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Fabrication of a composite electrode: CdS decorated Sb–SnO_2/TiO_2-NTs for efficient photoelectrochemical reactivity

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ABSTRACT

A CdS modified Sb–SnO_2/TiO_2-NTs hybrid electrode (CdS/Sb–SnO_2/TiO_2-NTs) with tailored architecture is studied for its photoelectrochemical applications. The visible light driven heterojunction photoelectrode was fabricated by anodic oxidation of titanium foil to obtain TiO_2 nanotube arrays firstly, and then solvothermally deposited with antimony doped tin oxide (Sb–SnO_2) thin coating onto the TiO_2 nanotube walls, followed by the successive ionic layer adsorption and reaction (SILAR) process to deposit certain amount of CdS nanoparticles. The obtained heterostructure was characterized by FE-SEM, EDS, XRD, XPS and UV–Vis techniques. The photoelectrochemical performance of this hybrid electrode demonstrated that the photocurrent under UV–Vis light illumination was remarkedly enhanced up to 17.48 mA/cm^2 under 1.0 V vs. Ag/AgCl. The enhanced photocurrent can be partially attributed to the narrow bandgap CdS nanoparticles, which allows for more visible light harvesting. On the other hand, the effect of Sb doping content on the photo-electrochemical activities of the composites was crucial. Thus a detailed investigation was carried out and the results showed that the nominal value of 2%(molar ratio) antimony loading exhibited the best photo-electrochemical performance. It is expected that the novel CdS/Sb–SnO_2/TiO_2 nanotube array hybrid system could serve as promising photoanode for effective hydrogen evolution from water splitting to meet the urgent problems of energy demand.

1. Introduction

Facing the urgent issue of energy requirement and environmental purification in modern world, one-dimensional (1-D) nanomaterials such as highly ordered nanowires or nanotubes have aroused a huge interest in recent years due to its unique properties compared to their bulk counterparts. Among many excellent properties of 1-D nanomaterials, the transport characteristics of electrons and holes in semiconducting materials, as well as the specific surface area are both critical factors influencing the performance of materials in many aspects, especially the application of photocatalysis [1]. In contrast with the slow electron transfer typically occurring in randomly packed nanoparticle film systems, the precisely oriented nanotubular structure provides excellent electron percolation pathways for vectorial charge transfer between interfaces [2]. Additionally, nanotubes with both inner surface and outer surface allow more light harvesting and active sites accessible to reactants in the aqueous environment.

Titanium dioxide (TiO_2), due to its high photochemical stability, abundance, low cost and nontoxicity, is highly functional in many fields such as photocatalysis [3,4], water-splitting [5], sensors [6] and dye-sensitized cells [7]. Therefore, combining the one-dimensional architecture with TiO_2 seems appealing in many aspects. Regarding the synthesis of TiO_2 nanotubes, there are a variety of methods including deposition into a nanoporous alumina template [8], sol–gel [9,10], hydrothermal processes [11,12] and microwave irradiation [13]. However, among the various nanotube fabrication routes, the electrochemical anodization approach seems attracting the most interest because of its easy and precise control on the dimensions of TiO_2 nanotubes. Grimes and co-workers [14] initially fabricated the TiO_2 nanotube arrays with controllable dimensions using the electrochemical anodization method in 2001. Since then on, significant attempts have been made to investigate the mechanism of TiO_2 nanotube formation and to further improve the length-to-width aspect ratio that would demonstrate superior performance in practical applications [15–18].

Despite the advantages of TiO_2 with 1-D architecture, there still are some shortcomings that limit the practical photocatalytic application of TiO_2 in large scale. As we know, TiO_2 can only utilize ultraviolet rays with wavelength shorter than 379 nm due to its large band gap of 3.2 eV [19]. Nevertheless, UV light merely accounts for 5% in solar spectrum. Thus, how to modify the electronic band structure of TiO_2 to make further use of visible light ($\lambda > 420$ nm) which accounts for 43% in solar energy, is quite an important aspect [20]. Large quantities of work has focused on the

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red-shifting of TiO_2 nanotube arrays by doping with N [18,19], C [21], dye sensitizing [22], or decorating CdS quantum dots or other narrow bandgap semiconductors such as CdSe and PbS onto the surfaces of TiO_2 nanochannels [22–26].

When used as photoelectrode, another barrier that limits the use of TiO_2 in photocatalysis is the poor charge transfer properties. Due to the poor conductivity of TiO_2 semiconductor, the electrons have difficulties in migrating in the tubular structure to the collecting electrode surface where chemical reactions usually take place. If the material with high electrical conductivity is filled into the interior of TiO_2-NTs, photogenerated carriers will be exported promptly and effectively. Therefore, enhancement of charge transport performance on TiO_2 surface is highly desirable.

As we know, antimony doped tin oxide (denoted as Sb–SnO_2) with suitable Sb doping level has favorable electrical conductivity [27], and it has been implanted into the TiO_2 nanotubes to increase the electrochemical performance on pollutant degradation by Guohua Zhao and other groups [28–30]. However, the photosensitive activity of Sb–SnO_2/TiO_2 nanotubes is comparatively poor because of the transparent property and the large band gap of SnO_2 (3.7 eV), which leads to a poor utilization of visible light. To the best of our knowledge, there is no relevant report that combines visible light responsive semiconductors such as CdS with electrochemically active Sb–SnO_2/TiO_2 nanotube arrays as photoanode materials to realize photoelectrocatalytic application.

