Communication

Enhanced Photocatalytic Hydrogen Generation by Optimized Plasmonic Hot Electron Injection in Structure-Adjustable Au-ZnO Hybrids

Youlong Chen ¹, Liang Ma ^{1,*} and Sijing Ding ^{2,*}¹ Hubei Key Laboratory of Optical Information and Pattern Recognition, Wuhan Institute of Technology, Wuhan 430205, China; chenyoulong2@126.com² School of Mathematics and Physics, China University of Geosciences (Wuhan), Wuhan 430074, China

* Correspondence: maliang@wit.edu.cn (L.M.); dingsijing@cug.edu.cn (S.D.); Tel.: +86-027-8799-2089 (L.M.); +86-027-6788-3091 (S.D.)

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Abstract: Plasmonic Au-ZnO hybrids with adjustable structures (including Au-decorated ZnO and core-shell Au@ZnO with dense and porous ZnO shells) and the optimized hot electron-driven photocatalytic activity were successfully prepared. It was found that the Au@ZnO core-shell hybrids with porous morphology had the highest plasmon-enhanced photocatalytic hydrogen generation activity under visible light irradiation. The wavelength-dependent photocatalytic tests verified that Au@ZnO with porous ZnO shells had the highest apparent quantum efficiency upon resonance excitation. The ultrafast transient absorption measurements revealed that Au@ZnO with porous ZnO shells had the fastest plasmon-induced hot electron injection, which was thought to be the reason for the improved photocatalytic activity. This work might provide a promising route to designing photocatalytic and photoelectric materials.

Keywords: nanoparticles; plasmon; photocatalysis; hot electron injection; metallic composites

1. Introduction

Hot electron-driven photocatalysis by plasmonic metal–semiconductor hybrids shows great potential in the field of solar energy conversion [1–10]. Hot electrons, which are generated from the nonradiative relaxation of localized surface plasmons, are more energetic than those generated by direct photoexcitation [11–15]. The maximum utilization of hot electrons is significantly important to improve the photocatalytic performance of metal–semiconductor hybrids [16–22]. Several strategies have been proposed to optimize the hot electron injection in plasmonic composites, such as enhancing the near field of plasmonic metal nanocrystals [23–25], selectively placing a semiconductor on the position, where a strong near field is located [26,27]. However, the current strategies mainly focus on adjusting the plasmonic properties of metal nanocrystals and the positions of semiconductors, and few reports concentrate on manipulating the morphology of semiconductors for better reception of hot electrons.

In this work, structure-adjustable Au-ZnO hybrids were used for optimizing hot electron-driven photocatalysis. Three types of Au-ZnO hybrids, including Au-decorated ZnO (Au/ZnO) and core-shell Au@ZnO with dense (Au@dense ZnO) and porous shells (Au@porous ZnO), were prepared for photocatalytic hydrogen generation from water splitting. It was found that core-shell Au@porous ZnO hybrids possessed the highest photocatalytic hydrogen generation under light irradiation ($\lambda > 420$ nm), which were 2.75, 1.34, and 1.14 times those of the pure ZnO, Au/ZnO, and Au@dense ZnO, respectively. The enhanced mechanism can be ascribed to the enhanced utilization efficiency of hot electrons caused by the porous ZnO shells.

2. Results and Discussion

The detailed morphologies of the structure-adjustable Au-ZnO hybrids are presented in Figure 1. The initial Au nanospheres had an average diameter of 18 ± 2 nm (see Figure 1a). Figure 1b displays the TEM image of the Au-decorated ZnO hybrids, demonstrating that the Au nanospheres were randomly attached on ZnO. The TEM image of the core-shell Au@porous ZnO is shown in Figure 1c. The ZnO nanoshells showed a well-defined porous structure and had an average thickness of 45 ± 3 nm. Figure 1d exhibits the TEM image of Au@dense ZnO. The ZnO nanoshells displayed a dense structure and had an average thickness of 44 ± 3 nm.

Figure 1. TEM images of Au (a), Au/ZnO (b), and Au@ZnO with porous (c) and dense (d) shells.

The high-resolution TEM (HRTEM) images and the XRD patterns were obtained to elucidate the detailed morphologies and crystalline structures of the Au-ZnO hybrids. Figure 2a,b displays the XRD patterns and EDS spectra of the structure-adjustable Au-ZnO hybrids. The phase of Au and ZnO can be observed in the three types of Au-ZnO hybrids. From the EDS results, the presences of Au, Zn, and O elements can be confirmed. Figure 2c exhibits the HRTEM image of single Au@porous ZnO nanoparticles and demonstrates that the holes (circled by a white dashed line) were randomly distributed in the whole shell region. The average diameter of the holes was approximately 4 nm. Figure 2d displays the lattice of the region labelled in Figure 2c. The well-resolved lattice plane distance of 0.261 nm can be ascribed to the (002) plane of ZnO. The corresponding fast Fourier transform (FFT) analyses of the red labelled region are shown in Figure 2e, which also indicated the existence of the ZnO lattice plane.

