

A Green Approach to Sustainable Energy using Quantum Dots

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Abstract: The sunlight is the potential renewable green energy source considering the availability of solar energy in abundance and the need for clean and renewable source of energy. The solar energy is dispersed largely in the electromagnetic spectrum including ultraviolet, visible and infrared regions. Quantum dots are semiconductor nanocrystals having considerable interest in photovoltaic research areas. Cadmium sulfide-sensitized solar cells are synthesized by Chemical bath deposition and titanium nanowires were fabricated by hydrothermal method. The synthesized CdS quantum dots are sensitized to nanoporous TiO₂ films to form quantum dots-sensitized solar cell applications. The introduction of TNWs enables the electrolyte to penetrate easily inside the film which increases the interfacial contact between the nanowires, the quantum dots and the electrolyte results in improvement in efficiency of solar cell. Green synthesis of quantum dots is also studied. Field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and ultraviolet-visible light (UV-VIS) spectrometer are used for characterization. An efficiency of 2.98% was achieved for the CdS quantum dots-sensitized solar cells via the current technique.

Index Terms: Green synthesis, QDSSC, quantum dots, solar cells, titanium nanowires

I. INTRODUCTION

Solar photovoltaics power generation is a clean sustainable energy technology. The direct conversion of light energy to electricity occurs without any environmental emissions, thus it is eco-friendly and green. Maximum conversion efficiency can be obtained based on the material nature. Quantum dot sensitized solar cells (QDSSCs) have the same device layout as that for DSSCs and the dyes are replaced with semiconductor quantum dots. Lot of semiconductor resources along with CdS, CdSe, CdTe, PbS, PbSe, InP, HgTe, Ag₂S, Sb₂S₃, Bi₂S₃, Cu₂S, CuInS₂ have

been investigated for applications in quantum dot sensitized solar cells. CdS, CdSe and PbS has bandgaps of 2.4-2.42 eV, 1.73-1.74 eV and 0.34-0.37 eV. Colloidal quantum dot based solar cells can be processed from solution at low expenditure. For solution processable solar cells to be practically applied, they should attain a photo conversion efficiency of 10 %. Quantum dots are prepared mostly from the second and sixth group elements of the periodic system - Cadmium Chalcogenides (CdS, CdSe, CdTe), Zinc (ZnSe, ZnS, ZnTe) and third and fifth group, Phosphides and Indium Arsenides. Quantum dots can be engineered for the fluorescence in different wavelength based on the physical dimension. The entire range of spectrum can be accessed by the application of diverse colloidal quantum dots for different parts of the visible spectrum.

Quantum dots absorb light photons and release longer wavelengths of photons for a period of time. The tuning of the quantum dot size gives a way to specific control on the wavelength of the emitted photons. That means the colour of the light emitted from the quantum dot can effectively be manipulated with our most important cost or with the use of nanotechnology. The smaller the size of the crystal, the band gap will be smaller, the energy between the highest valence band and lowest conduction band will be high. Thus requires upper frequencies of light after excitation of the dots because the crystal dimension goes smaller ensuing equivalent shift from high to low in light emission. As the nanomaterial becomes larger, the energy gap become smaller and the quantum dot change its colouration from violet to red.

In a conventional solar cell, light is allowed to pass through a thin layer of n-type semiconductor. If the photons have energy exceeding the bandgap of the semiconductor material, an e-h pair generates. The minimum amount of energy desirable to excite an electron from the valence band of semiconductor to the conduction band is termed as bandgap. Usually photons having lesser energies than the bandgap not get absorbed, while those with higher energies can quickly absorbed. Photons with energies equal to or higher than the bandgap energy get absorbed by the semiconductor material and

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the bandgap therefore determines the range of photons a solar cell can absorb from the solar spectrum. If electrons shift from the valence band to the conduction band, current can flow through the system.

The quantum dot sensitized solar cells applies nanotechnology and quantum mechanics theory to enhance the performance of ordinary solar cells. Quantum dot sensitized solar cell is a solar cell design that uses quantum dots as the absorbing photovoltaic material. In this solar cell, separating the photogenerated exciton and extracting free carriers should happen with as little energy loss as possible [1,2]. Quantum dots are most often incorporated into solar cells devices by the deposition of layers into a quantum dot film, and the highest achieved quantum dot solar cell efficiency is 10.7%. One of the factors limiting the efficiency of solution-processed quantum dot solar cells is the inefficient charge extraction from the active layer of the device to the electrodes [3]. Charges have to hop from dot to dot in order to be collected. Quantum dots are usually solution synthesized and the transport can be enhanced by changing the chemical environment around the quantum dots after deposition.

