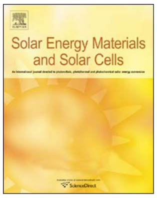
Solar Energy Materials and Solar Cells 180 (2018) 25–33

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Surface plasmon-driven photoelectrochemical water splitting of aligned ZnO nanorod arrays decorated with loading-controllable Au nanoparticles

Weiwei Zhang[a,b], Wenzhong Wang[a,*], Honglong Shi[a], Yujie Liang[a], Junli Fu[a], Min Zhu[a]

[a] *School of Science, Minzu University of China, Beijing 100081, China*
[b] *Kunming Institute of Physics, 31 Jiao-Chang East Road, Wuhua District, Kunming 650223, China*

ARTICLE INFO

Keywords:
Au nanoparticles
Plasmon resonance
ZnO nanorod arrays
Visible light
Photoelectrochemical water splitting

ABSTRACT

In this paper, we designed a series of well-aligned ZnO nanorod arrays decorated with loading-controllable Au nanoparticles and studied their surface plasmon-driven photoelectrochemical (PEC) water splitting performances. The PEC water splitting ability of Au-ZnO nanorod arrays was evaluated under illumination with $\lambda > 420$ nm light. These nanorod arrays show remarkable PEC water splitting performances and achieve the highest photocurrent density of 30 μA cm^{-2} at 0.8 V versus Ag/AgCl. Furthermore, the PEC performance for heterogenous nanorod arrays can be effectively adjusted by controlling loading amounts of Au nanoparticles. We experimentally demonstrate that the Au-ZnO nanorod arrays show enhanced visible light absorption ability. The superior PEC performance of Au-ZnO nanorod arrays is attributed to the synergistic effects of plasmonic Au nanoparticles, ZnO semiconductor and Schottky barrier built in heterogenous nanorod array. This work provides a facile strategy to manipulate the PEC water splitting activity of Au-ZnO hybrid nanostructures by simply controlling the loading amounts of metallic Au nanoparticles. Furthermore, our research offers a potentially efficient strategy for the design and fabrication of new types of plasmonic-metal/semiconductor hybrid nanostructures with a plasmonic-enhanced PEC water splitting activity under the visible light, which are as valuable photocatalysts for solar-to-chemical/electrical energy conversion.

1. Introduction

Visible-light-driven photoelectrochemical (PEC) water splitting is one of the most promising ways to provide a sustainable clean energy source, because PEC water splitting can convert solar energy to electricity or to chemical fuels directly [1–6]. Hence visible-light-driven PEC water splitting is highly important for exploiting clean and renewable solar energy to meet the steadily increasing energy demand [7–9]. Due to the intriguing photocatalytic properties, wide-band gap metal oxides such as TiO_2 and ZnO have been widely studied as PEC photoanode materials for water splitting [10,11]. As a common, important and cheap wide-band gap metal oxide, ZnO semiconductor has been considered as a promising photoanode material for PEC water splitting [11–13] due to its high electron mobility and transfer efficiency (115–155 $cm^2\ V^{-1}\ s^{-1}$) [14], large exciton binding energy (60 meV), intrinsic stability, non-toxicity, and favorable environmental compatibility [15].

Recently, fabrication and PEC water splitting performances of ZnO nanostructures with controllable morphologies have attracted numerous attentions, because these nanostructures are capable of facilitating fast transport of photogenerated carriers due to the shorter lateral length [16–18]. Among the nanostructures, vertically aligned ZnO nanorod/nanowire array is most ideal nanostructure for light-driven PEC water splitting because of its large surface area, large light absorption area and short diffusion length [13,19,20]. Nevertheless, as a wide-band gap metal oxide semiconductor, the main limitation of ZnO photoanode employed for PEC water splitting is that it is not capable of absorbing visible light owing to its wide-band gap feature (3.3 eV), hence only very few solar photons (~ 4%) can be applied to drive water splitting in this photocatalyst, imposing a significant restriction on the overall water splitting. Therefore many efforts have recently been devoted to fabricate visible-light-driven ZnO photocatalysts, such as doping with metal or nonmetal elements, fabricating heterogeneous nanostructures [21–23], and so on.