Figure 2. XRD patterns (a) and EDS spectra (b) of the structure-adjustable Au-ZnO hybrids. (c) High-resolution TEM (HRTEM) image of Au@porous ZnO. (d) HRTEM image recorded from the area marked with a red circle in (c). (e) Fast Fourier transform (FFT) pattern of the region indicated by a red dashed circle. (f) Extinction spectra of Au, ZnO, and structure-adjustable Au-ZnO hybrids. (g) Photoluminescence (PL) spectra of ZnO and the structure-adjustable Au-ZnO hybrids.

The extinction spectra of the structure-adjustable Au-ZnO hybrids are given in Figure 2f. The Au nanospheres exhibited a narrow plasmon peak around 520 nm. The plasmon peak of Au@dense ZnO red-shifted to 578 nm, caused by the increased refractive index of the surrounding medium. For Au@porous ZnO, the plasmon peak red-shifted to 614 nm. The plasmon peak of Au/ZnO red-shifted slightly, reaching 532 nm. The structure-adjustable Au-ZnO hybrids had a sharp and strong plasmon resonance in the visible light region, laying the foundation for hot electron-driven photocatalysis. Figure 2g displays the PL spectra of ZnO and the structure-adjustable Au-ZnO hybrids. The ultraviolet and blue emission intensities of the structure-adjustable Au-ZnO hybrids were remarkably decreased compared with those of the pure ZnO, verifying the efficient electron migration and energy between ZnO and Au.

The photocatalytic hydrogen generation activities of ZnO and the structure-adjustable Au-ZnO hybrids were investigated by using Na_2S and Na_2SO_3 as sacrificial agents under light irradiation

($\lambda > 420$ nm). As shown in Figure 3a,b, the pure ZnO had a low hydrogen generation rate of $0.044 \text{ mmol g}^{-1} \text{ h}^{-1}$. This is because ZnO had a weak visible light absorption and a fast recombination of electron–hole pairs. Noticeably, the Au@porous ZnO hybrids had the highest photocatalytic hydrogen generation rate, reaching $0.12 \text{ mmol g}^{-1} \text{ h}^{-1}$, which were 2.75, 1.34, and 1.14 times those of the pure ZnO, Au/ZnO, and the Au@dense ZnO hybrids.

Figure 3. (a,b) Photocatalytic hydrogen generation rates of ZnO and the structure-adjustable Au-ZnO hybrids. (c) Apparent quantum efficiency (AQE) of the Au@porous ZnO hybrids. (d) AQEs of the structure-adjustable Au-ZnO hybrids tested at their plasmon resonances. (e) Normalized time-resolved optical differential transmission for Au and the structure-adjustable Au-ZnO hybrids. (f) Schematic illustrating the possible hot electron injection processes in the structure-adjustable Au-ZnO hybrids.

To reveal the mechanism of the improved photocatalytic activity of Au@porous ZnO, the AQE of hydrogen generation was tested using monochromatic light irradiation. As shown in Figure 3c, the AQE of Au@porous ZnO matched well with its extinction spectrum, revealing that the plasmon excitation was the origin of the enhanced hydrogen generation. In addition, the AQEs of the three types of Au-ZnO hybrids, which were tested around their corresponding plasmon resonance peaks, were given to verify the plasmon-enhanced efficiency. The Au@porous ZnO hybrids had the highest AQE (0.21%) with the irradiation wavelength at the plasmon peak of 600 nm, whereas the AQEs of the Au/ZnO and Au@dense ZnO catalysts only reached 0.12% and 0.15%, respectively, with an irradiation wavelength of 550 nm. These results demonstrated that the Au@porous ZnO hybrids had the highest plasmon-enhanced photocatalytic conversion efficiency upon resonance excitation.

The structure-adjustable Au-ZnO hybrids had almost the same mass ratio of Au, and they had a similar plasmonic light-harvesting ability. However, they showed totally different photocatalytic hydrogen generation efficiencies upon resonance excitation. The different architectures played a key role, which may influence the utilization efficiency of plasmon-induced hot electrons. Ultrafast transient absorption measurements probed around the plasmon peaks were used to investigate the hot electron injection processes, thereby explaining the physical mechanism of a different photocatalytic activity upon resonance excitation. As shown in Figure 3e, the decay rate of Au/ZnO was faster than that of the Au nanospheres, which demonstrated that the hot electrons in the Au nanospheres were quickly injected into ZnO. The Au@dense ZnO hybrids showed a faster decay rate than Au/ZnO, indicating a higher hot electron injection efficiency from the Au nanospheres to the ZnO shells. Noticeably,

the Au@porous ZnO hybrids displayed the fastest decay rate, revealing the highest hot electron injection efficiency.