The QDSSCs are made in a sandwich configuration of two pieces of conducting glass. The main mechanism of the cell are the adsorption of quantum dots to wide band gap semiconductor and deposition on transparent electrode (photoanode), redox mediator electrolyte and counter electrode. FTO glass is chosen as the conducting substrate for the purpose in QDSSCs. The QDSSC revolution began essentially from the application of the n-type wide bandgap TiO_2 layer as semiconductor and extensively used as photoanode in QDSSCs [4,5]. The TiO_2 has many advantages with unique properties including high photosensitivity, high structure stability under solar irradiation and in solutions, non-toxic, low cost and a excellent absorber of the ultraviolet. Counter electrode in QDSSCs is graphite coated FTO glass. The role of counter electrode is to transport the electrons incoming from the external circuit reverse to the redox electrolyte.

In the present work, the quantum dots were synthesised via chemical as well as green route. Synthesized quantum dots were effectively applied in QDSSC. Titanium dioxide nanowires effect on structural and optical properties of QDs was premeditated. A variety of parameters of quantum dot sensitized solar cell were calculated.

II. MATERIALS AND METHODS

A. Preparation of CdS quantum dots

For CdS quantum dots synthesis, Cadmium sulphate is used as the Cd^{++} ion source and thiourea as an S^{--} ion source. Ammonium hydroxide is added dropwise to cadmium sulphate solution at 50°C to adjust pH to 11. Thiourea is

added dropwise to this results in yellow colour precipitate of CdS quantum dots. The precipitate is washed numerous times by double distilled water and kept in oven for drying at 70°C to collect yellow powders of CdS quantum dots.

B. Preparation of CdS Quantum Dots Using Leaf Extract

Moringa oleifera leaves contains sulfur-containing amino acids in higher levels. Moringa oleifera extract was prepared by taking 20g of dry Moringa oleifera leaves, washed, dried and finely crushed mixed with 50ml of deionized water. Boil the mixture at 80°C for 15 min and cooled to the room temperature and the extract filtration is done by Whatmann filter paper. Cadmium sulphate is used as a Cd^{++} ion source and leaf extract is used as S^{--} ion source. Ammonium hydroxide is added dropwise to cadmium sulphate solution at 50°C to adjust pH to 11. Moringa oleifera extract is added dropwise to these results in yellow colour precipitate of CdS quantum dots. The precipitate is washed continuously with double distilled water and kept in oven at 70°C for drying to collect grayish yellow powders of CdS quantum dots.

C. Preparation of TiO_2 nanowires

0.1gram of anatase TiO_2 and 40 ml of 10 M NaOH heated under stirring at 100°C for 5 hours. The mixture is kept in oven at 200°C for 24 hours. The resultant sample is filtered. The filtrate was taken and 1M HCl was added dropwise under stirring until the pH became 7. The precipitate formed is filtered, washed with ethanol and double distilled water continuously. The sample is dried in hot air oven at 70°C for 8 hours. A fibrous white product was obtained.

D. Preparation of TiO_2 Electrode Films

An optically transparent conducting glass, FTO was cleaned with ethanol and deionized water for 10 minutes in ultrasonic bath. Immersed the FTO glass in TiCl_4 aqueous solution for 30 minutes at 70°C to create excellent mechanical contact. A TiO_2 film of thickness 12 to $15\ \mu\text{m}$ was deposited on top of the pretreated FTO glass by means of doctor blading method and sintered over again at 450°C and 500°C for 15 minutes. This sintering process has a great impact on the films. The CdS quantum dots are sensitized by dip coating and the resultant electrode is dried at 60°C .

E. Assembly of the QDSCs

The working electrode used was TiO_2 coated FTO, sensitized with CdS quantum dots. The counter electrode was graphite FTO glass. The cell was fabricated in sandwich form by clamping working electrode and counter electrode, so as to take leads from both the electrodes. An effective working area of $0.25\ \text{cm}^2$ was



exposed to light source, while all other areas were masked. The electrolyte for the quantum dot sensitized solar cell was potassium iodide electrolyte. A solvent consisting of potassium iodide and ethylene glycol is prepared and stored in a dark container. Prior to clamping, one or two drops of electrolyte freshly prepared were placed above the working electrode. It should be ensured that the whole aperture was covered by the electrolyte and the electrodes were tightly held with the help of crocodile clip.

Photocurrent- voltage (I-V) characteristics of quantum dot sensitized solar cells were calculated with a Keithley electrometer on illumination and non-illumination conditions by using the sun simulator Oriol Sol 3A which includes a Xenon lamp at an intensity of 100mW/cm² (AM1.5). The active area of around 0.25 cm² (0.5 cm × 0.5 cm) of the resulting cell is exposed to light.

