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A novel process for sensitization and infiltration of quantum dots in mesoporous metal oxide matrix for efficient solar photovoltaics response

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ABSTRACT

Cadmium telluride (CdTe) quantum dots are integrated with mesoporous titanium dioxide "TiO_2" electrode using an in-situ sensitization approach for the first time, where water soluble N-Acetyl Cysteine capped CdTe quantum dots (diameter 4–5 nm) are grown hydrothermally inside mesoporous TiO_2 electrode matrix. This in-situ sensitization approach has shown the effective sensitization over the conventional reported sensitization processes. The in-situ CdTe sensitized TiO_2 electrodes are further unified with PbS counter electrode to realize the quantum dot sensitized solar cell (QDSSC). The fabricated CdTe QDSSC has shown the optimal short circuit current density 3.35 ± 0.21 mA/cm^2 and open circuit voltage 0.58 ± 0.01 V. The observed current density is the highest among such cell configurations, reported till date. The in-situ sensitized CdTe QDs are further treated with zinc sulfide for surface passivation to realize the reduced back recombination, if any. These ZnS passivated CdTe QDs sensitized solar cells in similar device configurations resulted into the significant reduction in the short circuit current density (20%) with the minimal change in open circuit voltage (5%). The impedance spectroscopy measurements suggest that the transmission resistance "R_{tr}" has increased after ZnS treatment for these electrodes, however, the recombination resistance R_{rec} has not changed much. The observed high R_{tr} might be responsible for the observed current deterioration after ZnS surface passivation. These studies suggest that in-situ QD sensitization may provide a new method of integrating QDs into mesoporous TiO_2 matrix for effective QDSSC device performance without any additional surface passivation.

1. Introduction

Silicon based solar photovoltaic devices and photovoltaic systems have shown promise and are in use for large scale power plants as well as distributed applications (Nayak et al., 2012). The solar photovoltaic potentials and promises have opened possibilities to explore the alternative photovoltaic materials and devices (Galliano et al., 2018; La Notte et al., 2017; Palma et al., 2017), which may provide efficient and cost effective solutions to the direct electricity generation. These new photovoltaic materials are not only promising candidates for future applications but also opens new challenges in understanding the underlying physical phenomenon as well. Quantum Dots are one such promising candidates, which have not only potential in solar photovoltaic, but also have shown promise in the other domains of science and technology such as sensors (Murphy, 2002), bio- imaging (Saha et al., 2013), photodetector (Konstantatos and Sargent, 2011), field effect transistors (Choi et al., 2012), light emitting diodes and color displays (Jang et al., 2010). Colloidal quantum dots are exciting for photovoltaic applications because of their interesting physical properties like size tunable band gap (Alivisatos, 1996), large extinction coefficient and possibility of multiple exciton generation phenomena (Nozik, 2008). These interesting properties place Quantum Dot solar cell under third generation photovoltaic systems (Beard et al., 2013), where detailed balance calculation has shown that the theoretical efficiency of QDSSCs may cross Shockley Queisser limit (Klimov, 2006). Several configurations are under investigations for Quantum Dots based solar cells such as quantum dot sensitized solar cell, heterostructure quantum dot solar cell (Nozik, 2002). The configuration of quantum dot sensitized solar cells (QDSSCs) is similar to that of the dye sensitized solar cells (DSSCs) (Sugathan et al., 2015), as shown in the schematic diagram in Fig. 1, which explains the integrated subcomponents for a QDSSC structure. The respective electronic energy levels of CdTe quantum dot with TiO_2 is shown schematically in the zoomed view of Fig. 1. The schematic process also explains the incident photon

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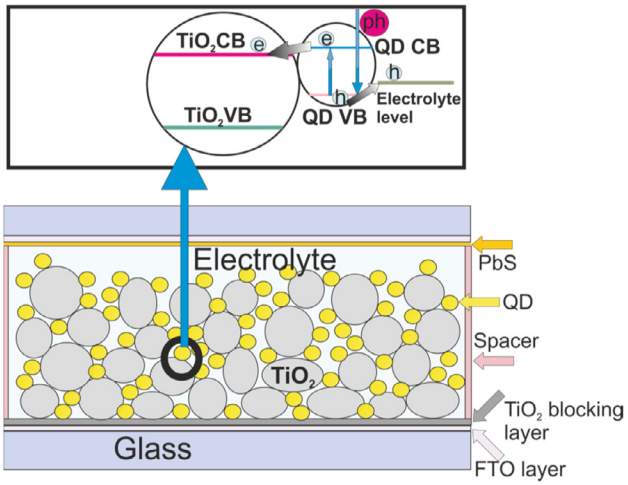

Fig. 1. The schematic structure of quantum dot sensitized solar cell with desired electronic processes, (shown in top of figure).

absorption across the quantum dot and exciton generation with electron transfer from CdTe quantum dot to the valence band of TiO_2 semiconductor. The only difference in structure lies in the fact that QDSSCs uses quantum dots as an absorber in place of the active dye, used in DSSCs.

