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High performance NiS-nanoparticles sensitized TiO₂ nanotube arrays for water reduction

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ABSTRACT

Nickel sulfide nanoparticles (NPs) have been grown on highly ordered vertically aligned TiO₂ nanotube arrays (TNAs) by the successive ionic layer adsorption and reaction (SILAR) method at room temperature. Using Fe-SEM, EDX, XPS, XRD and UV–Vis diffuse reflectance spectroscopy, the effect of synthesis conditions and post treatment procedure on the physico/chemical characteristics of the NiS NPs-sensitized TNAs was investigated. The photo-electrochemical properties of the different photoanodes were investigated for the water reduction reaction using aqueous solutions of Na₂S/Na₂SO₃ as sacrificial electrolyte under the whole spectrum of simulated solar light irradiation. The highest photocurrent was obtained as 7.68 mA/cm², for the optimized SILAR number of loading cycles equal to 4. The photo-activity was more than 10 times larger than the corresponding one achieved for pure TNAs. A high incident photon to current efficiency (IPCE) of about 45% was obtained. SILAR cycle numbers higher than 4, resulted in the unwanted increase of the size of NiS nanoparticles eventually transforming them in the form of electro-hole recombination centers. A mechanism based on density functional theory (DFT) calculations of the hexagonal bulk NiS electronic configuration is proposed to explain the observed enhanced photocatalytic activity for the optimum sample. The excellent performance of NiS NPs-sensitized TNAs cells allows the composite photo-electrode to have many potential applications as a photoanode material for photo-electrochemical applications such as H₂ production, nanoparticle sensitized solar cells and UV photodetector.

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Introduction

Solar energy is one of the most promising energy sources for the future. Moreover, it is sustainable and far more abundant. Recently, much attention has been given to photo-electrocatalytic water splitting technology as it has a great potential for low-cost and environmentally friendly solar-hydrogen production to support the future hydrogen

economy as a clean and green fuel [1]. The chemical process for hydrogen production via electrolysis of water under sunlight irradiation, namely the water splitting reaction, needs a suitable photocatalyst. Over the past years, an ever increasing number of investigations have focused on the development of photo-electrochemical (PEC) devices composed of photo-electrodes for oxidation/reduction of water under sunlight irradiation as well as finding an appropriate aqueous

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electrolyte containing a redox couple [2–5]. The most studied active photoelectrodes for hydrogen production comprehends metal oxide semiconductors, including TiO_2 [2,6–8], ZnO [9,10] and WO_3 [11,12]. Among the numerous types of semiconductor photocatalysts and all the TiO_2 nanostructured materials studied in the recent decades, TiO_2 nanotube arrays (TNAs) prepared by electrochemical anodization of titanium have attracted great attention due to their special features, such as outstanding photo-electrochemical stability in most aqueous solutions, low cost, fast electron transfer mechanism, chemical inertness and non-toxicity [13–18]. TiO_2 has a minimum conduction band higher than the $\text{H}_2/\text{H}_2\text{O}$ level and a maximum valence band lower than the $\text{H}_2\text{O}/\text{O}_2$ level. However, the PEC performance of this metal oxide semiconductor as a single material in solar hydrogen production is poor due to its wide band gap energy (3–3.2 eV) which usually restricts the light absorption just in the ultraviolet region ($\lambda < 385$ nm) and the fast recombination rate photogenerated electron–hole pairs among TiO_2 nanoparticles because of the short diffusion paths of charge carriers [2,7,19]. Therefore, it is necessary to design an efficient TiO_2 -based PEC water splitting system for photo-electrochemical hydrogen generation which can simultaneously combine the advantages of large light utilization (both UV and visible regions), slow recombination rate of excitations by cascade electron transport, fast carrier transport, well matched energy levels with H^+/H_2 and large surface area [7,9,13]. In this regard, a series of techniques have been used to increase the light harvesting in visible range, such as doping with different metal ions (cationic doping) like Ni [20] and Fe [21], nonmetal ion (anionic doping) like N [22] and S [23] to induce a red shift to the band gap and also coupling with narrow band gap semiconductors including CdS [24], CdSe [2,25], CdTe [26], PbS [8] and Ag_2S [27]. Actually, by coupling of a narrow bandgap semiconductor with a wide bandgap TiO_2 semiconductor facilitates combining large light utilization via light harvesting, interfacial charge transfer mechanism via multiple excitations by single photon absorption, fast carrier transport and well matched energy levels simultaneously. This leads to maximal power conversion efficiency of NP-based PEC cells and an increase in the photo-electrochemical efficiency for visible-light-driven hydrogen generation [2,7,9,28,29]. Among the low-band-gap semiconductors, nickel sulfide (NiS) is an attractive and promising semiconductor material responding in the whole solar energy spectra, due to its small direct band gap energy of about 0.9 eV [30]. NiS has been investigated for application in the areas of solar selective coatings, solar cells, photoconductors, sensors, IR detectors, and as electrode in photo-electrochemical storage device [31]. Liang et al. investigated the photo-electrochemical performance of coupled NiS/ ZnIn_2S_4 system for hydrogen evolution under visible light irradiation [4]. They have found that the directional migration of the photo-excited electrons from ZnIn_2S_4 to NiS (cascadal mechanism) can significantly enhance the H_2 production rate. Wei et al. also studied the effect of NiS loading on nanostructured CdS for H_2 evolution from lactic acid sacrificial solution under visible light [32]. Furthermore, some other reports claimed improvement in photo-electrochemical performance of nanoparticle-