III. RESULTS AND DISCUSSION

A. Scanning Electron Microscopy (SEM) observations of TiO₂ nanowires and CdS quantum dots

In Fig.1, SEM pictures revealed that CdS quantum dots and TiO₂ nanowires were successfully prepared. Fig.1 (a) shows a high yield of nanowires. The average length of the wires was about 2-4 μm and the average diameter was 40-50 nm. The CdS QDs were observed as spherical like structures that followed chemical bath deposition (CBD) method as in Fig. (b) and showed excellent crystalline natures. The average diameter of the resultant CdS quantum dots was about 6-8 nm by chemical synthesis and 7-9 nm by green synthesis, in Fig.1 (c).

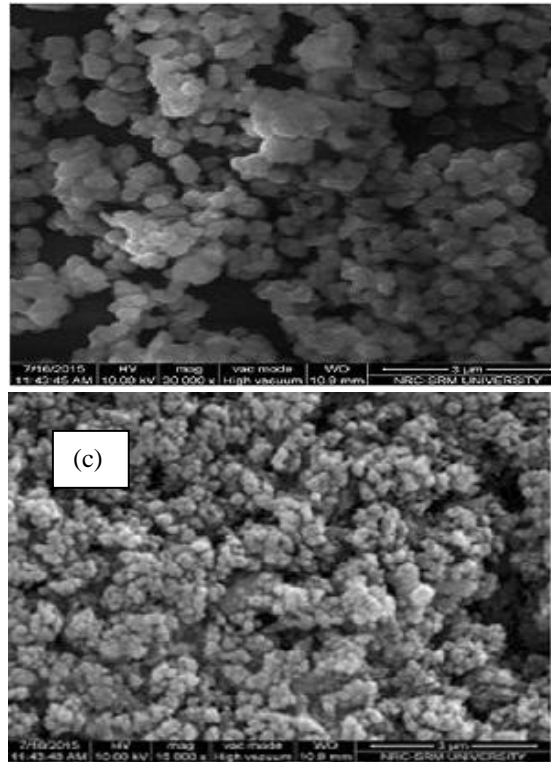
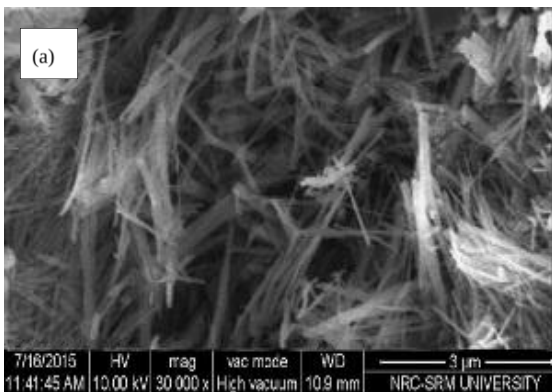


Fig. 1 SEM images of (a) TiO₂ nanowires, (b) CdS quantum dots by chemical method, (c) CdS quantum dots by green method

B. Powder X-Ray Diffractometry (PXRD)

Fig. 2 (a) shows the X-ray diffraction (XRD) pattern of TiO₂ nanowire annealed at 450 °C. In Case of TiO₂ nanowires, the prominent peaks observed at values 27.446 [110], 41.23 [111] and 62.75 [002]. The data clearly indicates good crystallinity of the TiO₂ anatase phase. Fig.2 (b) shows the XRD pattern of the CdS QDs deposited by the chemical bath deposition (CBD) method. The diffraction peaks in the pattern are correspond to the hexagonal phase of CdS. The X-ray diffraction profile is characterized for CdS sample at 55 °C .Peaks were obtained at 27.24 and on other relative weak peak at 2θ =44.27. The obtained X-ray diffraction pattern clearly indicates the formation of single phase cubic CdS quantum dot (JCPDS Card No.- 75-1546) with estimated particle size 1.1 nm The presence of peaks in Fig.2 (c) at 2θ = 27.14°(111), 44.24°(220) shows that the particle size of CdS is very small and was around 1.7 nm

(a) responding to the CdS quantum dots by green method.

