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Chalcogenide photosensitized titania nanotube arrays

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ABSTRACT

The spatially ordered and vertically oriented TiO_2 nanotube (TNT) arrays were prepared by a two-step anodization process. The TNT arrays (TNAs) were annealed at 450 °C for 30 min, yielding discrete, hollow nanotube structures with anatase phase. $CuInS_2$ (CIS) and In_2S_3 (InS) chalcogenide nanoparticles were deposited on the top surface, walls, and bottom of the TNAs by repeated drop-casting in ambient atmosphere. Suitable photosensitizer coverage was achieved with CIS5 and InS3CIS5, when exposed to visible light, efficiently generated photoelectrons that traveled uniformly into TNAs. The TNA/CIS10 nanostructures were oversaturated with CIS nanoparticles, resulting in more defects and an overly thick absorption layer promoting premature electron–hole pair recombination. Electrochemical impedance spectroscopy (EIS) analysis indicated that the mass transfer in polysulfide electrolyte occurred sufficiently quickly for the Nernst diffusion impedance (Z_d) to be neglected. The equivalent circuit of the TNA nanostructures in polysulfide electrolyte exposed to light was modeled by two serial RQ circuits. The impedance in lower frequency regions contributed to the mechanism of the interface charge transfer when exposed to light. When a positive bias was applied, the photosensitized electrons could travel from the CIS photoabsorption layer through the TNAs, and into Ti electrode more efficiently. The relaxation behavior of open circuit potential exhibited by the TNA/InS3CIS5 nanostructures showing that the enhanced lifetime of photo-induced electrons was a function of the InS3 buffer layer. The novelty of facile drop-casting chalcogenide photosensitive composition containing an excess of sulfur avoided the use of toxic H_2S gas and other toxic solvents. The charge transfer mechanisms were established on the basis of the behaviors of suitable photosensitive layers and function of buffer layer.

1. Introduction

Polycrystalline titania nanotube arrays (TNAs) have many interesting properties including a large specific surface area, enhanced light scattering abilities, self-aligned, spatially ordered dispersion, a vertically oriented shape, and fewer interfacial grain boundaries [1]. TNAs facilitate the transport of charge carriers with a greater efficiency than porously sintered TiO_2 nanoparticles and can minimize the loss of charge carriers at grain boundaries in one dimension [2]. Such one-dimensional TNAs are promising for photoelectrode and photoanode applications [3,4]. However, the large band gap of anatase phase TiO_2 (3.2 eV) and the relatively high recombination rate of photo-induced charge carriers in TNAs limit their suitability to the visible light region. The proposed strategies are “decorating” or “sensitizing” TNAs with narrow band gap nanoparticles such as $CuInS_2$, CdS, $BiFeO_3$, $ZnFe_2O_4$, thereby expanding the optical absorption spectrum of TNAs into the visible and infrared regions and increasing their solar energy harvesting ability [5–8]. Therefore, the main benefits of sensitization are increasing visible light absorption and reducing electron–hole recombination for TNAs.

$CuInS_2$ (CIS) has an optimal band gap for solar energy conversion ($E_g = 1.53$ eV), a large absorption coefficient (6×10^5 cm^{-1}), and good stability against solar radiation. It is also low cost and low toxicity compared with the selenium containing compounds currently in use [9–11]. The electronic properties of CIS can be further modified through the introduction of internal defects and non-stoichiometric ratios of the components. Copper-rich films

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exhibit larger grain sizes, good crystallinity, and high conductivity; however, they have a lower photosensitivity and are prone to non-uniform film surface composition [12]. Indium-rich films have low conductivity and crystallinity but show good photosensitivity as a light-absorbing layer. In general, films with equal amounts of copper and indium as well as an excess of sulfur show acceptable levels of photosensitivity, crystallinity, and conductivity [13,14]. It has been reported that one-dimensional titanias decorated by narrow band gap CIS can efficiently collect charges from the excited CIS, reducing the charge collection distance for the TiO_2 nanostructured electrodes [5,15,16].

Due to the photosensitization of CIS materials, the photo-excited electrons in CIS will transfer to CIS-decorated TiO_2 in order to achieve an effective separation of the electron–hole pairs [17]. CIS can be deposited into TiO_2 nanostructures by several approaches including chemical bath deposition of pre-synthesized colloids [17–20], successive ionic layer absorption and reaction (SILAR) [5,21,22], electrophoresis deposition [23], and extremely thin absorption layer [24] processes.

The presence of a buffer layer in solar, photoelectrochemical, and photosensitive cells may improve the electronic contact between the photon absorption layer and the semiconductor electrode. The buffer layer may also suppress the back flow of electrons, which could disrupt the photocurrent [25]. The n-type semiconductor indium sulfide (In_2S_3) has a band gap of 2.0–2.3 eV and either a cubic or tetragonal crystal structure. It has been reported that In_2S_3 may substitute highly toxic cadmium sulfide (CdS) in the buffer layer of chalcogenide-type solar cells [26,27]. For these reasons, In_2S_3 was selected as the buffer layer for CIS-photosensitized TNAs in this work.

During the low-pressure annealing step of chalcogenide film fabrication, the phase of CIS layer was weakened by the sublimation of In_xS if Cu_yS was deposited prior to In_xS [28]. Cu was found to diffuse from $CuInS_2$ [29] and CuSCN into In_2S_3 (InS) when the annealing temperature reached 200 °C [30]. This may be due to Cu-interdiffusion at the absorber/buffer interface. However, it has been reported that annealing above 300 °C may damage solar cells with an InS buffer layer due to the formation of a $CuIn_5S_8$ phase [31].

