Solar Energy Materials and Solar Cells 178 (2018) 208–222

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

$CuInS_2$ quantum dot sensitized solar cells with high $V_{OC} \approx 0.9$ V achieved using microsphere-nanoparticulate TiO_2 composite photoanode

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ARTICLE INFO

Keywords:
Nanocomposites
TiO_2
QDs
Solar cell
Microsphere
$CuInS_2$

ABSTRACT

$CuInS_2$ (CIS) based solar cell devices are fabricated by sensitizing TiO_2 photoanodes with CIS quantum dots (CIS-QDs). Morphologically different TiO_2, *viz*. Degussa P25 nanoparticles, smooth and fibrous microspheres (SμS and FμS respectively) are used to fabricate photoanodes. CIS-QDs are synthesized using dodecanethiol (DDT), CuI and $In(OAc)_3$ precursors by solvothermal method. DDT surfactant present on the CIS QDs surface is replaced with 3-mercaptopropionic acid in a single phase one step procedure to enable efficient loading of QDs onto photoanode and as linker molecule for charge carrier extraction. The CIS QDs sensitized on SμS and FμS microsphere photoanode layers exhibit a photoconversion efficiency (η) of 3.2% and 1.6%, respectively, in comparison to $\eta \approx 2.1\%$ for nanoparticulate TiO_2 (Degussa P25). Further increase in efficiency is obtained (3.8% for SμS and 2.5% for FμS) when composite photoanode films made of porous microspheres filled with nanoparticulate P25 are used. A maximum efficiency of 3.8% (with $J_{SC} \approx 6.2$ mA, $V_{OC} \approx 926$ mV and FF ≈ 66 for cell area ≈ 0.25 cm^2 and thickness ≈ 20 μm) is realized when 4.6 nm CIS QDs sensitized on composite photoanode (consisting of 80 *wt.* % SμS and 20 *wt.* % P25) is used. High V_{OC} observed is unprecedented and is possible due to combined effect of SμS + P25 composite photoanode properties such as fewer defects, good connectivity between particles, effective light scattering, minimum recombination, and effective electron transport and size optimized $CuInS_2$ QDs. Electrochemical impedance spectroscopy studies reveal a low interfacial resistance and longer electron life time in SμS + P25 composite photoanodes.

1. Introduction

Third generation solar cell devices aim at achieving low-cost earth abundant materials with ease of device fabrication and enhanced photovoltaic performance [1]. Towards this effort several optimization studies in the sensitized solar cells are being extensively pursued, especially on the photoanodes such as titanium dioxide (TiO_2), zinc oxide (ZnO) and tin oxide (SnO_2) and sensitizer materials such as dyes, quantum dots (QDs), perovskites and semiconductor thin films [2–4]. In spite of reported higher efficiency in dye and perovskite sensitized solar cells (DSSCs and PSCs), the main challenge lies in keeping up the efficiency high on large area solar cells in addition to establishing the stability of these devices for long duration [5,6]. Inorganic quantum dots (QDs) and semiconductor thin film sensitized solar cells offer promising alternative to these sensitizers [7]. The tunability of bandgap by tailoring the size of semiconductor QDs and by tailoring the composition in thin films offer large flexibility to optimize the optical properties and maximize solar absorption of sensitizer materials [8]. Out of several semiconductors studied, copper indium disulfide (CIS), a non-toxic chalcopyrite semiconductor, is an ideal sensitizer for capturing sunlight owing to its high absorption coefficient (10^5 cm^{-1}). Further, the direct bandgap of CIS with $E_g \sim 1.53$ eV offers the maximum achievable efficiency as predicted by the Shockley-Queisser limit [9–11]. Hence, CIS sensitized solar cells have shown significant progress in recent years due to its tunable bandgap, low fabrication cost, long term stability, etc [12–15].

