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Higher open-circuit voltage set by cobalt redox shuttle in SnO_2 nanofibers-sensitized CdTe quantum dot solar cells☆

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ABSTRACT

In this study, we report an efficient CdTe-SnO_2 quantum dot (QD) solar cell fabricated by heat-assisted drop-casting of hydrothermally synthesized CdTe QDs on electrospun SnO_2 nanofibers. The as-prepared QDs and SnO_2 nanofibers were characterized by dynamic light scattering (DLS), UV–Vis spectroscopy, photoluminescence (PL) spectra, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The SnO_2 nanofibers deposited on fluorine-doped tin oxide (SnO_2) and sensitized with the CdTe QDs were assembled into a solar cell by sandwiching against a platinum (Pt) counter electrode in presence of cobalt electrolyte. The efficiency of cells was investigated by anchoring QDs of varying sizes on SnO_2. The best photovoltaic performance of an overall power conversion efficiency of 1.10%, an open-circuit voltage (V_{oc}) of 0.80 V, and a photocurrent density (J_{SC}) of 3.70 mA/cm^2 were obtained for cells with SnO_2 thickness of 5–6 μm and cell area of 0.25 cm^2 under standard 1 Sun illumination (100 mW/cm^2). The efficiency was investigated for the same systems under polysulfide electrolyte as well for a comparison.

1. Introduction

Quantum Dots (QDs) are nanocrystals of a semiconducting material which were first reported in 1981 [1–4]. The band-gap of QDs can be tuned as a function of size which is one of their most peculiar characteristics. QDs have shown multi-exciton generation (MEG) effect with which a single photon can provide more than one exciton [5–14]. Also QDs of same material can be tuned to absorb whole of the visible spectrum [15,16]. Thus QDs are widely investigated for their practical applications in new generation solar cell technologies [17–22]. Inexpensive methods of colloidal synthesis of QDs, high compatibility with solid-state device technology, tunable band-gap of QDs, MEG, and good stability against conventional dyes used in dye-sensitized solar cells (DSSCs) make them an ideal sensitizer that can be used in third generation solar cells [23]. The specialty of this third generation solar technologies would be flexible or non-flat solar cell devices fabricated with QDs or other sensitizers embedded in nanomaterial semiconducting polymer films.

Effective deposition of QDs or sensitizers onto metal oxide films of TiO_2, ZnO or SnO_2 is one of the problems in QDSCs. Successive Ionic Layer Adsorption Reaction (SILAR) has been one of the easy and effective ways of QD deposition onto photoanodes. But in the case of CdTe, the precursors of CdTe are not favorable for an easy SILAR deposition. Dyes used in DSSCs could be easily loaded onto the photoanode material because of the chemical affinity of dyes to photoanode material like TiO_2. This kind of chemical attachment is absent between QDs and general photoanode materials (ZnO, SnO_2 and TiO_2). Hence surface ligands can be used in chemically attaching QDs to the photoanode material (TiO_2 or SnO_2) and in stabilizing the QD colloidal solution but the chain length of ligands (most of them being insulators in nature) causes more resistance thereby causing recombination. Previously, Thioglycolic acid (TGA) was widely used with CdTe as stabilizer. Here, we have used MPA (3-mercaptopropionic acid) as the stabilizing agent or ligand [24,25]. The carboxylic group of MPA would bind to the metal oxide while the thiol group (-SH) would bind CdTe. Also preparation of water soluble QDs with this hydrophilic MPA ligand is favorable for the effective adhesion of QDs onto the hydrophilic SnO_2 film.

CdTe is used as the sensitizer in this work which is a semiconductor with a direct band-gap of around 1.5 eV at 300 °C. Considerable amount of research exists on QDSCs with TiO_2 as the photoanode and cadmium chalcogenide as the sensitizer [26–30].