C. Fourier Transform Infra-Red (FTIR) Spectroscopy

The relative IR absorbance significantly depends on oxygen coordination around cations in the lattice, crystal geometry and oxidation state of its cations. The IR spectrum of the sample was recorded on a NaCl crystal which is shown in Fig.3. TiO₂-anatase form nanowires having typical peaks at 638, 513 and 397 cm⁻¹ were observed in the FTIR spectrum. An initiation of the prominent peak from 404 cm⁻¹ is a specifically characteristic of TiO₂ anatase. A broad absorption band around 3400 cm⁻¹ is assigned to O-H vibration of absorbed H₂O. The absorption band present at 644 cm⁻¹ corresponds to Cd-S stretching. The band around 1500 cm⁻¹ is due to NH₂ bending. The band near 2353 cm⁻¹ can be attributed to C=O residue probably due to atmospheric CO₂.

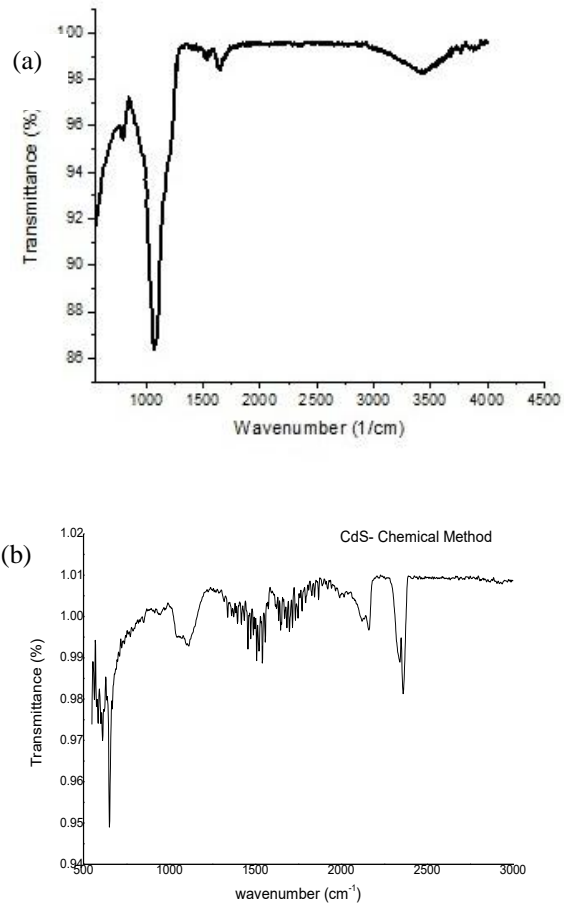
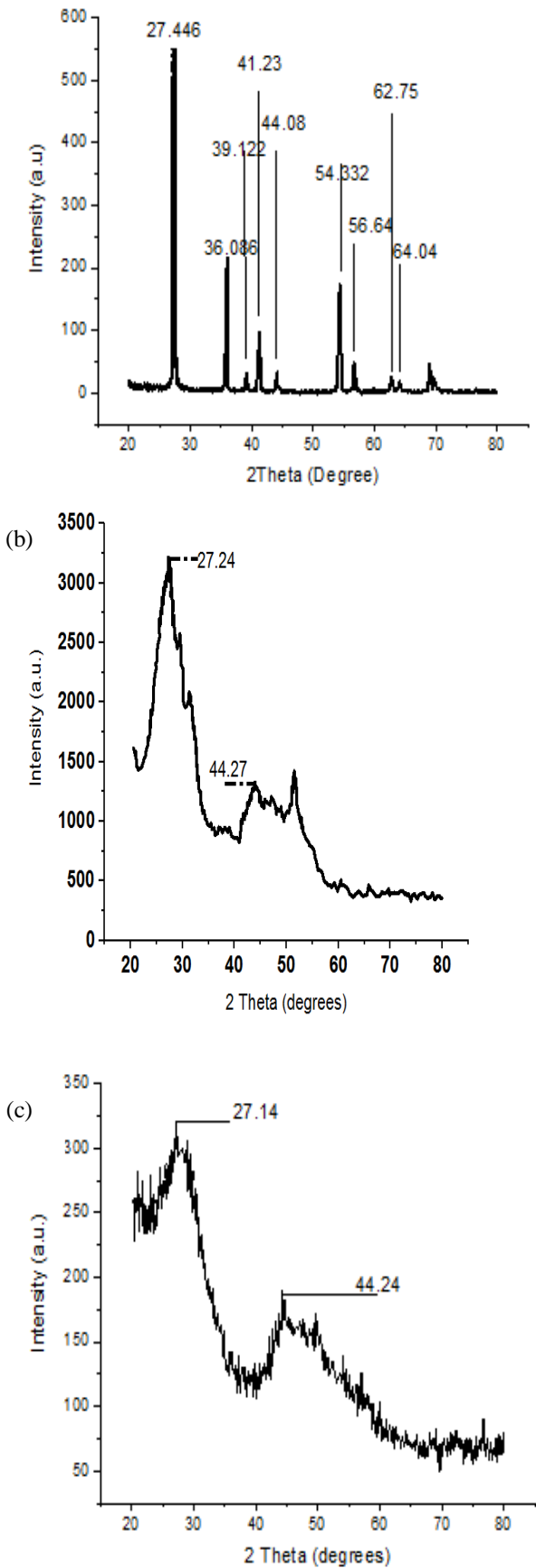


