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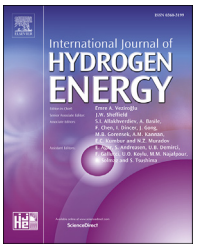

Photoelectrochemical hydrogen generation on TiO_2 nanotube arrays sensitized with $CdS@Sb_2S_3$ core shell particles

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ABSTRACT

In this work, we propose the sensitization of TiO_2 nanotube arrays with CdS and Sb_2S_3 (TNTs-$CdS@Sb_2S_3$), in order to improve the visible light absorbance, and the photoelectrochemical performance as photoanodes in photoelectrochemical cells for hydrogen production. It is the first time that these materials have been synthesized by an electrochemical/thermal/chemical method. TNTs-$CdS@Sb_2S_3$ were characterized by X-Ray Diffraction, UV–Vis diffuse reflectance spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy. The diffuse reflectance spectrum obtained for TNTs-$CdS@Sb_2S_3$ confirms a total coverage of the firstly electrodeposited Cd particles by Sb forming a core@shell type structure. The photoelectrochemical behavior of the TNTs-$CdS@Sb_2S_3$ photoelectrodes and their hydrogen production capacity, were evaluated in a homemade H-type photoelectrochemical cell using a sulfide-free electrolyte. By performing gas chromatography experiments, it was determined a higher hydrogen production using the TNTs-$CdS@Sb_2S_3$ photoelectrode (10.23 μmol h^{-1}), being 1.5 and 4.5 times higher than that reached for the TNTs-CdS and TNTs-Sb_2S_3 photoelectrodes, respectively. Additionally, the chalcogenide core@shell structure shows better photostability and photocurrent response than that of each of the components separately.

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Introduction

The implementation of a Hydrogen Economy in which hydrogen can be used as an energetic vector is one of the dearest dreams of the scientific community [1,2]; however, in order to make the dream come true, various technological developments should be realized. Among them, one of the most important is the implementation of a method capable to produce high purity hydrogen from abundant resources at rates of technological interest. Photoelectrochemical hydrogen production is currently being considered as a potential clean and renewable route for energy generation [3,4], for this, is of fundamental importance the development of materials capable to adsorb most of the solar spectra while avoiding the recombination process of charge carriers. TiO_2 nanotube arrays (TNTs) are interesting photoanodes with potential use in photoelectrochemical cells for hydrogen production. Due to the TNT 1D geometry, the recombination processes is diminished while the electron transport is accelerated towards the counter electrode, where the electrons are subsequently scavenged by hydrogen ions on the Pt cathode forming hydrogen bubbles [5]. Moreover, the low fabrication cost, chemical stability, high specific surface area, photosensitivity, and catalytic potential, make TNTs valuable materials as photocatalytic and photoelectrocatalytic supports [5]. However, the optical absorption range of TiO_2 (<387 nm) limits its practical use [6]. Sensitization with narrower band gap semiconductors such as CdS [6,7] and Sb_2S_3 [8,9] has been attempted to improve the TNTs photoresponse in the visible region, transforming them into suitable materials for applications in photoelectrochemical hydrogen production employing solar energy [10]. CdS shows a band gap close to 2.4 eV [11], then, it is only capable to absorb the wavelengths of the visible spectrum shorter than 510 nm. On the other hand, although the band gap of Sb_2S_3 is close to the maximum of the solar spectrum on the Earth surface [12], its low band gap (1.7 eV) may cause an increase in the recombination of the photogenerated charge carriers. Thus, a core@shell structure composed of CdS in the core and Sb_2S_3 in the shell might improve the photoelectrochemical performance. This improvement can be due to the higher light absorbance promoted by Sb_2S_3 combined with the lower recombination process caused by CdS acting as a buffer layer which probably modifies the surface states and diminishes the recombination in Sb_2S_3 [13]. Moreover, it has been reported that core@shell structures have a high stability and activity in solar energy conversion applications [14–16]. Therefore, in this work we propose the fabrication of TNTs-CdS@Sb_2S_3 photoelectrodes. This material is obtained for the first time using an electrochemical/thermal/chemical method, previously reported in our group [17,18]. This method basically consists of three steps: 1) electrodeposition of precursor particles on the substrate, 2) thermal oxidation and 3) sulfurization in $H_2S_{(g)}$. To obtain the core@shell composite through this hybrid strategy, the first step was replaced by two consecutive electrodeposition steps, being the core precursor particles deposited on the TiO_2 support, whereas the shell precursor particles are preferentially deposited onto the firstly deposited particles. Therefore, this route assures better support-core and core-shell interfacial contact (and consequently lower ohmic drop); moreover, depending on the electrodeposition parameters, it is possible the control of the size, distribution and amount of the composite particles [18–20]. Also, the combination of electrodeposition with thermal treatments improves the crystallinity of the synthesized chalcogenide [18].

In order to elucidate if the core@shell structure can be obtained employing the electrochemical/thermal/chemical method, an extensive characterization analysis is performed. Furthermore, the photoelectrochemical response, hydrogen production capacity and photo-stability is evaluated, at an applied bias potential of 0.5 V vs Ag/AgCl (3 M KCl) using a sulfide-free electrolyte and TNTs-CdS@Sb_2S_3 photoelectrodes. For sake of comparison, the TNTs-Sb_2S_3 and TNTs-CdS systems are analyzed as well.

Experimental section

TiO_2 nanotubes synthesis

TNTs were obtained by potentiostatic anodization of titanium foils (Alfa Aesar, 0.25 mm thickness, 99.5% purity), following a procedure previously used by our group [18]. Ti foils were mechanically polished and degreased by sonication in acetone for 10 min before anodization. Anodic oxidation was carried out during 4 h at 55 V in a two-electrode cell set up using a Pt wire (Alfa Aesar, 99.99%) as counter electrode. An ethylene glycol solution containing 0.1 M NH_4F (Alfa Aesar, 96%) and 10% H_2O was used as the electrolyte, and kept under magnetic stirring during the anodic oxidation. After anodic oxidation, the as-prepared samples were rinsed with water and ethanol and heat treated in air at 450 °C for 0.5 h (heating rate, 10 °C min^{-1}) [21]. The TNTs prepared and annealed through this process present an average diameter of 100 nm and 5 μm length [18]. The annealed samples were sonicated in water for 10 min previous to the electrodeposition of the Cd and Sb precursors.

Pulsed electrodeposition on TNTs of cadmium and/or antimony precursor particles

The pulsed electrodeposition of Cd and/or Sb on TNTs, was carried out using an AUTOLAB (model PGSTAT302N) potentiostat/galvanostat, in a conventional three-electrode cell with TNTs as working electrode, a Saturated Calomel Electrode (SCE) and a platinum plate as reference and counter electrode, respectively. A high cathodic potential of −3 V vs SCE (E_{on}) was imposed for 0.005 s (t_{on}), before opening the external circuit cell (E_{off} = OCP) for 1 s (t_{off}) [18]. In order to elucidate more clearly the behavior and properties of the synthesized chalcogenides, an excess of precursor particles was electrodeposited using the number of electrodeposition cycles as indicated below.

TNTs-Cd and TNTs-Sb preparation

Cadmium was electrodeposited using an electrolyte with pH = 2, containing 0.002 M $CdSO_4$ and 0.1 M Na_2SO_4 in a water:ethanol solution (70:30, %v) [18], for 8000 cycles.

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