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$Cu_2ZnSnSe_4$ QDs sensitized electrospun porous TiO_2 nanofibers as photoanode for high performance QDSC

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ABSTRACT

An earth-abundant and relatively less toxic, quaternary $Cu_2ZnSnSe_4$ (CZTSe) quantum dots (QDs) were prepared by hot injection method at low temperature to use as a sensitizer for QDSC. The formation of tetragonal phase and stoichiometry were confirmed by X-ray diffraction (XRD), Raman spectroscopy and energy dispersive X-ray (EDX) analysis, respectively. The UV–Vis-NIR and photoluminescence spectroscopy was used to determine the bandgap (1.66 eV) and narrow emission (1050–1130 nm) range. Moreover, transmission electron microscopy (TEM) was used to find out the average size of CZTSe QDs and it was found to be ~5 nm. It can highly adsorb on the porous TiO_2 nanofibers (NFs) and enhance the absorbance due to its smaller size. The photoconversion efficiency was investigated using the prepared CZTSe QDs sensitized porous TiO_2 NFs based QDSC and its photoconversion efficiency (PCE) was found to be 3.61% which is higher than that of the conventional TiO_2 NFs based QDSC ($\eta \approx 2.84\%$).

1. Introduction

Energy crisis is the major issue concerning the world at present and researchers are working intensively to improve the performance of electrochemical energy devices such as dye sensitized solar cell (Liu et al., 2017), perovskite solar cell (Qiang et al., 2017; Hu et al., 2017; Qinzhi et al., 2018), Li-ion batteries (Lin et al., 2018), supercapacitors (Deng et al., 2018), fuel cells (Huayun et al., 2018), water splitting (Anantharaj et al., 2017) etc, because of their potential to generate and store energy in a sustainable and environmental friendly and make it accessible upon demand. Among various renewable energy sources, solar energy has the potential to contribute a significant fraction of the world's energy demand. Over the past decades, quantum dots sensitized solar cell (QDSC) has drawn a lot of attention because of the possibility of boosting the photoconversion efficiency (PCE) beyond the traditional Shockley and Queisser limit of conventional silicon solar cells. QDSC has shown the exponential increase in PCE and has recently achieved the milestone of 11.6% efficiency as reported by Jun Du et al. (Du et al., 2016) which have shed light on the future potential of quantum dots in the commercialization of QDSCs. Colloidal quantum dots are attractive due to their superior optical properties such as bandgap tuning, higher absorption coefficient, a unique property of multiple exciton generations, facile synthesis process and can have a wide range of solar spectrum by size control etc., (Kim, 2015; Kouhnavard et al., 2014). Besides the binary QDs (Shengyuan et al., 2014; Sudhagar et al., 2009), multinary (ternary and quaternary) QDs (Li et al., 2015a; Mcdaniel et al., 2013; Du et al., 2016; Guijarro et al., 2014; Li et al., 2015a; Mcdaniel et al., 2013) have been reported as a promising candidate for future QDSCs, due to their fascinating properties such as direct bandgap ~1–1.5 eV that can harvest wide solar spectrum from visible to near-infrared (NIR), high absorption coefficient ($\sim 10^5\ cm^{-1}$) along with good photostability and low toxicity when compared to toxic Cd and Pb based QDs (Dun et al., 2014; Engberg et al., 2015).

The concept of making alloy devoting more research in case of multinary QDs such as $CuInSe_2$/ZnS that could improve the properties of photovoltaic devices. The ternary QDs have also attained much attention as an efficient sensitizer in the last few years and reported to obtain efficiency of < 6% (Li et al., 2015b). However, synthesis of alloy QDs ($CuInSe_2$-ZnS and $CuInSe_2$-ZnSe) leave behind the cohabitation of two phases which led to a mismatch in the crystal formation and hence create the defect (Nelson et al., 1993; Takei et al., 2014). To overcome these limitations, In-situ QD alloys have been synthesized which suppresses back electron recombination and favours conduction band upliftment inside the cell. Very recently, Bai et. al. has prepared defect free quaternary Cu_2ZnSnS_4 QDs to use as a sensitizer for QDSC and reported 3.29% efficiency (Bai et al., 2015). Its high bandgap energy of