As a result, given the importance of effective electron transfer as well as the efficient sunlight utilization, we proposed a hybrid nanostructure material as shown in Scheme 1. In this nanostructure, CdS is supposed to serve as sensitizer to absorb solar energy to generate photo-electrons and holes; Sb–SnO_2 could act as the conducting line to transfer photo-generated electrons injected from the conduction band of CdS promptly, avoiding the fast recombination of charge carriers; titanium dioxide nanotube arrays would functionalize as a template to provide highly ordered nanochannels for charge carriers' transport, and also guarantee the intimate contact between CdS and Sb–SnO_2 to facilitate efficient charge transfer based on its confinement effect.

Herein, we report the fabrication of such composite photoelectrode to investigate its photoelectrochemical water-splitting performance. The effect of one critical parameter, the concentration of antimony doped in tin dioxide, on the current properties was investigated in detail. The results obtained demonstrate that with proper Sb doping level the CdS/Sb–SnO_2/TiO_2-NTs hybrid structure could exhibit significant enhancement in photocurrent density compared with the previous CdS/TiO_2 NTs nanostructure, which means better photoelectrochemical performance than before can be realized. We assume the novel fabricated functional material would be quite promising in application of electric field assisted photocatalytic hydrogen evolution from water as alternative energy resource.

2. Experimental

2.1. Preparation of TiO_2 nanotube arrays

The titanium foil (>99.6% purity, BaoTi Co. Ltd, China) with a thickness of 0.5 mm was firstly cut into small pieces with a dimension of 2 × 3 cm, and then mechanically polished with different abrasive papers, followed by immersing into the aqua regia for 24 h to remove organic compounds from the surface. Prior to the electrochemical anodization, the Ti foils were cleaned in absolute ethanol under ultrasonic bath (KQ2200DB, 80 W, 40 KHz, Kunshan Ultra Co. Ltd, Jiangsu, China) and deionized water (D.I.), then dried in air atmosphere.

The electrochemical potentiostatic anodization performed in a two-electrode system, in which the Ti foil served as anode and Pt as cathode, with a distance of 2 cm approximately. The electrolyte consisted of EG (ethylene glycol) containing 0.3 wt% NH_4F (99.5%) and 2 vol% H_2O according to the literature [2]. A constant voltage of 60 V was applied to the electrochemical system (provided by a DC power supply) with magnetic stirring for one hour at room temperature (25 °C). After the process, the anodized Ti sample was rinsed thoroughly with deionized water and then subjected to ultrasonication (80 W, 40 KHz) [31] to remove the precipitates. The as-prepared TiO_2 nanotube arrays were amorphous, thus an annealing step conducted in air at 500 °C for 120 min was required to induce crystallization, with both heating and cooling rates of 1 °C/min.

2.2. Deposition of TiO_2 NTs with Sb–SnO_2

The fabrication of Sb–SnO_2/TiO_2 nanotubes were prepared by the solvothermal synthesis approach. In this step, it should be noted that the precursor solution of $SnCl_4{\cdot}5H_2O$ and $SbCl_3$ has to be freshly prepared because of its poor stability. In a typical synthesis process, 0.05 M $SnCl_4{\cdot}5H_2O$ and a certain amount of $SbCl_3$ in ethanol was sealed in a Teflon lined autoclave with the as-prepared TiO_2 NTs sample placed inside, and then ultrasonicated for 30 min, finally heated to 160 °C maintaining for 6 h. After the solvothermal process, the samples were annealed in air at 500 °C for 1 h, with a heating rate of 5 °C/min.

2.3. Sensitization of Sb–SnO_2/TiO_2 NTs with CdS

The fabrication of CdS/Sb–SnO_2/TiO_2 nanotube arrays was conducted based on the previously reported SILAR method [23,26]. Typically, the Sb–SnO_2/TiO_2 NTs sample was sequentially dipped in four different beakers for 1 min separately, accompanied by magnetic stirring to ensure the uniform deposition. The first contained 0.05 M Cd $(Ac)_2$ solution, the next contained 0.05 M Na_2S solution, and the rest two contained D.I. water to rinse the excess ions adsorbed on the sample. Such procedure was repeated for 5 times to deposit desired amount of CdS on the Sb–SnO_2 coatings. In the end, the prepared samples were thoroughly cleaned with D.I. water and then dried out in an air oven at 60 °C overnight.

2.4. Characterization

The surface morphology and elemental composition of prepared samples were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) equipped with an EDS (energy-dispersive X-ray spectroscopy) detector. The crystal structure of prepared samples were identified by an X'pert PRO MRD diffractometer using Cu-K_α source ($\lambda = 0.15416$ nm), with a scanning angle (2θ) range of 10–80°. The light absorption property was recorded using a Hitachi U-4100 spectrophotometer with a wavelength range of 300–800 nm. Chemical states of Sb in the CdS/Sb–SnO_2/TiO_2-NTs heterostructure were identified by X-ray photoelectron spectroscopy (XPS) on a Ultra DLD Electron Spectrometer (Al Kα radiation; $h\nu = 1486.71$ eV). XPS data were calibrated using the binding energy of C1 s (284.6 eV) as the standard.

2.5. Cyclic voltammetry test

The electrochemical performance of as prepared electrodes was measured by the cyclic voltammetry test conducted in a three-electrode system, with Pt foil as counter electrode and a saturated Ag/AgCl as reference electrode. The 0.1 M Na_2SO_4 solution was used as the supporting electrolyte. The scanning voltage range