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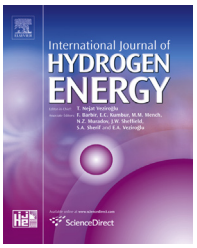

Impact of In_2S_3 shells thickness on the electrochemical and optical properties of oriented ZnO/In_2S_3 core/shell nanowires

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ABSTRACT

In this paper, we address the effect of shell thickness and core/shell structure on the electrochemical and photoelectrochemical cell (PEC) measurements properties of ZnO/In_2S_3 core/shell nanowires (NWs). The objective is to elucidate the mechanisms responsible for the extended photoresponse of ZnO/In_2S_3 core/shell NWs to solar radiation. Well aligned ZnO/In_2S_3 core/shell NWs were fabricated on indium tin oxide substrates using electrochemically grown ZnO NWs as the cores and electrodeposited In_2S_3 as the shells. The samples structure was characterized by X-ray diffraction, revealing the mixed wurtzite and tetragonal structures of both ZnO cores and In_2S_3 shells, and the improvement in the structure with the increases of In_2S_3 shell thickness. The optical properties were studied through optical absorbance and photoluminescence measurements, showing the optical properties featured with type-II heterogeneous nanostructures constructed from ZnO and In_2S_3. Electrochemical impedance spectroscopy (EIS) is employed and an equivalent circuit model is designed suggesting that the cell performances were affected by increasing In_2S_3 shell deposition times. From Mott–Schottky plots, several parameters such as flat-band potential and free carrier concentration were determined. Next, from (PEC) measurements, the highest photocurrent density produced by the In_2S_3 shell electrode prepared at deposition time of 5 min reached 9.30 mA cm^2 at an applied potential of 0.8 V vs. Ag/AgCl. This value was about 6.8 times as much as more than that measured on ZnO NWs one and provided the highest value of solar-to-hydrogen energy efficiency η (%). These results are very encouraging and suggest that In_2S_3 covered ZnO NWs nanostructures are valuable photo-anodes in order to build cheap devices for solar energy-to-hydrogen generation devices.

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Introduction

Recently, photoelectrochemical cell (PEC) water splitting has been extensively studied as a promising candidate for hydrogen energy production and renewable energy [1–4]. In fact, many investigations have demonstrated the feasibility of semiconductor metal oxides application in photoelectrochemical cells, including photocatalysis, solar water splitting cells and dye sensitized solar cells due to their high activity, environment-friendly feature and low cost [5–8]. Among the various oxide 1D nanostructured materials, zinc oxide nanowires (ZnO NWs) [9] have also attracted much attention due to their cheap fabrication, high specific surface area and wide applications in PEC water splitting [10–15]. However, the disadvantage of ZnO is that it large band gap ($E_g = 3.37$ eV). Consequently, only a small portion of the solar spectrum is absorbed since the UV spectrum represents only ca. 5% of sunlight. This greatly hinders the use of ZnO materials for solar energy harvesting [16]. To overcome this difficulty, many efforts have been devoted to create an heterojunction between ZnO NWs and another semiconductor which has spread visible light range. In the cases where the two materials recombine firmly, the absorption edge shifts towards the visible light region. As a result, it may be an interesting approach to improve the visible light driven PEC performances [16,17]. We have identified In_2S_3 as valuable candidate for visible decorated material combined to ZnO since it offers good stability and high carrier mobility [6,18,19]. In addition, the indium sulfide is a convention n-type binary chalcogenide semiconductor which appears highly desirable for use in solar energy conversion. Actually, the low band gap value ($E_g = 2.1$ eV) favors the utilization of a significant portion of the visible the solar spectrum. Despite these advantages, the core/shell structure involving ZnO/In_2S_3 nanowires does not widely studied.

Recently, in our previous work [6], we have developed novel core/shell ZnO/In_2S_3 nanowires by a simple route using two steps electrodeposition process. The typical type II band alignment and uniform In_2S_3 distribution deduced from optical measurements and morphological study contributed to the effective separation of the photogenerated electron–hole pairs and transportation of the electrons to the electrode surface. These effects lead to a significant enhancement of the photoelectrochemical performance. In addition, an excellent stability of the core/shell nanowires was also demonstrated. We have also shown in our other studies [20,21], that the deposition time or thicknesses of thin film have an influence on the physical and particularly electrical properties of a semiconductor.

On the basis of our recent study [6], in the present paper we will address the impact of the deposition time, which is closely related to the In_2S_3 shell thickness, on the photoelectrochemical properties as well as the electrochemical behavior taking place at the ZnO/In_2S_3 electrode – Na_2SO_4 electrolyte solution interface. A special attention will be put on the electrochemical impedance spectroscopy analysis.

Experimental sections

Sample preparation

All chemicals used in this study were of analytical reagent grade and were used as received without further purification. All aqueous solutions were prepared using deionized water.

Synthesis of the ZnO nanowires

The electrodeposition procedure was performed on a glass sheets coated with Sn-doped polycrystalline In_2O_3 (ITO, resistance of 10 Ω/sq). Prior to the electrodeposition, the ITO/glass substrates were cleaned sequentially with an acetone solution and isopropanol (for 15 min each) in an ultrasonic bath, and then thoroughly rinsed with abundant water. The sheets were immersed in an aqueous solution of $ZnCl_2$ (5.0×10^{-4} M) and KCl (1.0×10^{-1} M), under continuous bubbling of oxygen inside a classical three-electrode electrochemical cell with optimized potentiostatic conditions, as described recently by our group [22]. The electrodeposition of ZnO nanowires was performed at a fixed potential of −1 V versus Ag/AgCl, while the reaction temperature was kept at 80 °C [23].

Synthesis of the ZnO@In_2S_3 core/shell structure

ZnO/In_2S_3 core/shell nanowires arrays were prepared via an electrodeposition process. The previously deposited ZnO nanowires arrays were employed as working electrode. The plating was conducted in an aqueous solution containing 1 mM $InCl_3$ and 2 mM $Na_2S_2O_3$, as indium and sulfur sources, 0.1 M KCl supporting electrolyte and 2 mM Na_2 EDTA chelating agent. More details were given in our recent work [6]. The electrodeposition of In_2S_3 was carried out at a fixed potential of −1.2 V at room temperature. To modulate the shell thickness, the deposition time was varied between 1 min and 10 min. Finally, the as-synthesized samples were rinsed with distilled water and dried in air at room temperature. The produced samples will be called sample B, C, D and E respectively, in the further section, while bare ZnO/ITO one will be called sample A.

Samples characterization

The crystal phase of the obtained samples was identified by X-ray diffraction technique (XRD). The apparatus was an analytical Empyrean equipped with a multichannel detector (Pixel3D) using CuKα radiation in the 20–70° 2θ range, with a scan step of 0.026° for 297s. The morphology of the prepared samples was investigated by scanning electron microscopy (SEM) equipped with a Silicon Drift Diode (SDD) detector and operating at 10 kV. The elemental composition was obtained using an energy-dispersive X-ray spectrometer (EDX). The UV–visible absorption spectra of all samples were recorded using Perkin-Elmer-Lambda 1050 spectrophotometer equipped with a PTFE coated integration sphere within the range of 300–1500 nm. Finally, photoluminescence spectra (PL) were performed by exciting with the frequency of a pulsed Ar^+ laser at an excitation wavelength of 340 nm.

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