Stibnite sensitized hollow cubic TiO$_2$ photoelectrodes for organic-inorganic heterojunction solar cells

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ABSTRACT

Enhancing power conversion efficiency in organic-inorganic heterojunction solar cells faces several serious hurdles. Although standard TiO$_2$ nanoparticles-based heterojunction solar cells are moderately efficient, the TiO$_2$ nanostructure has several drawbacks including a disordered low surface area with poor pore structure. Thus, it is necessary to develop a new TiO$_2$ morphology for effective photon harvesting in organic-inorganic heterojunction solar cells. Hollow nanostructured electrodes are widely used in energy related devices because of their high surface area, larger pores, and superior light scattering properties. Here, we report the first successful application of hollow cubic TiO$_2$ (HCT) nanostructured photoelectrodes sensitized with stibnite for all solid-state heterojunction solar cells. The unique hollow nanostructure resolved several issues of organic-inorganic heterojunction solar cells, such as insufficient pore size for inorganic sensitizers, large grain boundary area, and poor penetration of organic hole conductors, thereby improving the cell efficiency. Device performance was strongly dependent on the thickness of stibnite, which could be controlled by deposition time. Devices optimized with HCT exhibited a high solar to power conversion efficiency (~3.5%), which was slightly higher than the TiO$_2$ nanoparticle-based devices.

1. Introduction

Heterojunction solar cells with inorganic-semiconductor sensitizers are weighed as favourable substitute to traditional dye-sensitized solar cells (DSC) (Kamat, 2008, 2012). Metal chalcogenides possess unique properties such as higher absorption coefficient compared with conventional ruthenium and organic sensitizers, multiple exciton generation, good stability, band tuning by size control, and larger dipole moment. Thus, as a sensitizer alternative, metal chalcogenides were widely studied as absorbers to achieve high solar cell performance (Abraham et al., 2010; Nozik et al., 2010; Barea et al., 2010; Kim and Ma, 2015; Chang et al., 2010).

For the last several years, Sb$_2$S$_3$ (stibnite) has been utilized as a absorber layer by various research groups in organic-inorganic heterojunction solar cells because of its high absorption coefficient (1.8×10^5 cm^{-1} at 450 nm) and a low bandgap of 1.7 eV, which can give high energy conversion efficiency (Chang et al., 2010; Messina et al., 2007; Versavel and Haber, 2007; Itzhaik et al., 2009, 2011; Choi

and Seok, 2015; Godel et al., 2015; Gui et al., 2012; Veerappan et al., 2015; Cardoso et al., 2012; Fukumoto et al., 2013). Until now, stibnite sensitizers have been synthesized by chemical bath deposition (Kim and Ma, 2015; Chang et al., 2010). Although a photovoltaic performance of more than 6.0% has been achieved in stibnite sensitized solar cells (Choi and Seok, 2015), the parameters that determine conversion efficiency have not been extensively studied (Chang et al., 2010; Itzhaik et al., 2011; Choi and Seok, 2015; Fukumoto et al., 2013; Tsujimoto et al., 2012). In stibnite devices, charge carrier generation takes place between stibnite-sensitized anatase TiO$_2$ and hole conducting materials. In general, nanostructured TiO$_2$ exhibits a heterogeneous interface with stibnite sensitizer that results in slow electron transfer, which is primarily attributed to an ambipolar diffusion mechanism controlled by trap sites and results in a lengthy path to the transparent conductive electrode (Dloczik et al., 1997; Kopidakis et al., 2000; Lagemaat et al., 2008; Martinson et al., 2008; Tetreault et al., 2011; Tetreault and Grätzel, 2012). Furthermore, TiO$_2$ nanoparticle films contain a high number of grain boundaries.

