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Graphene "bridge" in transferring hot electrons from plasmonic Ag nanocubes to TiO_2 nanosheets for enhanced visible light photocatalytic hydrogen evolution

Qingqing Lang[a], Yaohan Chen[a], Tianlong Huang[a], Lining Yang[b], Shuxian Zhong[a], Lanju Wu[a], Jianrong Chen[b], Song Bai[a,c,*]

[a] *Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, PR China*

[b] *College of Geography and Environmental Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, PR China*

[c] *Hefei National Laboratory for Physical Sciences at the Microscale, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui, 230026, PR China*

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ABSTRACT

The integration of plasmonic metal with wide-bandgap semiconductor is a promising approach to utilize the visible light without compromise of the redox ability of photogenerated charge carriers. However, a larger work function of metal than that of semiconductor is indispensable to enable the injection of hot electrons from plasmonic metal to semiconductor. In this paper, we demonstrated that reduced graphene oxide (rGO) nanosheets as conductive "bridge" can breakthrough the restriction and transfer hot electrons from Ag of smaller work function to TiO_2 of larger work function. In the design, both of the Ag nanocubes and TiO_2 nanosheets are co-deposited on the surface of rGO nanosheets to form Ag-rGO-TiO_2 structure, which was characterized by XRD, TEM, Raman and XPS spectra. On one hand, the Ag-rGO interface facilitates the transfer of hot electrons from Ag to rGO through conductor–conductor contact. On the other hand, the new formed Schottky junction on the rGO-TiO_2 interface further pumps the transferred electrons to the surface of TiO_2 for photocatalytic reduction reaction resulted from the larger work function of rGO than that of TiO_2. Enabled by this unique design, the hydrogen production activity achieved under visible light irradiation is dramatically enhanced in comparison with that of Ag-TiO_2 counterpart with the direct contact between the same Ag nanocubes and TiO_2 nanosheets. This work represents a step toward the rational interfacial design of plasmonic metal-semiconductor hybrid structures for broad-spectrum photocatalysis.

1. Introduction

Semiconductor based solar photocatalysis for chemical fuel production, such as production of H_2 from water splitting and reduction of CO_2 to hydrocarbons is an attractive and challenging approach to addressing global energy and environment issues [1–4]. The key to achieving high solar-to-chemical energy conversion efficiency is to develop high-efficient photocatalysts, which can absorb high proportion of solar photons, create high-energy electron-hole pairs, and efficiently transfer them to the surface for redox reactions [5–7]. Generally, both the light absorption ability of photocatalysts and redox ability of photogenerated carriers are greatly determined by the bandgap of the light-harvesting semiconductor (namely, the energy range between conduction band minimum (CBM, E_c) and valence band maximum (VBM, E_v)) [8,9]. In terms of redox ability of charge carriers, wide-bandgap semiconductors with more negative CBM and more positive VBM can offer higher energetic electrons and holes for reduction and oxidation half reactions in comparison with narrow-bandgap ones. However, semiconductors with wide bandgaps can only absorb UV light (wavelength (λ) $<$ 420 nm), which accounts for a very small fraction ($\approx$5%) of solar spectrum. While narrow-bandgap semiconductors can utilize photons from visible light (420 $< \lambda <$ 780 nm, $\approx$43%) or near-infrared (NIR) light (780 $< \lambda <$ 2500 nm, $\approx$52%) region, but the less negative CBM and positive VBM reduce the redox abilities of charge carriers.

To resolve the contradictions between the light absorption and

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[*] Corresponding author at: Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, PR China.

E-mail address: songbai@zjnu.edu.cn (S. Bai).

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redox ability of photogenerated charges, the wide-bandgap semiconductors are integrated with plasmonic metal nanostructures to form hybrid photocatalysts [8,10–16]. When the incident photons are absorbed by the free electrons of plasmonic metal, the electrons will leap over the Fermi level to a higher energy level. And the formed energetic hot electrons then inject into the conduction band (CB) of semiconductor in driving the photocatalytic reduction reaction [17,18]. On one hand, metal (e.g. Au, Ag and Cu) with plasmonic band in visible or NIR region can offer complementary light absorption to wide-bandgap semiconductors as long as the photon energy meets $h\nu \geq E_{c0} - E_f$ (which has a much smaller value than $E_c - E_v$; E_{c0} is the flat-band CB potential of the semiconductor, and E_f is the Fermi level of metal). On the other hand, the CBM of the wide-bandgap semiconductor maintain relatively high-energy level, which guarantees the high reduction ability of the injected hot electrons for photocatalytic reactions.

However, not the combination of every semiconductor and plasmonic metal can realize the effective hot electron injection for photocatalytic reactions. Generally, only when the work function of semiconductor (W_s) is smaller than that of metal (W_m) ($W_m > W_s$), can the Schottky barrier be formed between the metal and semiconductor, which can suppress the backflow of injected electrons from semiconductor to metal, making sure the transfer of electrons to the semiconductor surface for reduction reaction [19–21]. In the case of $W_m < W_s$, the Schottky barrier cannot be formed so that the injected hot electrons flow back to metal, reducing the efficacy of plasmonic effect [8]. This restriction makes some plasmonic metal can not function efficiently in some plasmonic metal-semiconductor photocatalytic systems due to the relatively small W_m (such as Ag and Cu) [22].

