersed in the solution by sonication and stored for further use. The concentration of Au NPs was measured by inductively coupled plasma mass spectrometry (ICP-MS).

The Au– TiO_2 {001} hybrid structure was obtained using MPA as an intermediate ligand [34]. In brief, TiO_2 NSs (20 mg) were added to a 50-mL quartz tube containing deionized water (20 mL), and then sonicated to form a uniform suspension. Then, MPA (50 μL) was dispersed in the suspension by stirring for 6 h. After the reaction, the sample was collected and washed with deionized water by centrifugation to remove the dissociated MPA. The obtained MPA-modified TiO_2 NSs were dispersed in deionized water (20 mL) by sonication in a 50-mL

quartz tube. Subsequently, the as-synthesized Au NPs (2 mg) were mixed with the suspension by stirring for 6 h. The product was isolated by centrifugation and washed with deionized water and ethanol several times. To remove MPA, the product was calcined at 200 °C for 1 h in an Ar atmosphere.

The Au-TiO₂{101} hybrid structure was fabricated by directly photodepositing Au NPs on the {101} facets of TiO₂ NSs. In a typical synthesis, deionized water (20 mL) was added to a 50-mL quartz tube and purged with Ar for 30 min to remove air. Then, TiO₂ NSs (20 mg), HAuCl₄·4H₂O (2 mL, 12.6 mmol/L), and methanol (1 mL) were added to the quartz tube, which was subsequently sonicated for 30 min. The stirred mixture was irradiated by a 300-W Xe lamp for 10 min. After the reaction, the product was isolated by centrifugation, washed with deionized water and ethanol several times, and dried at 60 °C under vacuum.

The Au-TiO₂{101}-Pt hybrid structure was fabricated by a chemical reduction method. In a typical synthesis, H₂PtCl₆·6H₂O (0.77 mL, 2 mmol/L) was added to deionized water (15 mL). As-synthesized Au-TiO₂{101} (12 mg) was dispersed in the solution, which was then stirred for 30 min. Then, NaBH₄ (1.5 mL, 10 mmol/L) solution was added to the suspension. After stirring for 10 min, the product was isolated by centrifugation, washed with deionized water and ethanol several times, and then dried at 60 °C under vacuum.

2.2. Characterization

The morphology of all samples was investigated by transmission electron microscopy (TEM; JEOL JEM-2100F, 200 kV) and high-resolution transmission electron microscopy (HR-TEM; FEI, G2 F30, USA). Powder X-ray diffraction (XRD) patterns were recorded using a Philips X'Pert Pro Super X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The concentrations of Pt and Au elements were measured with a Thermo Scientific PlasmaQuad 3 ICP-MS after dissolving the samples in a mixture of HCl and HNO₃ with a volume ratio of 3:1. The ultraviolet-visible-near infrared (UV-vis-NIR) diffuse reflectance spectra of as-synthesized samples were recorded in the spectral region of 200–1000 nm with a Shimadzu SolidSpec-3700 spectrophotometer. Photoluminescence (PL) measurements were carried out on a Jobin Yvon Horiba Fluorolog-3-Tau spectrofluorometer.

2.3. Photoelectrochemical measurements

The photoelectrochemical measurements were carried out in a three-electrode quartz cell filled with Na₂SO₄ electrolyte (0.5 mol/L) under irradiation of a 300-W Xe lamp (Solaredge 700, China). The Na₂SO₄ electrolyte was deoxygenated with Ar for 30 min prior to the measurements. TiO₂ NSs (2.0 mg) and Au-TiO₂ (2.4 mg) were dispersed in ethanol (1 mL) and then uniformly deposited onto a 2.5 × 2.5 cm indium tin oxide (ITO)-coated glass substrate (SC-1B, China) to form a photoelectrode. Pt gauze and Ag/AgCl were used as the counter and reference electrodes, respectively. The photoresponses of the prepared photoelectrodes (i.e., current (*I*)-time (*t*) curves)

were measured on a CHI 660D electrochemical station (Shanghai Chenhua, China) at a bias potential of 0.6 V (vs. Ag/AgCl) for 200 s. Visible or full-spectrum light as an illumination source was realized in the presence or absence of a 400-nm long-wave-pass cutoff filter (i.e., $\lambda > 400 \text{ nm}$).