One of the key considerations in fabricating any heterojunction or solid-state dye-sensitized solar cell (SDSC) is the nanoscale of the photoanode, which should have a good pore structure and favourable morphology for proper infiltration of a hole-conductor as well as an inorganic sensitizer. To address such issues, several novel TiO_2 nanostructures have been proposed in DSC and SDSC, which always surpass the efficiency of random TiO_2 structures (Tetreault et al., 2011; Tetreault and Grätzel, 2012; Veerappan et al., 2014; Yang et al., 2016; Vazquez et al., 2012; Crossland et al., 2013). However, for stibnite sensitized all solid-state heterojunction solar cells (Sb-HSC), only a few reports have been reported to date on TiO_2 nanostructure dependent power conversion efficiency (Gui et al., 2012; Veerappan et al., 2015; Cardoso et al., 2012). It is well known that porosity, morphology, and crystallinity of photoanodes occupy an important role in the photovoltaic conversion efficiency of 3rd generation solar cells (Hagfeldt et al., 2010). For instance, our group and Gui et al. reported TiO_2 nanoparticles of different sizes and the influence of Sb-HSC, which resulted in a larger pore size and enhanced power conversion efficiency (Gui et al., 2012; Veerappan et al., 2015). Recently, Cardoso et al. reported one-dimensional (1 D) TiO_2 nanostructures for Sb-HSC and showed an effective way to facilitate faster electron transport in achieving higher efficiency (Cardoso et al., 2012). However, the performance of these cells was inferior compared to liquid DSC. In general, 40–50 nm-sized irregularly structured TiO_2 nanoparticle based photoanodes are used in Sb-HSCs, which causes many drawbacks such as poor hole-conducting material penetration, poor electron transport, high charge carrier recombination, and insufficient pores for effective light scattering (Chang et al., 2010; Itzhaik et al., 2009, 2011; Choi and Seok, 2015; Godel et al., 2015; Fukumoto et al., 2013).

In the past several years, there have been significant achievements in engineering {0 0 1} facets of TiO_2 crystals through various morphology-controlled strategies, resulting in improved photocatalysts and solar cells (Liu et al., 2011; Zhang et al., 2010). However, the high energy {0 0 1} facets of anatase TiO_2 are more vulnerable to dissolution than {1 0 1} facets during hydrothermal reactions in corrosive hydrofluoric acid/H_2O_2 solutions, and thus the property of anisotropic corrosion of facets is expected to have interesting applications in developing hollow TiO_2 with faceted surfaces (Hu et al., 2009).

In this study, we report for the first time a self-tailored approach for the synthesis of highly exposed {1 0 1} faceted anatase hollow cubic TiO_2 (HCT) derived from cubic $TiOF_2$ crystals. We subsequently prepared HCT films on FTO coated glass, sensitized with stibnite and P3HT as a hole-conductor to achieve stibnite sensitized organic-inorganic heterojunction solar cells. We developed the Sb-HSCs by controlling the stibnite sensitization time on HCT and compared their performance with that of conventional TiO_2 nanoparticles based all solid-state heterojunction solar cells.

2. Experimental section

2.1. Synthesis of hollow cubic TiO_2

Cubic $TiOF_2$ crystals were synthesized by hydrothermal treatment of a mixture of 25 ml Ti(OBu)$_4$, 5 ml of hydrofluoric acid and 20 ml C_2H_5OOH at 180 °C for 24 h (Liu et al., 2011; Zhang et al., 2010). The resulting cubic $TiOF_2$ was washed thrice with deionized water and then mixed in ultrapure water (10 mg: 1 ml) by ultrasonication for 10 min. The dispersion was then placed in a 60 ml hydrothermal reactor and maintained at 120 °C for 24 h. The resulting hollow cubic TiO_2 was collected and washed with water until achieving a neutral pH, after which it was dried at 60 °C.