Graphene, a unique two-dimensional carbon structure, is considered as an ideal electron-transfer medium in photocatalysis mainly due to its various advantages including superior electron mobility, large surface area, excellent optical transparency, and low cost [23–26]. For instance, Amal et al. demonstrated that graphene could be used as a solid electron mediator for a Z-scheme photocatalytic water splitting system using $BiVO_4$ and $Ru/SrTiO_3:Rh$ as the O_2 and H_2 photocatalysts, respectively [27]. Yu et al. used graphene as an electron bridge between TiO_2 semiconductor and MoS_2 cocatalyst for photocatalytic H_2 evolution [28]. In this work, for the first time, we demonstrate that graphene nanosheets can breakthrough the limitation and act as “bridge” to transfer hot electrons from smaller work function plasmonic metal to semiconductor of larger work function for photocatalytic applications. In the design, TiO_2 nanosheets and Ag nanocubes are co-deposited on the reduced graphene oxide (rGO) nanosheets to form a ternary Ag-rGO-TiO_2 hybrid structure. It was found that the rGO nanosheets as conductive channels can successfully conduct the hot electron flow from Ag nanocubes to TiO_2 nanosheets. As a result, the photocatalytic performance is significantly improved by the rGO nanosheets in comparison with binary Ag-TiO_2 structure with Ag nanocubes directly deposited on the TiO_2 nanosheets.

2. Experimental

2.1. Chemicals

Poly(vinyl pyrrolidone) (PVP, M.W. ≈ 55000, Aldrich, 856568), NaSH (Sigma-Aldrich, 161527), ethylene glycol (EG, Sigma-Aldrich, 324558), natural graphite flake (~325 mesh, Alfa Aesar), and silver trifluoroacetate (Aladdin, S109509) were used in our synthesis. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in all experiments was de-ionized. All chemicals were used as received without further purification.

2.2. Synthesis of TiO_2 nanosheets

The TiO_2 nanosheets were synthesized with hydrofluoric acid as a capping agent, by modifying a method in literature [29]. In a typical synthesis, 10-mL of tetrabutyl titanate was added into a 50-mL dried Teflon autoclave. Then with vigorous magnetic stirring, 2.5 mL of hydrofluoric acid was added and the stirring was allowed to proceed for 5 min. Then the Teflon-lined stainless steel autoclave was heated at 200 °C for 24 h. After the autoclave had cooled down to room temperature, the resultant product was separated by centrifugation, and washed with water for several times. The final product was then dried at 45 °C for 12 h. Caution! Hydrofluoric acid is extremely corrosive and toxic, and should be handled with extreme care.

2.3. Synthesis of Ag nanocubes

In a typical synthesis [30], 10-mL EG was added into a 50-mL three-neck flask and pre-heated under magnetic stirring at 150 °C. 0.12-mL NaSH (3 mM in EG) was quickly injected into the heated solution. After 2 min, 1-mL HCl solution (4 mM in EG) was introduced into the reaction solution, followed by the addition of 2.5-mL PVP solution (20 mg/mL in EG) after another 2 min. Next, 2 min later, 0.8-mL solution of silver trifluoroacetate (282 mM in EG) was added. The reaction was allowed to proceed at 150 °C for 40 min. The product was collected by centrifugation, and washed with acetone and water several times to remove excess PVP. The as-obtained Ag nanocubes were redispersed in water for further use.

2.4. Synthesis of reduced graphene oxide

Graphite oxide was synthesized from natural graphite flake (~325 mesh, Alfa Aesar) by a modified Hummers method [31]. In a typical procedure, 2.0 g of graphite powder was added into concentrated H_2SO_4 (80 mL) in a 500-mL flask under ice bath. Under vigorous stirring, $KMnO_4$ (10.0 g) and $NaNO_3$ (4.0 g) were gradually added, while the temperature of the mixture was kept below 10 °C for 4 h. Subsequently, the reaction mixture was stirred at 35 °C for another 4 h until it became pasty green. The mixture was then diluted with water (200 mL), after which its color changed into brownish. The addition of water was performed in an ice bath to keep the temperature below 100 °C. The mixture was then stirred for 30 min, and 15 mL of 30 wt% H_2O_2 was slowly added to the mixture to reduce the residual $KMnO_4$, after which the color of the mixture changed to brilliant yellow. The mixture was re-dispersed in water and then was dialyzed for one week to remove residual salts and acids. The resulted solid was centrifuged and dried at 45 °C for 12 h. In a typical synthesis of reduced graphene oxide (rGO), 30 mg of graphite oxide was dispersed in 100 mL of water to form a graphene oxide (GO) aqueous suspension with probe sonication (Scientz-IID, China) for 1 h. Then 200 mg of PVP (K30) was added in and the mixture was stirred for 40 h at room temperature. The as-obtained suspension was pre-heated at 95 °C under magnetic stirring. Then 40 μL hydrazine hydrate and 200 μL ammonia were added to the mixture and the reaction was allowed to proceed at 95 °C for 1 h. The product was collected by centrifugation, washed with acetone several times, and re-dispersed in water for further use.

2.5. Fabrication of Ag-rGO-TiO_2, Ag-TiO_2, Ag-rGO and Eosin Y (EY)-rGO-TiO_2

In the synthesis of Ag-rGO-TiO_2, 2.5 mL (2 mg mL^{-1}) rGO aqueous dispersion was diluted with 10 mL water by sonication. Subsequently, 20 mg of TiO_2 nanosheets were added into the rGO aqueous dispersion, which was further sonicated for 10 min. Then 1.2 mL (10 mg mL^{-1}) of Ag nanocubes was added into the dispersion, and the sonication was allowed to proceed for another 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 rGO with TiO_2 and Ag. The Ag-TiO_2 and Ag-rGO were prepared under the same experimental