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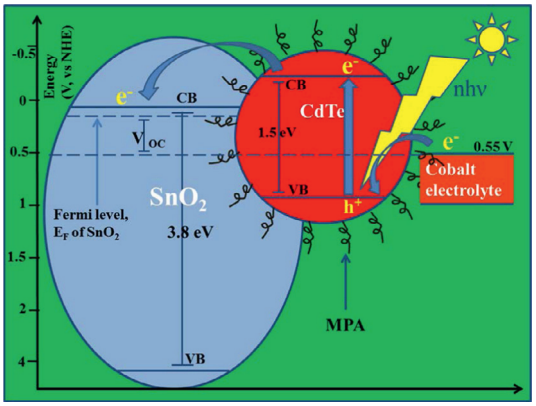

Fig. 1. Illustration of band alignment of materials used as photoanode (SnO_2), sensitizer (CdTe), and electrolyte (Co electrolyte).

The photoconversion efficiency of CdSe/CdS-sensitized SnO_2 solar cells is comparable to that obtained for CdSe/CdS-sensitized TiO_2 under 1-Sun illumination [31]. Since the SnO_2 nanostructures have higher electron mobility and much more negative conduction band minimum than nanostructures of TiO_2, we assume that the proposed solar cell would yield good efficiency when SnO_2 and CdTe are employed as photoanode and sensitizer, respectively. The band alignment of the materials used as photoanode, sensitizer and electrolyte in this study is ideal for a working solar cell as given in Fig. 1. Also one-dimensional (1-D) ballistic transport should facilitate guided electron transport pathways [32]. Hence the 1-D nanofibers of SnO_2 were synthesized by electrospinning. QDs of varying sizes and color were synthesized via hydrothermal route by varying either MPA concentration or duration of the hydrothermal process. A ZnS passivation layer was coated via SILAR method on CdTe sensitized SnO_2 films to avoid surface reconstruction.

Also the issues of electrolytes in QDSCs are still unsolved; we considered cobalt-based electrolyte which is little explored in QDSCs. Cobalt complex redox couples have yielded a very good photoconversion efficiency of 13.0% using tailored zinc-porphyrene dye [33,34]. Fast recombination of electrons in the photoanode (TiO_2) conduction band to the electrolyte limited the performance of cobalt electrolyte in DSSCs. This recombination is overcome by linking suitable steric groups onto the sensitizer in the adsorbed monolayer [35]. Hence cobalt based redox mediators are considered as promising alternative electrolytes for dye-sensitized solar cells (DSSCs). Cobalt electrolyte has only weak visible light absorption and also offers higher output voltage compared to polysulfide or iodine electrolyte. It is non-corrosive and non-volatile. It has tunable redox potential (0.43–0.85 V) which is achieved by changing the coordination sphere of complex molecules around cobalt species. The Li^+ ions in the cobalt based electrolyte increase the short-circuit current density (J_{sc}). Both Li^+ and 4-tert-butylpyridine (TBP) contribute to higher open-circuit voltage (V_{oc}) [36]. Hence the use of cobalt electrolyte would improve V_{oc} in the proposed QDSC considering the band edge positions of SnO_2 with respect to the electrolyte redox level (Fig. 1), and thereby should provide decent efficiencies without buffer layers or passivation layers. It is reported that Co complexes formed from structurally simple ligands could also be used as efficient electron transfer mediators. Hence any substituted bipyridine Co complexes should yield the same V_{oc} [36]. Polysulfide electrolyte is also used to compare the efficiencies and other characteristics of SnO_2-CdTe system. Hence this study also provides a comparison between the widely used polysulfide electrolyte and cobalt-based redox system in QDSCs.

