Journal of Colloid and Interface Science 413 (2014) 17–23

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Silver sulfide nanoparticles sensitized titanium dioxide nanotube arrays synthesized by in situ sulfurization for photocatalytic hydrogen production

Xu Liu [a,b], Zhongqing Liu [b,*], Jinlin Lu [a], Xuelian Wu [b], Wei Chu [b,*]

[a] School of Materials & Metallurgy, University of Science & Technology Liaoning, Anshan 114051, PR China
[b] College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China

ARTICLE INFO

Article history:
Received 7 April 2013
Accepted 16 September 2013
Available online 21 September 2013

Keywords:
In situ sulfurization
TiO_2 nanotube arrays
Photocatalytic
Hydrogen production

ABSTRACT

Titanium dioxide (TiO_2) nanotube arrays (TNAs) sensitized with silver sulfide (Ag_2S) nanoparticles (NPs) were synthesized via facile in situ sulfurization. Metallic silver NPs were first loaded on TNAs through a simple electrodeposition process. The as-prepared Ag/TNAs composites were further treated with a solution of acetonitrile containing sulfur (S_8) and dried in vacuum to obtain a new nanocomposite material comprising of TNAs sensitized with Ag_2S NPs. In these composite nanostructures, ultrafine Ag_2S NPs were well-dispersed and assembled on the exterior and interior walls of the TNAs. Owing to sensitizing with a narrow bandgap material like Ag_2S and the homogeneous distribution of the Ag_2S NP heterojunction structures over the surface of the TNAs, the synthesized nanocomposite samples exhibited remarkable capability to absorb visible light and showed a significant enhancement in the photocatalytic efficiency of hydrogen generation. Under visible light illumination (100 mW/cm^2), a maximum photoconversion efficiency of 1.21% and the highest hydrogen production rate of 1.13 mL/cm^2 h were obtained from the TNA electrodes sensitized with Ag_2S NPs.

1. Introduction

Tapping of solar energy has gained much attention currently, owing to the depletion of fossil fuel resources and the serious environmental pollution caused by the use of carbon-based fuels [1]. As a clean and sustainable energy source, hydrogen is a possible alternative for fossil fuels to resolve future energy problems. Photocatalytic splitting of water using semiconductor materials under irradiation of solar light presents a great promise for hydrogen generation [2]. Among semiconducting materials, films of ordered TiO_2 nanotube arrays (TNAs), with their superior performance, is one of the most promising 1D materials being investigated widely as photocatalysts [3,4]. The vertically oriented architecture of the nanotube arrays can specifically provide a unidirectional channel for electron transport and enhance the overall light absorption by increasing the optical path length of light traveling through the nanotubes [5]. Therefore, TNAs may exhibit great potential to use photoelectrons efficiently to generate H_2 [6,7].

However, the wide band gap (3.2 eV) limits the absorption of TiO_2 to only ultraviolet (UV) region of the solar spectrum and decreases the utilization ratio of solar power vastly. Many strategies have been explored to extend the optical absorption of TiO_2 into the visible light region including doping of metal or nonmetal ions [8,9], coupling with narrow band gap semiconductors [10–12], dye sensitization [13], surface modification [14], and supporting noble metals [15,16]. Among these, a remarkable enhancement in the photocatalytic efficiency of TiO_2 under visible light has been obtained by coupling low bandgap semiconductors such as CdS, CdSe, and CdTe [10,17–19]. In comparison to other semiconductors, Ag_2S, owing to its narrow band gap (Eg ~ 1.0 eV) and relatively high absorption coefficient of visible light, is considered to be an important chalcogenide sensitizer [11,12]. Hence, Ag_2S is a highly desirable material that can be used in photovoltaics and photoelectrochemisty [20–23]. The existing methods that are used to synthesize TNAs sensitized with semiconductor NPs include chemical bath deposition (CBD) [17,20], electrochemical deposition [10], bifunctional organic linker [24] and successive ionic layer absorption and reaction (SILAR) [25]. These methods have some inherent disadvantages. For example, nanotubes sensitized by semiconductor NPs are very short and these NPs distribute nonuniformly on the wall of the nanotubes and aggregate or even plug the top of nanotubes, which weakens light harvesting for photocatalysis or solar cells [26].