2.4. Photocatalytic hydrogen production measurements

To investigate the photocatalytic hydrogen production performance of the TiO₂-based catalysts, methanol was used as sacrificial agent to scavenge the photogenerated holes. The photocatalysts were dispersed in a methanol aqueous solution (15 mL, 25 vol% methanol) and deoxygenated with Ar. In the measurements for hot electron injection, Au-TiO₂{101} and Au-TiO₂{001} hybrid structures (12 mg) were used. To evaluate the photoactivity over the full light spectrum, the weights of TiO₂ NSs, TiO₂ NSs-Pt, and Au-TiO₂{001}-Pt used were 10, 10.3, and 12.3 mg, respectively. The light irradiation experiments were typically performed for 4 h under a 300-W Xe lamp (Solaredge 700, China) in the presence or absence of a 400-nm long-wave-pass cutoff filter (i.e., $\lambda > 400 \text{ nm}$). The amount of hydrogen evolved was determined using gas chromatography (GC; 7890A, TCD, Ar carrier, Agilent). Three replicates were collected for each sample with a relative error of <10%.

3. Results and discussion

TiO₂ is a typical UV-active wide-bandgap (~3.2 eV) n-type semiconductor [35–37]. The TEM image in Fig. 1(a) reveals that the TiO₂ NSs synthesized via a simple hydrothermal route [33] had an edge length of 25–35 nm and thickness of 6–7 nm. The as-synthesized TiO₂ NSs are enclosed by eight equivalent {101} facets and two {001} facets (Fig. 1(b)), and their crystal structure can be indexed to the anatase phase with lattice constants of $a = 0.352 \text{ nm}$ and $c = 0.378 \text{ nm}$ (JCPDS No.21-1272) [36] according to their powder XRD pattern (Fig. 1(c)). The HRTEM images of the TiO₂ NSs show that their lattice spacings are about 0.23 and 0.19 nm (Fig. 1(d) and (e)), consistent with the (001) and (200) planes of anatase TiO₂ [36], respectively. A “surface heterojunction” can form in TiO₂ NSs covered with {001} facets with higher E_F and {101} facets with lower E_F [27,36]. When irradiated by UV light, the photogenerated electrons will migrate from the {001} facets of anatase TiO₂ to the {101} facets, while the holes will transfer from the {101} facets to {001} ones, promoting the separation of photogenerated electrons and holes (Fig. 1(f)).

The second step of our design is to achieve the facet-dependent charge migration along with the injection of plasmonic hot electrons. Au NPs with an average size of 10 nm that exhibit a plasmonic band in the visible spectral range were selected as the plasmonic model in our research. We integrated the plasmonic Au NPs with TiO₂ NSs in two ways: (1) by assembly on the {001} facet of TiO₂ NSs through an intermediate ligand (denoted as Au-TiO₂{001}); and (2) anchoring on the {101} facet of TiO₂ NSs by photoreduction (denoted as Au-TiO₂{101}). To synthesize Au-TiO₂{001} (Fig. 2(a)), MPA

Fig. 1. (a) TEM image of TiO₂ nanosheets. (b) Schematic illustration of a TiO₂ nanosheet. (c) XRD pattern of TiO₂ nanosheets. HRTEM images of the side face (d) and top face (e) of TiO₂ nanosheets. (f) Schematic illustration of the {001} and {101} “surface heterojunction”.

Fig. 2. Schematics of Au-TiO₂{001} (a) and Au-TiO₂{101} (d) hybrid structures. TEM images of Au-TiO₂{001} (b) and Au-TiO₂{101} (e) hybrid structures. HRTEM images of Au-TiO₂{001} (c) and Au-TiO₂{101} (f) hybrid structures.

was selected as an intermediate ligand because its thiol and carboxylic terminal groups can interact with Au NPs and TiO₂ NSs, respectively [34]. MPA strongly bound to the NPs and NSs to efficiently load the Au NPs onto the TiO₂ NSs. MPA was then removed by annealing at 200 °C to enhance the interfacial contact between the NPs and NSs. The TEM images in Fig. 2(b) and (c) clearly show that Au NPs are predominantly and uniformly distributed on the {001} facets of TiO₂ NSs, which is attributed to the dominant (001) surface coverage and small thickness of the TiO₂ NSs. In the synthesis of Au-TiO₂{101} through photo-reduction (Fig. 2(d)), the photogenerated electrons on the {101} facets of TiO₂ NSs, which were transferred from the {001} facets, can reduce Au³⁺ to Au NPs to achieve the selective deposition of Au NPs on {101} facets (Fig. 2(e)). HRTEM (Fig. 2(f)) revealed that the Au NPs and TiO₂ NSs were in intimate

contact, indicating the strong interaction between Au and TiO₂ during the photoreduction process.

