Ba-ZnS passivation layer for improved performance of quantum dot sensitized solar cells

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Abstract

We report an inexpensive TiO_2 based quantum dot solar cell (QDSSC) with improved power conversion efficiency prepared by simple techniques. Barium doped zinc sulfide has been successfully deposited on cadmium sulfide quantum dots (QDs) by simple successive ion layer adsorption and reaction (SILAR) technique. The Barium doped zinc sulfide is utilized as a passivation layer in the QDSSC, which helped in better charge separation. The copper sulfide (Cu_2S) and reduced graphene oxide deposited on FTO was used as a counter electrode. The developed QDSSC showed superior performance when tested with AM 1.5 solar simulator using sulfide/Polysulfide electrolyte. The photoconversion efficiency of FTO/TiO_2/CdS/BaZnS/Cu_2S-Graphene oxide is better than that of FTO/TiO_2 /CdS/ZnS/Cu_2S-Reduced Graphene oxide.

Keywords: TiO_2, ZnS, passivation layer, solar cells, quantum dot.

Introduction

QDSSCs belong to the third generation solar cells, narrow band gap semiconductor quantum dots (QDs) are used as the sensitizer. The tunable band gap makes QDs very useful as sensitizers. A variety of semiconductor QDs, viz. PbS, CdS, CdSe and CdTe have been successfully employed as visible light sensitizers for Titanium Dioxide based photoanodes [1-3]. The use of QDs enables band gap tuning through control of the QD size, which allows one to control light absorption and injection of electrons to TiO2. The hole transporting electrolyte takes holes and generates photocurrent. High absorption coefficients, the multiple exciton generation phenomenon and short excitonic path length of QDs would lead to the enhancement of the conversion efficiency in QD sensitized solar cells. The quantum dot sensitized solar cells (QDSSCs) have superiority over dye sensitized solar cells in terms of stability and they are considered to be the good substitute for silicon based solar cells.[4,5]

The QDSSCs normally consists of a sandwich structure of photoanode sensitized with a quantum dot (QD) and counter electrode. Electrolyte used in QDDSCs is sulfur-polysulfide redox couple.

Many attempts were made by the researchers to enhance the photoconversion efficiency of QDSSCs. The reported maximum photo conversion efficiency for this kind of solar cells was 6.76%, which is quite low compared to dye sensitized solar cells (11%). The main reasons for low conversion efficiency are narrow absorption range of QDs, difficult to obtain well covered monolayer of QDs on mesoporous TiO_2 without agglomeration, electron-hole recombination at quantum dot-electrolyte boundary and energy loss at the boundary of electrolyte and counter electrode.[6]

The electron transfer process at the interface determines the conversion efficiency and it is often influenced by electron-hole recombination process. [6] ZnS layer is used as a separation or passivation layers, which inhibits the charge recombination process to some extent and increases the efficiency. We made an attempt to enhance the photoconversion efficiency of QDSSCs by doping ZnS with Barium.

Experimental

Materials/ Chemicals details

Fluorine doped tin oxide (FTO) glass of dimension 25mm x 25mm x 1.1mm were cleaned by distilled water and alcohol and dried. FTO was employed as substrate because of its good conductivity and resistance (<10Ω/sq). The chemicals used to prepare solar cells were procured from Sigma-Aldrich. All other reagents used were of analytical grade and were used without further purification.

Material synthesis / reactions/ device fabrications

1g of TiO_2 was added to2 ml of distilled water with small amounts acetic acid and SDS to make a paste. A thin film of TiO_2 was coated on FTO glass substrate by simple doctor blade technique. The deposited TiO_2 was heated at 450 ^{0}C in muffle furnace for 30 min. The incorporation of TiO_2 with CdS Quantum dots (QDs) sensitizer was done by successive ionic layer adsorption and reaction (SILAR) technique. Initially, the TiO_2photoanode was dipped in 0.1 M $Cd(NO_3)_2$ solution 2 min after that it was dipped in distilled water for 20 s to remove excess Cd^{2+} ions then it was dipped in 0.1 M Na_2S for 2 min and dipped in distilled water for 20 s. This procedure is repeated seven cycles to sensitize TiO_2 with CdS.