2. Experimental

2.1. Materials

PVP (Polyvinylpyrrolidone, $M_w = 1.3\times10^6$ g/mol, m.p. 300 °C, Sigma Aldrich), ethanol (absolute, Fischer scientific), DMF (Dimethylformamide, 99.8%, Sigma Aldrich), $SnCl_2$ (Tin chloride, 99%, Alfa Aesar), PEG (Polyethylene glycol, 99.8% Min, Merck Chemicals), FTO plates (fluorine-doped tin oxide, sheet resistance of 6–8 cm^{-1} fabricated in-house by spray pyrolysis deposition method), ultra-pure de-ionised water (Millipore-Direct Q3 UV system, India), S (Sulfur, 99.5%, Nice chemicals, India), KCl (99.5%, Fisher Scientific), $Na_2S{\cdot}9H_2O$ (Sodium sulfide nonahydrate, 98%, Sigma Aldrich), citric acid (L.R, 99.5%, Nice chemicals), Platinum (Pt) sputtered FTO glasses, 2-propanol (L.R., > 99%, Sigma Aldrich, Germany), Zn(Ac) (Zinc acetate, 99.9%, Sigma Aldrich), DBTDA (Dibutyltin diacetate, tech. grade, d= 1.32 g/mL at 25 °C, Sigma Aldrich), NH_4F (Ammonium fluoride, 99.99%, Sigma Aldrich), CH_3OH (Methanol, L.R., 99%, Sigma Aldrich), $CdCl_2{\cdot}5/2H_2O$ (Cadmium chloride semi-pentahydrate, 99.9%, Alfa Aesar), NaOH (sodium hydroxide, pellets, Fischer Scientific), TeO_2 (Tellurium dioxide, 99.9%, Alfa Aesar), trisodium citrate (Merck Chemicals), MPA (3-mercaptoproponoic acid, 99%, Sigma Aldrich), $NaBH_4$ (Sodium borohydride, Merck Chemicals), (Co^{II} $(bpy)_3(B(CN)_4)_2$) (Dyesol), (Co^{III} $(bpy)_3(B(CN)_4)_3$) (Dyesol), TBP (4-tert-butylpyridine, 96%, Sigma Aldrich) and $LiClO_4$ (Lithium perchlorate, 95%, Alfa Aesar) were all the chemicals and materials used in this project.

2.2. Preparation of FTO plates

FTO deposition was done following the procedures reported in literature [37]. FTO deposition was done on a glass substrate (Corning Eagle XG, USA) using spray-pyrolysis deposition (SPD) technique. FTO plates of size 2×2 cm^2 were thus fabricated with sheet resistance of 8–10 Ω per square. The precursors of the FTO were a 0.2 M solution of DBTDA in 2-propanol and 9 M solution of NH_4F in 33.33 mL water. The white precipitate was stirred for 1 h to get dissolved in the solution. This was further diluted with 430 mL of 2-proponol. This was sprayed on the glass substrate using SPD machine (KM-150, SPD Laboratory, Inc. Japan). The number of cycles of SPD deposition was optimized according to conductivity measurements.

2.3. Preparation of SnO_2 nanofibers and mesoscopic SnO_2 electrodes

SnO_2 NFs were prepared via electrospinning. A solution of 1.28 g of $SnCl_2$ in 40 mL solution of ethanol and DMF prepared in 1:1 ratio along with 5.6 g of PVP was stirred in a magnetic stirrer to dissolve the materials in the solution. Electrospinning was done in a climate-controlled electrospinning unit (IME Technologies, The Netherlands). After electrospinning, the SnO_2-PVP composite was sintered in a hot furnace at 500 K for 4 h in hot air. The remaining white flakes were recognized as SnO_2 NFs through various characterization techniques. NFs were mixed with a small amount of PEG and were ground by pestle and mortar to break up the agglomerates for smooth coating over FTO plates. This paste was doctor-bladed onto the FTO glass to get an appropriate thickness of about 10 μm with scotch tapes as thickness reference. The printed films were then sintered in air by heating at 500 °C for 3 h.

2.4. Preparation of CdTe quantum dots

A hydrothermal method was followed to prepare CdTe quantum dots [38]. In this method, Teflon containers were used to keep the solution inside the hot furnace. The temperature was maintained at 180 °C. The solution was prepared by adding the