In the XRD patterns of the Au-TiO₂{001} and Au-TiO₂{101} hybrid structures in Fig. 3(a), the diffraction peak of Au NPs is overlapped by that of TiO₂ NSs at 38°. However, the peak at 44.3° can be assigned to Au NPs, indicating the existence of Au NPs in the Au-TiO₂ hybrid structures. Compared with that of the TiO₂ NSs, the UV-vis-NIR diffuse reflectance spectra of the Au-TiO₂ hybrid structures (Fig. 3(b)) show that the addition of Au NPs can broaden the absorption spectral range to the visible and even near-infrared regions. The peak at 550 nm is ascribed to the plasmonic absorption band of Au NPs. As a result, the hybrid structures could achieve light absorption over a broad wavelength range.

To reveal the plasmonic effect of the Au NPs on the TiO₂ NSs,

Fig. 3. (a) XRD patterns of $\text{Au-TiO}_2\{001\}$ and $\text{Au-TiO}_2\{101\}$ hybrid structures. (b) UV-vis-NIR diffuse reflectance spectra of TiO_2 NSs and Au-TiO_2 hybrid structures.

photocurrent measurements and photocatalytic hydrogen evolution of TiO_2 and Au-TiO_2 samples were performed under visible-light irradiation. Because TiO_2 NSs cannot be excited by visible light, this measurement setup prevented the interference of photogenerated electrons from TiO_2 NSs. Fig. 4(a) displays the obvious photocurrent observed for $\text{Au-TiO}_2\{001\}$ and weak photocurrent from bare TiO_2 NSs. This phenomenon can be attributed to the injection of plasmonic hot electrons from Au NPs into TiO_2 NSs. Compared with $\text{Au-TiO}_2\{101\}$, the $\text{Au-TiO}_2\{001\}$ hybrid structure shows dramatically higher photocurrent densities. This indicates that the plasmonic hot electrons can be more efficiently injected into TiO_2 NSs through their $\{001\}$ facets than through their $\{101\}$ facets. To evaluate the photocatalytic activity of the Au-TiO_2 materials, their photocatalytic hydrogen evolution from water was selected as a model reaction (Fig. 4(b)), because it can exactly reflect the behavior of electrons in the photocatalytic process. No hydrogen evolution was observed for the bare TiO_2 NSs under visible-light illumination because TiO_2 only absorbs UV light. Likewise, no hydrogen production was detected for the $\text{Au-TiO}_2\{101\}$ hybrid structure. Most likely, this results from the lack of a driving force to steer the migration of injected electrons towards the surface of TiO_2 NSs for reduction reactions. In contrast, the $\text{Au-TiO}_2\{001\}$ hybrid structure exhibits apparent photocatalytic activity. This suggests that the interface between Au and $\text{TiO}_2\{001\}$ facets indeed favors the injection of plasmonic hot electrons to facilitate reduction reactions.

The next question is how the $\{001\}$ and $\{101\}$ facets of TiO_2 NSs affect the behavior of injected hot electrons from plasmonic Au NPs to the TiO_2 NT surface. Because the work function of Au NPs (~ 5.1 eV) [32] is higher than that of TiO_2 NSs (~ 4.9 eV) [38], a Schottky junction can form at the interface between Au NPs and TiO_2 NSs. Under visible light, the plasmonic hot electrons photogenerated at Au NPs are injected into the CB of TiO_2 NSs across the Schottky junction, while the holes are left on the Au NPs. If the injected electrons cannot be