In sensitized solar cell, the photoanode made of nanostructured semiconductor metal oxide is the heart of system. The semiconductor metal oxides such as TiO_2, ZnO and SnO_2 are commonly employed as photoanodes [2]. TiO_2 is preferred as a suitable candidate for photovoltaic applications due to its inherent advantages that include high chemical inertness, non-toxicity, photo-stability, wide bandgap (3.2 eV) and eco-friendliness [16,17]. Even though TiO_2 exists in three different phases, anatase phase shows better photovoltaic performance compared to other phases [18]. Apart from the phase of TiO_2, the morphology also highly influences the efficiency of the solar cells. Photovoltaic studies using various morphologies of TiO_2 such as ordered nanotubes, nanoparticles, nanoporous microstructures, microspheres,

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https://doi.org/10.1016/j.solmat.2018.01.018
Received 23 October 2017; Received in revised form 22 December 2017; Accepted 13 January 2018

nanoarrays, and hierarchical nanotubes confirm the influence of morphology on the solar cell performance [19–24]. In addition to morphology, TiO_2 photoanode films should have high surface area for maximum sensitizer loading, more light scattering for effective light harvesting and good connectivity between particles for better electron transport. The surface area and the light scattering property of photoanode depends on morphology, particle size of TiO_2 and thickness of photoanode [22]. Better light scattering is achieved by using the suitable morphology and particle size of TiO_2 (> 100 nm). For example, the larger particle size TiO_2 of different morphology such as microsphere [22], nano-rods [25,26], nano-tubes [27], nano-spindles [28], nano-fibers [29], photonic crystals [30], nano-wires [31], nano-sheets [32], nano-disks [33], nano-plates [34], nano-petals [35], and nanocubes [36] are found to have better light scattering property. Several of these TiO_2 nanostructures are being used in the photoanode to get effective light scattering to increase the incident light path length thereby enhancing the light harvesting efficiency of sensitizers. Two types of light scattering structures are being used in the photoanode layer: (1) a "double-layer structure" in which a light scattering particle is deposited over a TiO_2 nanocrystallite layer and (2) a "composite structure" i.e. incorporation of larger particles as scattering centers into TiO_2 nanocrystallites [37]. These two types of light scattering were found to be effective and seem to enhance the optical absorption of the sensitized photoanodes in solar cells. However, in double layer film structure the scattering layer does not have any significant role in increasing the surface area for sensitizer loading. Also the thickness of the film is larger than desired for SSC devices. The optimized thickness of photoanode film is ~ 15–20 μm for achieving best efficiency in DSSC and QDSSC solar cells [38]. The more thickness of photoanode film in double layer structure leads to an increase of interfacial resistance which affects the efficiency of solar cell [38]. The composite film structure, on the other hand, could be made with optimized film thickness to yield better efficiency. Photoanodes with mesoporous microsphere and nanoparticle composite increases the surface area for sensitization, and provide good connectivity between particles for electron transport. Efficiency as high as 9% was achieved in a large area (0.5 cm^2) DSSC solar cells made from well-connected micron sized smooth sphere (SμS) and P25 nanoparticle (80:20 ratio of SμS and P25) composite TiO_2 photoanode films [39]. SμS-nanoparticle composite TiO_2 film possesses essential attributes necessary for an efficient photoanode *viz*. large surface area for sensitizer adsorption, good connectivity between nanocrystallites for the efficient electron transport, and higher scattering properties for better light harvesting efficiency.

In the present study, the CIS QDs are used as sensitizers on TiO_2 photoanodes made of smooth and fibrous microsphere morphologies and their composite with nanocrystalline P25. CIS quantum dots of various sizes synthesized by solvothermal method are loaded onto TiO_2 nanostructures using 3-mercaptopropionic acid (MPA) as linker molecule. The efficiency of solar cell devices with the CIS QDs sensitizers on TiO_2 microspheres and their composite with nanoparticulate P25 photoanode are studied under 1 sun illumination. We discuss the photovoltaic performance of CIS QDs of various sizes loaded on TiO_2 microsphere (SμS and FμS) and their composite (SμS/FμS + P25) photoanode. A maximum efficiency of 3.8% is obtained for CIS-QD sensitized composite photoanode film. Interestingly, CIS QDSSCs exhibit high open circuit voltage (≈0.9 V), which is unprecedented in any of the QD sensitized solar cells. Electrochemical impedance spectroscopy (EIS) studies are carried out to understand the electronic and ionic conduction process of CIS sensitized photoanode film made of individual and microsphere-nanoparticulate TiO_2 composite.