The sensitization of mesoporous wide band gap semiconductor electrode ("TiO_2" in our case), plays an important role in the performance of QDSSCs (Guijarro et al., 2009a,b). The physical attachment of QDs as absorber to the mesoporous electrode is quite crucial for good photovoltaic performance (Guijarro et al., 2010). Various sensitization approaches for mesoporous electrode have been explored in the past like direct adsorption (Lai et al., 2014), chemical bath deposition (CBD) (Gorer and Hodes, 1994), electrophoretic deposition (EPD) (Tachibana et al., 2008), linker assisted direct adsorption (Lai et al., 2014), successive ionic layer adsorption and reaction (SILAR) (Lee et al., 2009) as summarized in Fig. 2, with their respective advantages and disadvantages. Each of these sensitization schemes lead to different quantum dot loading fractions and different size control, thus, directly

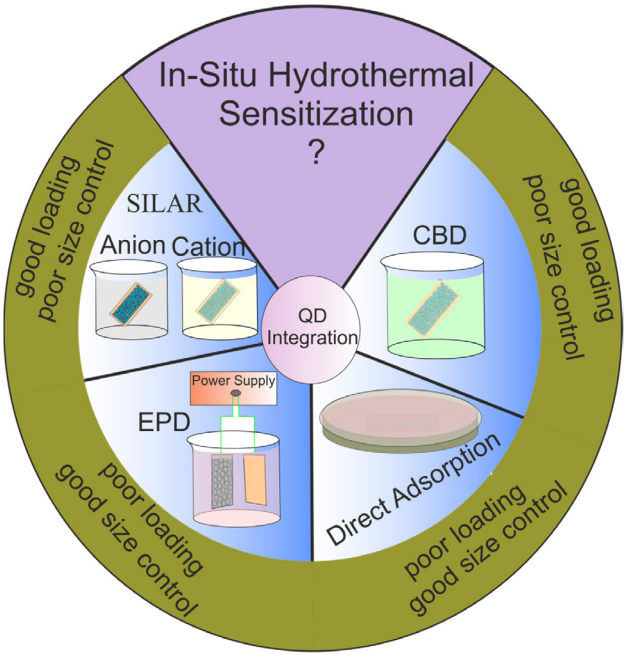

Fig. 2. The Schematic diagram showing comparison of various sensitization schemes used for quantum dot sensitized solar cell fabrication.

affecting the performance of QDSSCs (Guijarro et al., 2009a,b). For example, in direct adsorption, size and shape of quantum dots can be controlled, but it contributes to the poor loading of the quantum dots (Lai et al., 2014), where as in case of chemical bath deposition, high loading of quantum dot can be achieved but aggregation of quantum dots result in enhanced recombination (Hodes and Gorer, 1994). For example, in SILAR, number of cycles need to be optimized for proper QD loading, where less QD loading may lead to the poor absorption and large QD loading may cause the enhanced recombination (Lee et al., 2009). The electrophoretic deposition process is not suitable in general for water soluble quantum dots because of the limited operating voltage range for water, as electrophoretic process requires higher electric field (Poulose et al., 2012).

In this work, a new methodology is developed for effective quantum dot sensitization in mesoporous electrode. The initial direct adsorption of water soluble N-Acetyl Cysteine (NAC) capped CdTe quantum dots into mesoporous TiO_2 matrix has resulted into poor sensitization even after direct dipping of mesoporous TiO_2 electrodes in QD solutions for 48 h under dark conditions. In contrast to the direct adsorption constraints such as long duration and inefficient sensitization, the developed in-situ sensitization process, where TiO_2 mesoporous electrodes are sensitized in-situ during hydrothermal growth of quantum dots in an autoclave, led to the enhanced sensitization. Thus, the developed process may provide an efficient and easy way to integrate the water soluble quantum dots into the mesoporous electrode matrix.

Further, to understand the limitations of the developed process, in addition to in-situ sensitization, the surface modification of sensitized electrode has also been investigated using zinc sulfide "ZnS" thin film coating with SILAR. This ZnS is supposed to reduce back recombination, if any, as reported earlier (Guijarro et al., 2011). The observations suggest that transmission resistance has increased after sensitization, while recombination resistance remained nearly unaffected after ZnS surface treatment of CdTe QDs.

2. Experimental details

2.1. Materials required

Cadmium chloride (99.99%, Alfa Aesar), N-Acetyl-L-cysteine (NAC) (99%, Sigma-Aldrich), Tellurium powder (99.8%, 200 mesh, Sigma-Aldrich), Sodium borohydride (96%, Sigma-Aldrich), Titanium (IV) chloride solution in 20% HCl (0.09 M, Sigma Aldrich), Sodium sulfide hydrate (assay > 60%, Sigma-Aldrich), Sulphur powder (Merck), Potassium chloride (99.5%, Vetec), Sodium Hydroxide pallets (Merck), Zinc Nitrate Hexahydrate (98%, Alfa Aesar) and TiO_2 paste (wer-2, Dyesol) were purchased and used as received without any modifications. Fluorine dope tin oxide (FTO) with 7–10 ohm/sq resistivity was purchased from Global Nanotech and used for fabricating quantum dot sensitized solar cells.

2.2. Mesoporous TiO_2 electrode preparation & in-situ sensitization of CdTe quantum dots during hydrothermal growth process

The fluorine doped tin oxide (FTO) coated glass substrates are cleaned thoroughly to remove any surface impurities (Grinis et al., 2010). A thin amorphous TiO_2 blocking layer is deposited prior to the deposition of mesoporous TiO_2 electrode. A 40 mM solution of titanium (IV) chloride ($TiCl_4$) was prepared in 30% HCl solution and cleaned FTO substrates were dipped at 70 °C for 30 min in this solution, followed by the calcination at 450 °C for 30 min. The TiO_2 paste is applied above amorphous TiO_2 layer using Dr. blade method in conjunction with scotch tape to maintain the uniform thickness. These synthesized mesoporous TiO_2 electrodes were dried at 100 °C for 1 h, followed by the final sintering at 500 °C for 1 h under normal ambient conditions.

A 30 mM Cadmium chloride and NAC was dissolved in water in a three neck flask under inert ambient maintained using continuous flow