Another efficient strategy for fabricating visible-light photocatalyst is the photosensitization of semiconductor with plasmonic metal Au, Ag, and Cu nanoparticles (NPs), because these metal NPs are capable of absorbing visible light through localized surface plasmon resonance (LSPR) induced by the interaction with light [24]. For hybrid nanostructure photocatalysts fabricated by coupling plasmonic metal NPs

---

[*] Corresponding author.
E-mail address: wzhwangmuc@163.com (W. Wang).

https://doi.org/10.1016/j.solmat.2018.02.020
Received 12 November 2017; Received in revised form 12 January 2018; Accepted 11 February 2018

with semiconducting nanostructures, LSPR of plasmonic metal NPs can significantly improve the solar energy conversion efficiency of semiconductor photocatalyst through plasmonic energy-transfer enhancement [25], because the energy stored in the oscillating electrons or local plasmonic field can be transferred from metal to a semiconductor via direct electron transfer [26,27] and/or plasmon-induced resonant energy transfer [28].

As mentioned above, plasmonic metal NPs can efficiently extend the light absorption region and then significantly improve the solar energy conversion efficiency of semiconductors [25], thus many attempts have been tried to design plasmonic semiconducting photocatalysts for potential applications in visible-light-driven PEC water splitting. For instance, plasmonic Au NPs were successfully applied to couple with wide-band gap TiO_2 nanostructures to fabricate visible-response photocatalysts for PEC water splitting [4,5]. However, the fabrication and PEC water splitting performance of plasmonic ZnO photocatalysts is limited. The previous literature showed that matchlike ZnO/Au heterostructure exhibited the enhanced PEC water splitting performance under solar illumination [29]. ZnO nanopencil arrays sensitized with plasmonic Au NPs exhibited the improved PEC water splitting performance [30]. Nonetheless, in these studies, the PEC water splitting activities of the ZnO nanostructures sensitized with Au NPs were mainly investigated under the simulated solar light illumination. Furthermore, to the best of our knowledge, there are no any reports on the effects of loading contents of plasmonic metal NPs on the PEC water splitting performance for ZnO nanostructures under visible light irradiation. As demonstrated in previous literature, rational increase loading of plasmonic metal NPs can remarkably improve the water splitting performance of semiconducting photocatalyst [31]. Thus it is highly important for designing plasmonic semiconducting photocatalyst with superior photocatalytic activity by manipulating loading content of plasmonic metal NPs.

In this work, we designed a series of well-aligned ZnO nanorod arrays decorated with loading-controllable Au NPs (denoted as Au-ZnO nanorod arrays) and studied their visible light PEC water splitting performances. The highly aligned Au-ZnO nanorod arrays are fabricated via a facile seed-assisted electrochemical deposition and photodeposition strategy. The loading contents of the Au NPs can be easily controlled by varying the photodeposition time. The visible-light-driven PEC water splitting activities of ZnO nanorod arrays were systemically investigated to elucidate the specific role of the loading contents of the Au NPs. The Au-ZnO nanorod arrays exhibit improved PEC water splitting activity under visible light illumination ($\lambda > 420$ nm). The results achieved in this work have demonstrated that a rational increase for the loading of plasmonic Au NPs can significantly improve the PEC water splitting ability of ZnO nanorod arrays.

2. Experimental section

2.1. Synthesis of ZnO nanorod arrays

The ZnO nanorod arrays were synthesized by a facile seed-assisted electrochemical deposition method. A typical synthetic procedure was given as follows. Firstly, the fluorine-doped tin oxide (FTO) glass (1.0 × 1.5 cm) substrates were separately cleaned by deionized water, ethyl alcohol and isopropanol for 5 min in an ultrasonic cleaner(KQ5200DE, Shumei, China). Secondly, a few drops of 5 mM zinc acetate ($(CH_3CO_2)_2Zn$) ethanol solution were dropped on the cleaned FTO substrate and dried at 80 °C to form a thin $(CH_3CO_2)_2Zn$ film. After repeating 10 times of the above process, the FTO substrate with a thin $(CH_3CO_2)_2Zn$ film was annealed at 350 °C for 30 min in air to form a thin ZnO seed layer on the substrate. Thirdly, a facile seed-assisted electrochemical deposition method was applied to synthesize ZnO nanorod arrays. The experiments were conducted in a three-electrode electrochemical cell at 80 °C, in which the FTO substrate coated with thin ZnO seed layer was used as the working electrode, a Pt plate was applied as the counter electrode and an Ag/AgCl (KCl saturated) was employed as the reference electrode. The electrolyte was a 25 mM $(CH_3CO_2)_2Zn$ aqueous solution with 25 mM hexamethylenetetramine (HMT). The electrochemical deposition was performed for 1 h at a potential of − 1.10 V versus Ag/AgCl reference electrode. Finally, the FTO substrate grown with ZnO nanorod arrays was rinsed with deionized water and then dried.