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~1.5 eV enables the Cu_2ZnSnS_4 QDs to absorbs less in near-infrared region, which might be the reason for the reported low efficiency. Hence, to increase the absorption range in the near infrared region with a narrow bandgap, we have chosen $Cu_2ZnSnSe_4$ QDs as the sensitizer. It has been recognized as a suitable sensitizer because of its bandgap of ~1.0 eV (Yang et al., 2016), less toxicity and higher conduction band edge to semiconductor metal oxides which are the necessary factors to increase the electron kinetics inside the cell and photocurrent density (Wang et al., 2014).

The PCE of QDSCs is not only dependent on the selection of the sensitizer but also on the performance of the photoanode material. The photoanode material plays a crucial role that decides the quantity of QDs uptake and penetration of liquid electrolyte which seems to influence the fill-factor and photovoltage of the cell. In case of TiO_2 nanoparticles, grain boundaries among nanoparticles will increase the probability for recombination of electrons and thereby reducing the photovoltaic performance (Choi et al., 2010). To overcome this problem, we prepared one-dimensional TiO_2 NFs by electrospinning technique to improve the photovoltaic performance of QDSC. In the present work, we used polyvinylpyrrolidone (PVP) as a polymer template to produce one-dimensional TiO_2 NFs. Besides that, we prepared $Cu_2ZnSnSe_4$ QDs by simple one-pot hot injection method and investigated their morphological, structural and optical properties. Its first-time applicability to use as a sensitizer in QDSC with porous TiO_2 NFs based photoanode is also studied in detail.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (TiP, 99%), polyvinyl pyrrolidone (PVP, M_w = 1300,000), copper chloride ($CuCl_2{\cdot}2H_2O$, 99.9%), zinc chloride ($ZnCl_2$, > 97%), tin tetrachloride ($SnCl_4{\cdot}5H_2O$, 98%), selenium powder (99.9%), oleylamine (Technical grade, 70%), 1-Dodecanethiol (> 98%), were procured from the Sigma-Aldrich. Methanol (> 99.5%), ethanol (> 99%), chloroform (> 95%), acetic acid glacial (99–100%) and glycerol (GR 87%) were procured from the Merck India Ltd. and used without further purification.

2.2. Synthesis of $Cu_2ZnSnSe_4$ quantum dots

CZTSe QDs were synthesized by one-pot hot injection method as per our previously reported procedure (Nisha et al., 2017) by using phosphine-free oleylamine (Mourdikoudis and Liz-Marzán, 2013) as the solvent and 1-Decanethiol as the capping agent to obtain the narrow distribution of QDs. This typical synthesis follows two steps; First, 2 mmol of Se powder in 10 mL of oleylamine was taken in a two neck round bottom flask and refluxed at 150 °C for 1 h to form Se-OAm complex under stirring. Second, 0.2 mmol of $CuCl_2{\cdot}2H_2O$, 0.1 mmol of $ZnCl_2$ and 0.1 mmol of $SnCl_4{\cdot}5H_2O$ were taken with 10 mL of OAm and 1 mL of 1-DDTin a 50 mL round-bottom flask and heated up to 170 °C under N_2 gas atmosphere. At 200 °C, the pre-prepared Se-OAm solution was quickly injected into this homogenous precursor solution under continuous stirring to form QDs that was evident by the colour change into black. Later, the reaction was maintained for 10 min to undergone the growth process and then allowed to cool followed by precipitation using 10 mL of cold methanol. The pure form of CZTSe QDs was obtained by centrifugation for 3 times using ethanol and methanol. Finally, these QDs were dispersed in chloroform for further studies (Fig. 1).