Ba doped ZnS passivation layer was coated by SILAR Method. The CdS sensitized TiO_2 photoanode was dipped in the solution containing 0.1 M $Zn(NO_3)_2$ and 0.01 M $BaCl_2$ for 2 min after that it was dipped in distilled water for 20 s to remove excess Zn^{2+} and Ba^{2+} ions then it was dipped in 0.1 M Na_2S for 2 min and dipped in distilled water for 20 s. This procedure is repeated for two cycles to coat BaZnS Passivation layer.

To compare with bare ZnS, we followed the same procedure to coat ZnS on TiO_2/CdS photoanode without using $BaCl_2$.

Reactions that take place during SILAR technique for coating CdS is;

$$Cd^{2+} + S^{2-} \longrightarrow CdS$$

Reactions that take place during SILAR technique for coating BaZnS passivation layer is;

$$Zn^{2+}, Ba^{2+}\ (10{:}1) + S^{2-} \longrightarrow BaZnS$$

Reactions that take place during SILAR technique for coating ZnS passivation layer is;

$$Zn^{2+} + S^{2-} \longrightarrow ZnS$$

The counter electrode was prepared by depositing Cu_2S-reduced Graphene oxide (Cu_2S-rGO) composite on FTO substrate. Graphene oxide was prepared by modified Hummer's method [7]. The Cu_2S-rGO was prepared using a procedure reported by Radich *et al*[8]. The two electrodes are sandwiched using a spacer and electrolyte sulfur-polysulfide was prepared by mixing 0.2g of Na_2S, 0.6g of sulfur and 0.1 M NaOH in 10 ml water and injected between the two electrodes.

Characterizations

For characterization of photoanode, a Siemens X-ray Diffractometer (CuK_α source) (XRD) AXS D5005 was used.

Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer equipped with integrating sphere (Perkin Elmer, Waltham, MA, USA) was used to record diffuse reflectance spectra.

The Photovoltaic performance of QDSSCs were tested by integrated J-V test station (PVIV-211V) and Oriel Sol3A solar simulator (AM 1.5).

Results and discussion

The schematicdesign of fabrication process of photoanode is shown in **Fig. 1**. The first step involves coating a layer of TiO_2 on FTO glass substrate by doctor blade technique. The second step involves sensitization with CdS QDs by SILAR method and finally the same SILAR method is employed to deposit barium doped zinc sulfide on TiO_2/CdS.

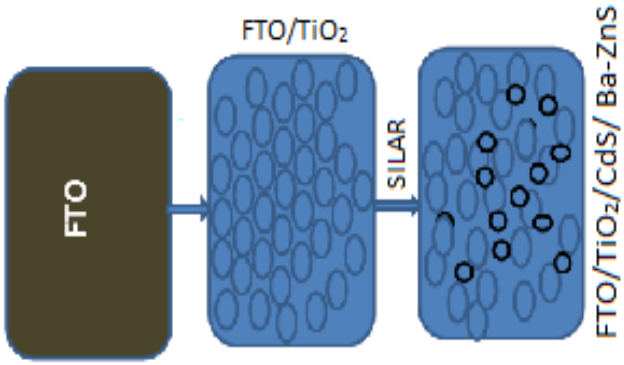

Fig. 1. Schematic presentation of fabrication process of photoanode.

When light strikes the solar cell, the photons are absorbed by CdS QDs generating electron hole pairs. The generated electron-hole pairs are immediately partedinto electrons and holes. The electrons are pushed into TiO2 nanoparticles and holes are scavenged by electrolyte sulfur-polysulfide redox couple. The redox couple then transfers the holes to Cu_2S-rGO counter electrode

The diffuse reflectance spectrum shown in **Fig. 2** was taken using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer. Diffuse reflectance spectra were recorded in the range 2000 – 200 nm using Barium sulfate as a reflectance standard.