sensitized solar cell using a highly efficient nickel sulfide based thin film counter electrode [33,34]. However, to our knowledge, there were very few reports on the synthesis, characterization and photo-electrochemical properties of NiS NPs-sensitized TNAs. In this work, NiS nanoparticles were deposited onto the TiO_2 nanotube arrays by using a successive ionic layer adsorption and reaction (SILAR) process. The SILAR method has emerged as one of the most common, simplest, and convenient methods to deposit a variety of compound materials in thin film form for fabricating PEC for large-scale production [35]. Using SEM, EDX, XPS, XRD and UV–Vis diffuse reflectance spectroscopy, the effect of synthesis conditions and post treatment procedure on the physico/chemical characteristics of the coupled NiS/TNAs system has been investigated. The photo-electrochemical properties of the NiS NPs-sensitized TNAs (narrow/wide-bandgap semiconductor) system have been extensively studied under whole spectrum of light irradiation. Furthermore, a mechanism is proposed to explain the photocatalytic hydrogen evolution from aqueous solutions of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ under light irradiation.

Experimental details

Preparation of pristine TiO_2 nanotube arrays (TNAs)

The 0.8 mm thick titanium foils (99.6% purity), and all chemical materials were purchased from Alfa-Aesar (Ward Hill, MA, USA) and Sigma–Aldrich. Briefly, prior to anodization, the titanium foils were cleaned and degreased by sonicating for 30 min in ultra pure water, acetone and finally ethanol, followed by rinsing with distilled water, and then drying under a flowing air stream. Afterwards they were chemically etched by immersing in a mixture of 3.2 M HF and 5.4 M HNO_3 for 40 s, and immediately rinsed with deionized water, dried under an air stream and used immediately. Anodic growth experiments were performed by potentiostatic anodization in a conventional two-electrode compartment electrochemical cell. After pre-treatment, the polished Ti disk (2 cm in diameter) was used as a working electrode (anode) and a Ti rectangular foil with a size of 20×45 mm² served as a counter electrode (cathode).

The Ti disk with an active anode area 3 cm² was kept between a set of O-rings in the sample holder and a copper wire was connected to both anode and cathode as the electrical contact. The anodization was performed in an ethylene glycol based electrolyte consisting of NH_4F (0.4 wt %) and H_2O (1.8 wt %), and placed in a Teflon vessel for 2 h at 40 V and at room temperature using a DC power supply (Keithley 2602) with a ramp rate of 660 mV/s. Using such a high ramp results in the production of a highly defect-less initial TiO_2 surface for further electrochemical etching at 40 V constant voltage and obtaining of proper TiO_2 nanotubes. Such a treatment resembles somehow electro-polishing in anodization processes.

After anodization, the obtained nanotube electrodes were rinsed immediately with ultra pure water for a couple of minutes to avoid dissolution of the TNAs, and then dried in an air stream. The prepared samples were annealed at 100 °C for

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