2.3. Preparation of CZTSe QDs sensitized porous TiO_2 NFs

The highly porous TiO_2 NFs were prepared by solvosonication process by mixing conventional TiO_2 NFs with glycerol (pore-forming medium). The ultrasonication (Leela Sonic, 50 W, and 30 kHz) was done for 90 min. Then, NFs are separated from glycerol and calcined at 300 °C for 10 min in a muffle furnace (Technico, India) to get highly porous TiO_2 NFs (Singh et al., 2018). This porous TiO_2 NFs has interconnected porous structure with higher porosity and surface area than the conventional TiO_2 NFs (Singh et al., 2018).

The porous TiO_2 NFs paste was prepared by a standard method (Subramania and Zaahir Salam, 2014). Briefly, the FTO glass plates were cleaned with de-ionized water, acetone and ethanol in an ultrasonic bath for 5 min, and then dried in a hot air oven. The prepared TiO_2 paste was coated on the FTO substrate by doctor blade technique using adhesive scotch tape so the thickness of ~11–12 μm was maintained. This coating was sintered at 450 °C for 30 min and cooled to 80 °C. This coated substrate was directly dipped into CZTSe QDs colloidal solution (5 mg CZTSe QDs dispersed in 5 mL of chloroform) for 24 h to complete the adsorption of CZTSe QDs onto the porous TiO_2 NFs. The resultant photoanodes were finally rinsed with chloroform and then dried to get CZTSe QDs sensitized porous TiO_2 NFs.

2.4. Physical characterization

The crystal structure and phase purity of prepared CZTSe QDs were confirmed by X-ray diffraction analysis (Rigaku Ultima IV) using Cu-Kα (1.54 Å) source over the scan range of 20–80° with an increment of 0.02°. The existence of secondary phase in CZTSe QDs was recorded by Raman spectroscopy (Renishaw, Model: RM 2000) equipped with the confocal microscope using a 488 laser with 30 s of exposure time and 0.05% optical power. The oxidation states of CZTSe QDs were determined by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra DLD (Kratos Analytical Ltd.), with an X-ray source of mono Al Kα (1486.71 eV, 5 mA) and an operation power of 75 W. The average size distribution of CZTSe QDs was confirmed by using dynamic light scattering (DLS) technique as well as transmission electron microscope (FEG-TEM, JSM-7600F) with recorded selected-area electron–diffraction (SAED) pattern. The absorbance spectra were recorded by using UV–Vis-NIR spectrophotometer (Perkin Elmer, Model: L-650) and the photoluminescence spectra were recorded by using luminescence spectrometer (Nanolog, Horiba, Jobin Yvon) with Xenon lamp as the source of excitation.

2.5. Fabrication of QDSCs

The photoanodes were prepared as in Section 2.3 and for the counter electrode part, Cu_2S nanoparticles paste was prepared by using 95 wt% of Cu_2S nanoparticles in 5 wt% N-methyl-2-pyrrolidone (binder) and then coated on pre-treated FTO glass plate by doctor blade technique (Saranya et al., 2016). The prepared photoanodes and the counter electrodes were sealed using 60 μm surlyn hot melt spacer. The space of cell was filled with polysulfide redox electrolyte containing 2 M Na_2S, 2 M S, 0.2 M KCl in 3:7(v/v) mixture of methanol and de-ionized water through the predrilled holes on the counter electrode. Later, the holes were closed by using a surlyn strip and left as such for few hours so that complete diffusion of electrolyte into the photoanode as well as the counter electrode takes place. The active area of the cell was 0.30 cm^2.

The photoconversion efficiency of fabricated QDSCs were determined by a calibrated AM 1.5 solar illumination (Newport, Oriel Instruments, USA, 150 W, Model: 67005) with a light intensity of 100 mW cm^{-2} calibrated using standard silicon solar cell (Newport, Oriel instruments, Model: 91150V) and a computer-controlled digital source meter (Keithley, Model: 2420). A series of photoconversion efficiency for three different fabricated QDSCs based on CZTSe QDs sensitized porous TiO_2 NFs as photoanode were studied and an average of these three cell efficiencies was taken as the final cell efficiency. The electrochemical AC-impedance measurements (Biologic-VSP, France) were carried out under AM 1.5 sun illumination at room temperature in the frequency range of 1–100 kHz with an AC amplitude of 10 mV