2.2. Synthesis of Au nanoparticle-decorated ZnO nanorod arrays

Au NPs were deposited on the ZnO nanorod arrays by an easy photoreduction method. Firstly, 20 μL of 20 mg mL^{-1} gold chloride ($HAuCl_4{\cdot}3H_2O$) was added into 60 mL deionized water to prepare $HAuCl_4$ aqueous solution. After that, the FTO glass grown with ZnO nanorod arrays was put into the $HAuCl_4$ aqueous solution, followed by irradiating with a 300 W Xe lamp under 420 nm for different time to grow Au NPs on ZnO nanorod arrays through reducing the Au^{3+} to Au°. Finally, FTO glass grown with Au nanoparticle-decorated ZnO nanorod arrays was washed with deionized water for several times, dried in air and then annealed in a tube furnace at 400 °C for 1 h. The loading content of Au NPs is controlled by adjusting photodeposition reaction time and is determined by inductively coupled plasma massspectrometry (ICP-MS). The samples with Au nanoparticle loading contents of 0.7 wt%, 2 wt% and 3.8 wt% Au NPs were prepared with photodeposition reaction time of 1 min, 3 min and 5 min, which were denoted as Au-ZnO (1 min-0.7% Au), Au-ZnO (3 min-2% Au) and Au-ZnO (5 min-3.8% Au), respectively.

2.3. Characterizations

The composition and phase pure of achieved Au nanoparticle-decorated ZnO nanorod arrays were characterized by X-ray diffraction (XRD) (XD-D1, Shimadzu, Japan) applying Cu Kα irradiation. The morphology and size of the samples were evaluated by scanning electron microscopy (SEM) (Hitachi, SEM-4800, Japan). The crystallinity and microstructure feature of the samples were investigated by transmission electron microscopy (TEM) and high resolution (HRTEM) (JEOL 2100, Japan). A Lambda 950 UV/Vis/NIR spectrometer (Perkin-Elmer, USA) was applied to study the optical absorption properties of the obtained ZnO nanorod arrays decorated with Au NPs.

2.4. PEC water splitting performance evaluation

The PEC water splitting performance of prepared Au-ZnO nanorod arrays was investigated in a three-electrode electrochemical cell, in which the fabricated Au-ZnO nanorod array was applied as working electrode, a Pt wire and Ag/AgCl were used as counter and reference electrode, respectively. The electrolyte solution was 0.1 M Na_2SO_4 buffer solution (100 mL) with pH value of 7. Before measurements, the electrolyte solution was degassed with N_2 for 30 min. The working electrode was illuminated by a 300-W Xenon lamp during the whole measurements. The chronoamperometric J–t plots for bare ZnO and Au-ZnO nanorod arrays were collected in 0.1 M Na_2SO_4 electrolyte solution under irradiation with $\lambda > 420$ nm light (AM 1.5G, 100 mW/cm^2). The linear sweep voltammograms (VLS) for bare ZnO and Au-ZnO nanorod arrays were recorded in applied potentials from 0 to 1 V versus Ag/AgCl at 5 mV/s under irradiation with $\lambda > 420$ nm (AM 1.5G, 100 mW/cm^2). The scan rate is 50 mV/s in the PEC measurements.

3. Results and discussion

3.1. Morphology and structure characterization

The morphology feature and size of the ZnO nanorod arrays and Au-ZnO nanorod arrays on ITO glass substrate were characterized by SEM as shown in Fig. 1A. As seen in SEM image, highly aligned nanorods