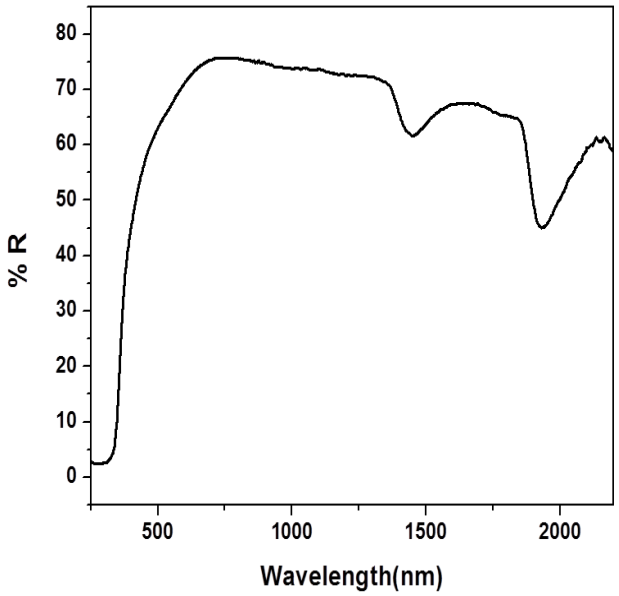

Fig. 2. The Diffuse reflectance spectra of TiO_2/CdS/BaZnS

The diffuse reflectance spectrum shows absorption at various wavelengths indicating wide tunability of QDs.

The X-ray diffraction pattern of TiO_2/CdS/BaZnS electrode is shown in **Fig. 3**. The diffraction peaks related to TiO_2, CdS and ZnS were identified. The peaks with 2θ angles 25.2, 38.0, 48.2, 53.9, 55.0 and 62.5 corresponding to 101, 004, 200, 105, 211 and 204 were assigned tolattice planes anatase TiO_2. The peaks with 2θ angles 26.8, 44.4 and 52.6 corresponding to 111, 220 and 311 were assigned to lattice planes CdS. Other peaks are due to ZnS and FTO. The reduction in the intensity of peaks can be attributed to doping of Ba on ZnS or some amorphous substance might have been formed.

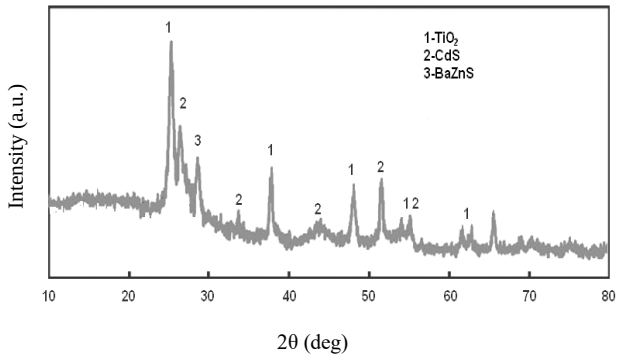

Fig. 3. XRD pattern of photoanode FTO/TiO_2/CdS/BaZnS

The performance of the fabricated QDSSCs were tested with AM 1.5 solar simulator using sulfur – polysulfide electrolyte

The photovoltaic parameters, open Circuit voltage, V_{oc}, Short circuit current, J_{sc}, Fill Factor, FF and the photoconversion efficiency η are reported in the **Table 1.**

Table 1. Photovoltaic parameters* of prepared solar cells.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
TiO_2/CdS/ZnS/Cu_2S-rGO	0.58±0.03	6.20±0.03	0.46±0.02	1.65±0.15
TiO_2/CdS/BaZnS/Cu_2S-rGO	0.61±0.03	7.06±0.05	0.48±0.03	2.06±0.22

*Results are tabulated and calculated for three tested cells.

The results suggest that the photoconversion efficiency of FTO/TiO_2/CdS/BaZnS/CuS-rGO is better than that of FTO/TiO_2 /CdS/ZnS/CuS-rGO.

Conclusion

TiO_2/CdS QDSSCs were fabricated successfully using simple SILAR Method.

The BaZnS passivation layer enhances the efficiency of QDSSCs by 19.9% compared to ZnS as passivation layer.

The photoconversion efficiency of fabricated QDSSC with BaZnS passivation layer was 2.06%

The photoconversion efficiency of fabricated QDSSC with ZnS passivation layer was 1.65%

Author's contributions

Conceived the plan: NHA, DRK and RMK; Performed the expeirments: DRK, RMK; Data analysis: NHA, DRK, RMK; Wrote the paper: DRK, NHY, RMK. Authors have no competing financial interests.

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