transported away quickly enough, the electrons accumulated in TiO_2 will flow back to the Au NPs through the Schottky junction and recombine with the holes left in Au, lowering the activity of reduction reactions. It is thus believed that the major reason for the limited photoactivity of $\text{Au-TiO}_2\{101\}$ is the lack of a driving force to steer the migration of the injected electrons and prevent the electrons from flowing back to recombine with holes. A “surface heterojunction” can play an important role in driving the migration of the injected electrons from the $\{001\}$ to $\{101\}$ facets of TiO_2 NSs. As illustrated in Fig. 4(c), the plasmonic hot electrons injected through the $\{001\}$ facet can sequentially migrate towards the $\{101\}$ facet and separate from the holes via the “surface heterojunction”, resulting in the higher photocatalytic activity of $\text{Au-TiO}_2\{001\}$ hybrid structure than that of the $\text{Au-TiO}_2\{101\}$ one. In sharp contrast, the $\text{Au-TiO}_2\{101\}$ interface does not offer the facet-dependent driving force for charge transfer, and as a result, the electrons injected through the $\{101\}$ facet may flow back to the Au NPs through the Schottky junction (Fig. 4(d)) [38].

To better resolve the facet-dependent charge transfer behavior of the structures, the facet-selective photodeposition of Pt NPs was carried out under visible-light irradiation. With the photogenerated electrons from the Au-TiO_2 hybrid structures, free Pt^{4+} in solution can be reduced to Pt^0 NPs and deposited on the hybrid structures. During this process, the migration behavior of photogenerated electrons can be determined. As shown in Fig. 4(e), Pt NPs can be clearly observed on the TiO_2 NSs in the $\text{Au-TiO}_2\{001\}$ hybrid structure, in good agreement with the proposed mechanism in Fig. 4(c). It is worth noting that the plasmonic hot electrons generated under visible-light irradiation are unlikely to migrate over a long distance to reach the $\{101\}$ facet in the absence of a co-catalyst given their short lifetime. For this reason, most Pt NPs are deposited on the $\{001\}$ facets near Au NPs, as shown in Fig. 4(e). Nevertheless, the driving force provided by the “surface heterojunction” can prevent the hot electrons from flowing back to recombine with

Fig. 4. (a) Photocurrent *versus* time (*I*-*t*) curves of TiO₂ NSs and Au-TiO₂ hybrid structures measured in Na₂SO₄ solution (0.5 mol/L) under visible-light irradiation ($\lambda > 400$ nm). (b) Average rates for photocatalytic hydrogen evolution using Au-TiO₂{001} and Au-TiO₂{101} as catalysts under visible-light irradiation. Schematics of the injection of hot electrons in Au-TiO₂{001} (c) and Au-TiO₂{101} (d). TEM images of Au-TiO₂{001} (e) and Au-TiO₂{101} (f) with deposited Pt NPs.

holes. In contrast, the photodeposition of Pt NPs on the Au-TiO₂{101} hybrid structure merely takes place near the Au NPs (Fig. 4(f)) because of the backflow of electrons to Au NPs. The facet-selective photodeposition observed here confirms that the integration of Au NPs with the {001} facet of TiO₂ NSs is an effective approach to separate the injected electrons from holes and steer the migration of injected electrons towards the TiO₂ NT surface. For this reason, the Au-TiO₂{001} hybrid structure was selected for further research.

To further explore the possibility of using the hybrid structure to realize full-spectrum photocatalysis, photocatalytic hydrogen evolution over Au-TiO₂{001} was performed under full-spectrum irradiation, during which TiO₂ NSs and Au NPs were simultaneously excited to produce photogenerated electrons. As shown in Fig. 5(a), the hydrogen production rate by Au-TiO₂{001} is slightly lower than that of the bare TiO₂ NSs at

the same weight of TiO₂. This performance degradation is essentially caused by the competition between the injection of plasmonic hot electrons and the Schottky junction-driven electron transfer. In comparison, Au-TiO₂{001} shows higher photocatalytic activity than that of the bare TiO₂ NSs under UV irradiation. This behavior reflects the ability of the Schottky junction to suppress charge recombination when only TiO₂ is photoexcited. As illustrated in Fig. 5(b), the TiO₂ NSs and Au NPs in Au-TiO₂{001} are simultaneously excited to produce photogenerated electrons and plasmonic hot electrons under full-spectrum irradiation, respectively. In this case, the injection of plasmonic hot electrons from Au NPs to TiO₂ NSs would be counteracted by the transfer of photogenerated electrons from TiO₂ NSs to Au NPs through the Schottky junction, thereby resulting in a fairly low efficiency of photocatalytic hydrogen evolution.