To explain the different hot electron injection efficiencies of the three types of hybrids, the possible hot electrons injection processes were proposed. As shown in Figure 3f, for the three types of Au-ZnO hybrids, the hot electron injection occurred at the interface between the Au nanospheres and the ZnO shells. However, the small contact area of the Au/ZnO hybrids limited their hot electron injection efficiency. For the core-shell Au@dense ZnO hybrids, they had a much larger interfacial contact area than that of the Au/ZnO hybrids, therefore resulting in faster hot electrons injection. Interestingly, the Au@porous ZnO hybrids had the highest hot electron injection efficiency, even though such structures almost had the same thickness of the ZnO shell and contact area compared with Au@dense ZnO. This is because porous ZnO nanoshells had abundant holes for hot electron transfer. Hence, hot electrons can not only be injected into the inner ZnO, but also transfer to the outer ZnO. Therefore, the Au@porous ZnO hybrids exhibited the highest photocatalytic hydrogen generation rate.

3. Materials and Methods

Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99.99%), sodium hydroxide (NaOH, 99.7%), L-ascorbic acid (AA, 99.7%), sodium sulfite (Na_2SO_3 , 99.5%), sodium sulfide (Na_2S , 99.5%), sodium borohydride (NaBH_4 , 96.0%), zinc acetate (99.5%), hexamethylenetetramine (99.0%), were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Hexadecyltrimethylammonium bromide (CTAB, 99.0%) was purchased from Amresco, Inc. (Solon, OH, USA). Deionized water with a resistivity of about $18.25 \text{ M}\Omega \text{ cm}$ was used as the solvent in all experiments. Au nanospheres were prepared as previously reported [28]. For the synthesis of structure-adjustable Au-ZnO hybrids, 2 mL of zinc acetate (0.1 M), 2 mL of ascorbic acid (0.1 M), and 5 mL of hexamethylenetetramine (0.1 M) were added to 10 mL as-prepared Au nanospheres in an aqueous solution. The mixture was kept at 85°C for 8 h in a vacuum oven. The product (labelled “A”) was centrifuged, washed by water and dried at 60°C . To obtain Au@dense ZnO, the as-prepared “A” powder was annealed at 200°C for 1 h in air. To obtain Au@porous ZnO, the as-prepared “A” powder was dispersed in ultrapure water and annealed at 200°C for 1 h in air. To obtain Au-decorated ZnO, the as-prepared “A” powder was transferred to a stainless steel autoclave and annealed at 200°C in a vacuum oven.

Photocatalytic hydrogen generation measurements were conducted as previously reported [29]. Visible-light photocatalytic hydrogen production tests were conducted with a commercial photocatalytic evaluation system. Briefly, 50 mg of photocatalyst powders were dispersed in 50 mL of an aqueous solution containing Na_2SO_3 (0.25 M) and Na_2S (0.35 M) as sacrificial reagents. The light source was a 300 W Xenon lamp (Zhongjiaojinyuan, Beijing, China) equipped with an ultraviolet cutoff filter ($\lambda > 420 \text{ nm}$). The amount of hydrogen gas was automatically analyzed by an online gas chromatograph (Tianmei GC-7920, Beijing, China). The apparent quantum efficiency (AQE) was measured using a series of quartz bandpass filters to obtain the monochromatic light. The photo flux of the incident light was tested by a Ray virtual radiation actinometer (Prefectlight, Beijing, China). The morphologies were obtained with TEM (Hitachi, Tokyo, Japan). XRD patterns were tested on an X-ray diffractometer (Panaco, Holland). The optical properties of the products were analyzed with extinction and photoluminescence (PL) spectra. Femtosecond transient absorption experiments were performed at room temperature by using a pump-probe method. The wavelengths of the pump and the probe were tuned to 560 nm.

4. Conclusions

In summary, we have successfully prepared structure-adjustable Au-ZnO hybrids, including Au-decorated ZnO, core-shell Au@dense ZnO, and Au@porous ZnO, for hot electron-driven photocatalytic hydrogen generation. Under light ($\lambda > 420 \text{ nm}$) irradiation, the Au@porous ZnO hybrids exhibited the highest photocatalytic hydrogen generation activity from water splitting. The enhanced mechanism can be ascribed to the enhanced utilization efficiency of hot electrons, which was

caused by the porous ZnO. This work might provide a promising route to designing photocatalytic and photoelectric materials.

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