2.2. Device fabrication

Hollow cubic TiO_2 powders were made into paste by mixing with alpha-terpineol and ethyl cellulose (Veerappan et al., 2015). A 70 nm thick compact TiO_2 layer (CL-TiO_2) was deposited onto the fluorine-doped tin oxide (FTO) glass substrates. Prior to use, all the FTO substrates were etched and cleaned using ethanol and acetone. Using doctor blade method, the HCT photoelectrodes were deposited onto the CL-TiO_2/FTO and annealed for 30 min at 500 °C. To enhance the connectivity between each TiO_2 particles, 0.2 M $TiCl_4$ treatment was done at 70 °C for 12 h and annealed at routine temperature (30 min at 500 °C). For comparison, a standard TiO_2 nanoparticle (NP) electrode was also prepared by doctor blading with a particle size of 50 nm, received from EnB Korea. Around 1.0 μm thick TiO_2 photoelectrodes were prepared using the traditional nanocrystalline TiO_2 and HCT TiO_2 pastes. Chemical bath deposition (CBD) was used for coating the TiO_2 electrodes with Sb_2S_3 by varying the dipping time to get the desired coverage (Chang et al., 2010; Messina et al., 2007; Veerappan et al., 2015). All the TiO_2 electrodes were dipped into a CBD solution consisting of 0.650 g $SbCl_3$ in 2.5 ml acetone, 25 ml of 1 M $Na_2S_2O_3$ aqueous solution, and 72.5 ml deionized water at 6 °C for various times (90, 150, 210, and 270 min). Orange colored amorphous stibnite layers formed on TiO_2 electrodes for different deposition times in the bath were sintered at 330 °C in an argon atmosphere for 30 min (Chang et al., 2010; Messina et al., 2007; Itzhaik et al., 2009, 2011; Choi and Seok, 2015; Godel et al., 2015; Gui et al., 2012; Veerappan et al., 2015; Cardoso et al., 2012; Fukumoto et al., 2013). Hole transporting material (P3HT solution) (HTM) was deposited onto HCT/Sb_2S_3 electrodes by spin coating (Veerappan et al., 2015). Then, the PEDOT:PSS layers were formed using five times diluted PEDOT:PSS solution in isopropyl alcohol by spin coating at 2000 rpm for 30 s to efficiently extract the holes and the devices were finished by depositing strip type gold contact using thermal evaporation.

2.3. Characterization

Phase, crystallinity, and surface area of HCT powders and electrodes were measured by X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) analyses. The nanostructure morphology of HCT powder and films, as well as the composition of stibnite were studied by FE-SEM (JEOL JSM-7500F Japan) and HR-TEM. Influence of sintering effect on stibnite films were characterized by UV–Vis absorption spectroscopy (UV3600, SHIMADZU). The current-voltage (I-V) characterization of Sb-HSCs were studied under AM 1.5 simulated solar light irradiation and calibrated with a standard Si solar cell for 1 sun. The incident photon to current conversion efficiency (IPCE) was studied using specially made system from PV Measurement, Inc. for all the devices. Electrochemical impedance spectroscopy was done in a frequency range of 100 mHz–100 kHz using an Zahner IM6 impedance analyzer.

3. Results and discussion

A scheme illustrating the mechanism for the generation of novel HCT is shown in Fig. 1a. $TiOF_2$ crystals were first hydrolyzed into TiO_2 and HF, during which HF as an etching agent exhibited a tendency to quickly dissolve low energy {0 0 1} facets, thereby gradually narrowing {0 0 1} facets until they nearly disappeared. On the other hand, the etching ratio of high energy {1 0 1} facets was lower than that of {0 0 1} facets, resulting in the formation of HCT with exposed {1 0 1} facets. Fig. 1b and c shows the diagrammatic representation of the stibnite sensitized HCT device and the band energy level positions and charge carrier transferring route in the Sb-HSCs, respectively.
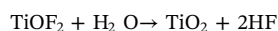
$$TiOF_2 + H_2O \rightarrow TiO_2 + 2HF$$

Fig. 2a shows the XRD spectra of the as-synthesized cubic $TiOF_2$ crystals and hollow cubic TiO_2 nanoparticles. After hydrothermal treatment of $TiOF_2$, the cubic crystals were converted into HCT at 120°C. XRD results demonstrate that, the as-synthesized HCT powders are composed of pristine anatase TiO_2 phase with no other contamination peaks. The peak intensities at 25.32° (1 0 1) and 37.93°