Here, we demonstrate the synthesis of TNAs sensitized with Ag_2S NPs by a facile in situ sulfurization route. We also report on the photocatalysis characteristics of the sensitized TNAs. TNAs

---

* Corresponding authors. Fax: +86 28 8546 1108.
E-mail addresses: lzq_301@126.com (Z. Liu), chuwei1965_scu@yahoo.com (W. Chu).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.09.031

loaded with well-dispersed Ag NPs were first fabricated by a soft electrodeposition method. The Ag NPs were subsequently transformed by sulfurization to Ag_2S NPs. The Ag_2S NPs were uniformly distributed on the surface of the TNAs retaining the configuration of Ag NPs in the TNAs. The photocatalytic properties of Ag_2S/TNA heterostructures were investigated under the irradiation of visible light. The structures exhibited high activity and stability toward hydrogen generation in an aqueous solution containing S^{2-}.

2. Experimental section

2.1. Loading of Ag NPs TNAs

Ti foils were first cleaned with ethanol in an ultrasonic bath for 10 min, then rinsed in deionized water, and were finally dried in air. The TNAs were prepared by anodization at 60 V for 4 h in ethylene glycol system containing 0.3 wt% NH_4F and 2.0 vol% deionized water. After anodization, the samples were rinsed with deionized water and then air dried. Then the as-prepared electrodes were directly annealed at 450 °C for 2 h in an atmosphere of air.

Loading of Ag NPs on the TNAs was carried out by facile electrodeposition. The photochemical experiments were carried out using a three-electrode system with the TNA as the working electrode (1×1 cm^2), a Pt foil counter electrode (2×2 cm^2), and a quasi-reference electrode made of Ag wire. Aqueous solution containing 0.01 M $AgNO_3$, 0.1 M $NaClO_4$, 0.6 M ethylenediamine, and 0.02 M thiopropionic acid was used as the electrolyte. The deposition was carried out at -0.6 V. After deposition, the samples were washed with ethanol and dried in vacuum.

2.2. Preparation of Ag_2S NPs sensitized TNAs electrode

The TNAs sensitized with Ag_2S NPs were synthesized from the TNAs loaded with Ag NPs using a facile in situ sulfurization method. The TNAs loaded with Ag NPs were immersed in a 100 mL solution of acetonitrile containing 1×10^{-2} M S_8 for 10 min at 60 °C. After reaction with S_8, the samples obtained were rinsed with acetonitrile, ethanol, and deionized water. Finally, the as-prepared samples were dried in vacuum.

2.3. Characterization

The morphology of the electrode was observed by field-emission scanning electron microscopy (FESEM, FEI Corporation) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin). X-ray photoelectron spectroscopy (XPS, Kratos XSAM-800 spectrometer) was carried out using an Al Kα X-ray source generated at 12 kV and 15 mA (with incident energy of 1486.6 eV) and the analytical instrument was corrected using standard Au and Ag samples. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. UV–vis diffuse reflectance spectroscopy (DRS) was carried out at room temperature (Tu-1901 photospectrometer, Pgeneral, China). Energy dispersive X-ray (EDX) spectra were also obtained (using an Oxford detector).

All photoelectrochemical (PEC) experiments were carried out in a specially designed rectangular quartz cell with a three-electrode configuration composed of the samples photoelectrode (1×1 cm^2) as a working electrode, Pt foil cathode as a counter electrode, and an Ag/AgCl as a reference electrode. An external Xenon lamp was used as the light source. A cutoff filter was inserted between the Xenon lamp and the side of the TNAs electrode so that light with a wavelength of less than 430 nm can be filtered. The illumination intensity of white light was measured as 100 mW/cm^2. A solution containing 0.05 M Na_2S, 0.05 M Na_2SO_3, and 0.1 M $NaClO_4$ was used as the electrolyte. The working electrode potential and current were controlled by an electrochemical workstation (CHI 660D, CH Instruments). The amounts of H_2 generated were analyzed by gas chromatography.