Fig. 5. (a) Average rates of photocatalytic hydrogen evolution using TiO_2 and $Au-TiO_2\{001\}$ as catalysts under full-spectrum and UV irradiation. (b) Schematic of the migration of charge carriers in the $Au-TiO_2\{001\}$ hybrid structure under full-spectrum irradiation. (c) TEM image of TiO_2 -Pt hybrid structures. (d) Photoluminescence spectra of TiO_2 , $Au-TiO_2\{001\}$, and TiO_2 -Pt.

To tackle the limitations of the $Au-TiO_2\{001\}$ hybrid structure and achieve full-spectrum photocatalysis, we introduced another metal as a co-catalyst to induce the flow of photogenerated electrons from TiO_2 NSs to the co-catalyst and suppress their transfer back to Au NPs. Pt metal is generally used as a co-catalyst because it can establish a Schottky junction with a semiconductor. Such a co-catalyst can not only trap the electrons from TiO_2 , but also provide highly active sites for hydrogen evolution [39]. The uniform distribution of Pt NPs on TiO_2 NSs was achieved through a chemical deposition method (Fig. 5(c)). PL spectroscopy (Fig. 5(d)) was used to examine the effect of the Pt co-catalyst on the separation and transfer of photoexcited charge carriers in the system because charge recombination generally induces luminescence. The PL spectrum of bare TiO_2 NSs reveals the obvious recombination of photoexcited electrons and holes. The addition of metal NPs to TiO_2 NSs strongly quenched the PL, indicating the role of the Schottky junction in suppressing charge recombination. In particular, the introduction of Pt NPs caused substantially stronger PL quenching than was the case for Au NPs. This suggests that the photogenerated electrons from TiO_2 NSs can be efficiently captured by Pt NPs to prevent their recombination with holes.

The information presented above has demonstrated the outstanding ability of Pt NPs as a co-catalyst to extract electrons from TiO_2 NSs. We investigated the effect of Pt NPs in the

$Au-TiO_2\{001\}$ hybrid structure (namely, $Au-TiO_2\{001\}$ -Pt) on its photocatalytic hydrogen evolution under full-spectrum irradiation. The TEM image in Fig. 6(a) shows that the Pt NPs are well dispersed on $Au-TiO_2\{001\}$ following their photodeposition. In addition, XPS analysis of the $Au-TiO_2\{001\}$ -Pt hybrid structure revealed Pt $4f_{5/2}$ and $4f_{7/2}$ peaks at 74.4 and 71.0 eV, respectively (Fig. 6(b)), indicating the formation of Pt NPs [40]. The Pt NPs supported on TiO_2 NSs served as co-catalysts to promote charge separation, as manifested in photocatalytic hydrogen evolution. Compared with that of bare TiO_2 NSs, TiO_2 -Pt exhibited an increased hydrogen production rate under full-spectrum irradiation, demonstrating the ability of the Pt co-catalyst to capture electrons from TiO_2 NSs. Similarly, when $Au-TiO_2\{001\}$ was coated with Pt NPs, the hydrogen evolution rate reached about 155 and 206 times those of bare TiO_2 NSs and $Au-TiO_2\{001\}$, respectively (Fig. 6(c)). In the $Au-TiO_2\{001\}$ -Pt hybrid structure (Fig. 6(d)), the hot electrons injected from Au NPs to TiO_2 NSs can be steered by the “surface heterojunction” inside the TiO_2 NSs, and be captured by Pt NPs for hydrogen evolution upon reaching $TiO_2\{101\}$ facets. Meanwhile, the electrons excited from TiO_2 NSs can also be captured by Pt NPs instead of flowing to Au NPs. As a result, the $Au-TiO_2\{001\}$ -Pt hybrid structure displays dramatically enhanced performance in full-spectrum photocatalytic hydrogen evolution compared with that of bare TiO_2 NSs.

Fig. 6. (a) TEM image of the Au-TiO₂{001}-Pt hybrid structure. (b) Pt 4f XPS spectrum of the Au-TiO₂{001}-Pt hybrid structure. (c) Average rates of photocatalytic hydrogen evolution with TiO₂, TiO₂-Pt, and Au-TiO₂{001}-Pt hybrid structures as catalysts under full-spectrum irradiation. (d) Schematic of the migration of charge carriers in the Au-TiO₂{001}-Pt hybrid structure under full-spectrum irradiation.