To prepare photosensitive solar cells in a cost-effective and scalable way, it is essential to develop a solution-based coating method. However, depositing chalcogenide quantum dots (QDs) or nanoparticles on TNAs via solution synthesis or molecular precursor decomposition is difficult because of the small aperture of the TNAs. This results in QDs and nanoparticles depositing primarily on the top surface of the TNAs rather than penetrating through the nanochannels of the structures [32,33]. In this work, the chalcogenides of CIS and InS solutions were drop-cast onto TNAs, producing TNA/CISy and TNA/InSxCISy photosensitive nanostructures. By utilizing the pre-formulated precursors containing excess of sulfur, the drop-casting method avoided the use of toxic H_2S gas and other toxic solvents. The microstructure, crystallinity, photosensitivity, impedance, and charge-transfer related mechanisms of the TNA nanostructures were evaluated for their use in photosensitive cell applications.

2. Experimental procedures

2.1. Preparation of spatially ordered TNAs by two-step anodization

The electrochemical anodization system used to prepare the TNAs with spatially ordered dispersion had a two-electrode configuration. Titanium foil with an area of 2.5 cm × 2.0 cm and a thickness of 150 μm was used as the anode. A platinum sheet (99.99%) was used as the cathode. The electrolyte composition in the anodization system was 3 wt.% NH_4F (98%, RDH) dissolved in ethylene glycol (99.5%, RDH) with 9 vol.% de-ionized water (D.I.-H_2O).

Prior to anodization, the Ti-foil was cleaned with ethanol, acetone, dilute hydrogen chloride, and D.I.-H_2O, in that order. The two-step anodic oxidation was performed using a dual-range DC power supply (GWINSIEK Co., SPD-3606). First, the anodization potential was applied at 40 V for 1 h. The resulting anodized TNAs were removed with 3M™ adhesive tape. Next, the Ti/TO_2 sheet was anodized again, after removing the 1 h-anodized TNAs, with a potential 40 V for 5 min. This yielded free-standing, discrete TNAs, approximately 1 μm long. After the second anodic oxidation, the TNAs were washed with D.I.-H_2O and dried with nitrogen gas. The dried specimens were annealed at 450 °C for 30 min in air and then cleaned via ultrasonication for 10 s.

2.2. Preparation of $CuInS_2$ and In_2S_3/$CuInS_2$ photosensitizers on TNAs

An inorganic photoabsorption layer, $CuInS_2$ (CIS), and buffer layer, In_2S_3 (InS), were deposited onto the anodized TNAs using a drop-casting (DrC) method. The starting materials were $CuCl_2$ (98%, SHOWA), $InCl_3$ (99.99%, Alfa Aesar), and $(NH_2)_2CS$ (98.5%, RDH). The starting materials were each dissolved in a 50 vol.% ethanol/50 vol.% D.I.-H_2O solution and mixed via ultrasonication to reach equilibrium. The concentrations of the precursors were 0.05 M $CuCl_2$, 0.05 M $InCl_3$, and 0.4 M $(NH_2)_2CS$. These solutions were then used to prepare a 0.05 M $CuInS_8$ solution. 0.1 M $InCl_3$ and 0.6 M $(NH_2)_2CS$ were used to prepare a 0.05 M In_2S_{12} solution. The excess of sulfur in $CuInS_8$ and In_2S_{12} allowed for sulfur compensation during the annealing process without the use of H_2S gas.

In the DrC procedure, 0.01 mL $CuInS_8$ solution (0.05 M) was dropped onto the prepared area of 2.0 cm × 2.0 cm TNAs. The solvent was evaporated in an air-evacuated desiccator then the sample was dried at 200 °C for 10 min in air. The dropping-drying procedure could be repeated for several cycles, referred to as "CISy" where "y" equals to the number of CIS cycles. After the CISy was completed, the sample was annealed at 400 °C for 30 min in an Ar atmosphere to form the TNA/CISy photosensitive structure. In the DrC procedure for the TNA/InS/CIS structures, 0.01 mL In_2S_{12} (0.05 M) was dropped onto the prepared TNAs. Again, the solvent was evaporated in an air-evacuated desiccator followed by drying at 200 °C for 10 min in air. The dropping-drying procedure for InS could be repeated several cycles, referred to as "InSx" where "x" is the number of InS cycles. After InSx was completed, the sample was annealed at 400 °C for 30 min in an Ar atmosphere to form the TNA/InSx structure. The CISy procedure was repeated on the TNA/InSx substrate, followed by annealing at 400 °C for 30 min, resulting in a TNA/InSxCISy photosensitive structure.

2.3. Characterization of photosensitized TNA nanostructures

Several key properties of the TNA nanostructures including bare TNAs, TNA/CISy and TNA/InSxCISy type structures were characterized after fabrication. Crystal structures for all of the samples were characterized by X-ray diffraction (XRD, BRUKER, D2 Phaser). The microstructures and the morphology of the bare TNAs and chalcogenide photosensitized TNAs (i.e., TNA/CISy and TNA/InSxCISy) were determined using field emission-scanning electron microscopy (FE-SEM, Hitachi Field-Emission S-4800).

The test area of the TNA nanostructures was approximately 1.0 cm^2. The photosensitivity of the chalcogenide sensitized TNAs was determined by measuring the photocurrent-time (I-t) and voltage-time (V-t) changes under on/off visible light cycling, generated by a Xenon lamp (Khlamp KHX-13 W) with a visible light filter. The I-t and V-t measurements were done by Keithley 2400