3. Results and discussion

The illustrative FESEM images of the top and cross-sectional portions of self-assembled TNAs prepared by anodization in ethylene glycol solution containing fluorine ions are shown in Fig. S1. These images show that the crystalline TNAs exhibit a regularly arranged structure [3,4], with average inside diameter, thickness, and length of the nanotubes found to be ~80 nm, ~10 nm, and ~8 μm, respectively. The highly ordered, vertically aligned, and crystalline TNAs were chosen as the substrate for deposition of Ag NPs. After electrodeposition at a constant direct potential of -0.6 V for 60 s in an aqueous solution containing Ag, some Ag NPs could be observed at the mouths of the TiO_2 nanotubes, as shown in Fig. 1a. The morphology of the TNAs remained unaltered after loading of the Ag NPs (Fig. 1b). Fig. 1c and d, and e correspond to the sections c, d, and e, respectively, shown in Fig. 1b. From these images, it can be observed that the facile electrodeposition process used for the synthesis resulted in uniformly distributed and well-dispersed Ag NPs. Furthermore, from the contrast between the TNAs and the Ag NPs loaded shown by the FESEM images, the well-separated Ag NPs were observed to be almost uniformly distributed across the entirety of the nanotubes, including the top, the middle, and the bottom sections.

TEM analyses provided further evidence of the nanoscopic structure of the Ag NPs on TNAs. The TEM images (example provided in Fig. 2a) showed spherical Ag NPs with uniform size of ~5 nm that were unagglomeratesd and distributed homogeneously on both the inner side and outer sides of the nanotubes. Fig. 2b displays the high resolution TEM (HRTEM) image of the Ag NPs deposited on the TNAs. The lattice distance measured ranged to of 0.235 nm, which corresponded to the (1 1 1) lattice distance of Ag (JCPDS: 04-0783). HRTEM image also revealed clear lattice fringes of 0.352 nm which was in good agreement with the (1 0 1) lattice distance of anatase-type TiO_2 (JCPDS: 21-1272) [20,27]. The selected -area electron diffraction (SAED) patterns showed polycrystalline diffraction rings, which could be indexed to (1 0 1), (0 0 4), (2 0 0), and (2 1 1) planes of anatase TiO_2 (shown in Fig. 2c) [10], and also revealed the presence of crystalline Ag (as shown by the dots enclosed in red circles in Fig. 2c) [27]. The EDX spectrum showed the presence of Ag besides Ti and O and the atomic percentage of Ag was about 2% (Fig. 2b). The chemical state of Ag was estimated by XPS (as shown in Fig. S2) and the results indicated that Ag mainly existed as Ag^0 on the TNA electrode [15]. Xie et al. and Zhang et al. have successfully prepared composites of TNAs and metal NPs by a pulse current deposition (PCD) method [15,28]. However, obtaining well-dispersed and uniform Ag NPs was challenging and the metal NPs could assemble or even plug the mouths of the nanotubes. In our case, thiopropionic acid, which is frequently used for stabilizing and protecting metal NPs during synthesis, was introduced into the electrolyte. The existence of S in thiopropionic acid can inhibit the growth of Ag NPs and also boost the formation of Ag nuclei during electrodeposition. This has been demonstrated by Nagasuna et al. [12].

Fig. 3 shows the results of the XPS analysis of TNAs sensitized with Ag_2S NPs that were synthesized by the in situ sulfurization of metallic Ag NPs loaded on TNAs. The reaction occurring during synthesis can be described concisely by the following reaction.

$$2Ag^0 + S_x \rightarrow Ag_2S + S_{x-1} \quad (x \leqslant 8). \tag{1}$$

The XPS profile (Fig. 3a) of the TNAs decorated with Ag_2S NPs indicated the peaks corresponding to Ti, O, Ag, and S. As shown in Fig. 3b, the peaks at 368.5 and 374.5 eV could be assigned to