4. Conclusions

In summary, we designed a hybrid catalyst structure to realize enhanced full-spectrum photocatalytic hydrogen evolution. This structure allows the photogenerated electrons from TiO₂ NSs and plasmonic hot electrons from Au NPs to simultaneously contribute to photocatalysis by steering their migration by synergizing the “surface heterojunction” with the Schottky junction. In this design, the efficient injection of plasmonic hot electrons from Au NPs is achieved by integration with the {001} facets of TiO₂ NSs under the driving force of the “surface heterojunction”. Meanwhile, the photogenerated electrons from TiO₂ NSs together with the injected hot electrons from Au NPs are captured by the Pt NPs present as a co-catalyst to induce hydrogen evolution. As a result, this hybrid structure showed dramatically enhanced performance in photocatalytic hydrogen production under full-spectrum irradiation compared with that of TiO₂ NSs. This work opens a new window for the rational design and synthesis of efficient hybrid structures to achieve plasmon-enhanced full-spectrum photocatalysis.

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Graphical Abstract

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Steering plasmonic hot electrons to realize enhanced full-spectrum photocatalytic hydrogen evolution

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An efficient strategy is developed to steer the migration of plasmonic hot electrons using a well-designed hybrid structure that synergizes a “surface heterojunction” with a Schottky junction to achieve highly efficient full-spectrum photocatalytic hydrogen production.

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基于等离子激元热电子调控的全谱光催化产氢增强

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摘要: 等离子激元效应在光催化体系中的集成为实现广谱光吸收提供了一个新的途径, 然而等离子激元热电子的较低迁移率和不确定扩散方向使得其光催化效率仍较低. 等离子激元金属与n型半导体接触后, 其界面间会形成肖特基结. 在特定波长太阳光照射下, 等离子激元金属将其表面等离子体能量聚集在表面自由电子上, 进而产生热电子. 当这些热电子具有的能量高于肖特基势垒时, 热电子便可注入到半导体导带上. 与此同时, 半导体上的电子可以通过肖特基接触发生回流, 与金属上的空穴复合, 进而降低半导体-等离子激元金属复合材料的光催化性能. 因此, 为了提高光催化效率, 如何调控等离子激元热电子迁移和充分利用等离子激元效应是一个重要挑战.

本文尝试将“表面异质结”与肖特基结相结合的复合结构, 得以有效地调控等离子激元热电子的迁移. 在该复合结构中, 金纳米颗粒和铂纳米颗粒分别作为等离子激元吸光单元和助催化剂, 集成在TiO₂纳米片表面. 其中“表面异质结”是由TiO₂纳米片的两种不同表面晶面所构成, 我们选择由{001}和{101}两组晶面组成的TiO₂纳米片作为半导体衬底. 该结构中的{001}晶面导带能级高于{101}导带能级, 因而电子由高能级的{001}流向低能级的{101}晶面, 可以用来引导等离子激元热电子从可见光响应的金纳米颗粒向TiO₂进行高效转移. 通过巯基丙酸的桥联作用, 将等离子激元Au纳米颗粒锚定在TiO₂纳米

片的{001}晶面上, 获得Au-TiO₂{001}样品. 另一方面, 利用TiO₂纳米片自身光生电荷导向性光沉积, 得到与{101}晶面结合形成的Au-TiO₂{101}样品. 我们对两组样品进行光电流和光催化产氢实验对比, 确认在“表面异质结”诱导下Au-TiO₂{001}样品中Au产生的光生热电子可以更好地注入到TiO₂纳米片导带上. 我们进一步通过光沉积Pt纳米颗粒来判定光生电子所能到达的区域, 验证了以上结论. 与此同时, 肖特基结由铂纳米颗粒与TiO₂纳米片所形成, 可以促使电子由TiO₂向铂纳米颗粒进行转移, 而避免发生向金纳米颗粒的反向迁移, 从而在Au-TiO₂体系中实现高效的单向载流子转移. 基于该设计, 等离子光催化剂实现了明显改善的全谱光催化产氢性能. 本文为全谱光催化的复合结构理性设计提供了一个新的思路.

关键词: 等离子; 表面异质结; 肖特基结; 光催化产氢; 全谱光照

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