2. Experimental

2.1. Materials

(i) TiO_2 sysnthesis: Titanium (IV) isopropoxide (97%; Alfa Aesar), Degussa P25-TiO_2 nanocrystallites, glacial acetic acid (AR > 99.8%; Vetec), ethanol (AR-99.9%). (ii) *CIS QDs:* copper iodide (99.99%; Alfa Aesar), indium acetate- (99.99%; Alfa Aesar), 1-dodecanethiol (98%; Alfa Aesar), 1-octadecene (90%; Alfa Aesar). (iii) *Electrolyte:* Acetonitrile (HPLC grade 99.8%), butanol (> 99%; Emplura), lithium iodide (LiI), Iodine, 4-tertiary butyl pyridine (TBP, 96%; Aldrich). (iv) *Solar cell fabrication:* Poly ethylene glycol 4-tert-octyl phenyl ether (Triton X-100; SRL), and fluorine doped tin oxide (FTO) coated transparent glass (8 Ω/Sq, 2.2 mm thick). All the chemicals were purchased and used without any further purification.

2.2. Synthesis of TiO_2 microsphere

Anatase TiO_2 microsphere with smooth and fibrous morphology (SμS and FμS) are synthesized by solvothermal and hydrothermal methods, respectively [39]. Smooth surface TiO_2 microsphere (SμS) synthesized by using ethanolic solution of titanium (IV) isopropoxide (1.25 M) with pH of the solution was adjusted to 3 using glacial acetic acid. The solution was maintained at 200 °C for 2 h in an autoclave. After the solvothermal treatment, the remaining solvent was filtered to get a white powder. This powder was washed with de-ionized water and then calcined at 450 °C for 3 h to obtain crystalline anatase TiO_2 nanoparticles. Hollow/ fibrous TiO_2 microsphere (FμS) is synthesized by taking Degussa P25 particle (0.1 g) in 60 mL of 10 M NaOH and 8 mL of hydrogen peroxide solution mixture. The solution was maintained at 160 °C for 2 h in an autoclave. The white powder obtained was filtered and washed several times with de-ionized water and then calcined at 450 °C for 3 h to obtain crystalline TiO_2 microsphere.

2.3. Synthesis of $CuInS_2$ (CIS) QDs

$CuInS_2$ (CIS) QDs are synthesized by solvothermal method [40]. In a typical synthesis of CIS QDs, 1 mmol (0.2919 g) of $In(OAC)_3$, 1 mmol (0.1904 g) of CuI, 15 mL of 1-octadecene (ODE) and 5 mL of 1-dodecanethiol (DDT) were added to three-neck flask (100 mL) and stirred under N_2 atmosphere for 30 min at 100 °C. The temperature of reaction mixture was slowly increased to 210 °C. The reaction of metal precursors with DDT leads to the formation of CIS at 210 °C and the color of reaction mixture gradually turned from colorless to yellow, orange, red, dark red and brown in that order as the reaction proceeded. Based on the color change of the solution we can infer the typical size and bandgap of CIS nanocrystallites. As the reaction proceeded small aliquots of reaction mixture of various colors comprising of different size of CIS-QDs were collected. The collected CIS-QDs samples were cooled down to room temperature and purified using acetone to remove excess solvent and unreacted precursor. The purified CIS QDs were dispersed in chloroform for further characterization. Five CIS QDs samples with typical solution colors of yellow, orange, red, dark red and brown collected at different time intervals are named as CIS-a, CIS-b, CIS-c, CIS-d and CIS-e respectively (Table 1).

2.4. Fabrication of TiO_2 photoanode

TiO_2 paste was prepared by mixing TiO_2 powder, ethanol solvent and TritonX-100 binder with a mortar and pestle. TiO_2 layers were coated on FTO/glass substrates by applying the paste using the doctor blade technique. These TiO_2 layers were annealed at 450 °C for 3 h in air. Tiny TiO_2 nanocrystals were also nucleated on these annealed TiO_2 photoanode by immersing the films in 40 mM $TiCl_4$ solution at 70 °C for 30 min and washing three times with water before annealing again at 450 °C for 30 min. For the fabrication of composite photoanode, TiO_2 microsphere and P25 nanocrystallites (weight ratio of 80 + 20 for SμS + P25 and 75 + 25 for FμS + P25) were mixed together initially and then films were prepared by following the above mentioned method. The thickness of fabricated photoanode is ~ 20 μm and the area is ~ 0.25 cm^2. The coating thickness and area were kept constant for all the