Fig. 2 XRD images of (a) TiO₂ nanowires, (b) CdS quantum dots by chemical method, (c) CdS quantum dots by green method

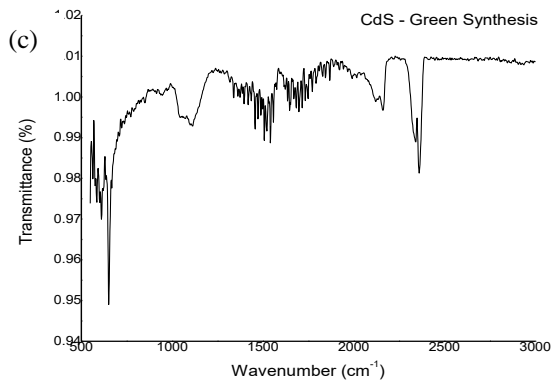


Fig. 3 FTIR spectra of (a) TiO₂ nanowires (b) CdS quantum dots by chemical method and (c) CdS quantum dots by green method

D. U-V Visible Spectroscopy

Fig.4 shows the absorption spectrum obtained and the peak at 252 nm indicates the absorption due to anatase TiO₂. The spectrum shows that the optical absorption peak of CdS quantum dots are shifted to the lower wavelength side comparative to bulk CdS (~530 nm) crystals.

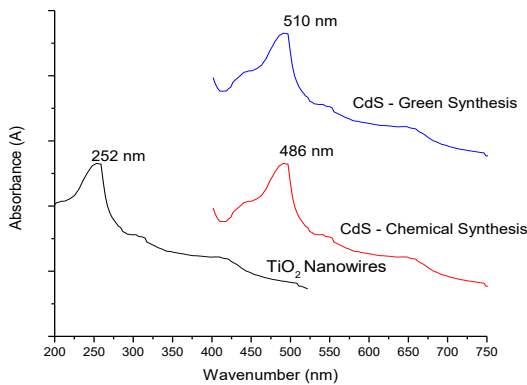


Fig. 4 UV-Visible images of TiO₂ nanowires, CdS quantum dots by chemical method and CdS quantum dots by green method

E. Photocurrent- voltage (I-V) characteristics QDSCs

The I-V characteristics of quantum dot sensitized solar cell (FTO/TiO₂/CdS QDs/Graphite/FTO) were calculated with solar simulator and the results are shown in Fig. 5, Fig. 6 and Fig. 7. The photocurrent is defined as the current produced under light irradiation owing to the production of free charge carriers by absorption of photons inside the depletion layer. The efficiency of solar cell under illumination and non-illumination conditions (with light (wl) and without light (wol)) is also calculated.

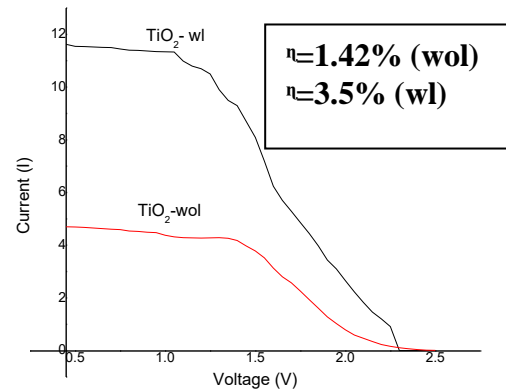


Fig. 5 I-V characteristics of TiO₂ nanowires with light (wl) and without light (wol)

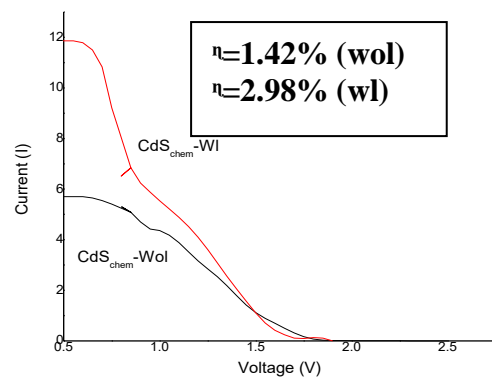


Fig. 6 I-V characteristics of CdS quantum dot solar cell by chemical method with light (wl) and without light (wol)

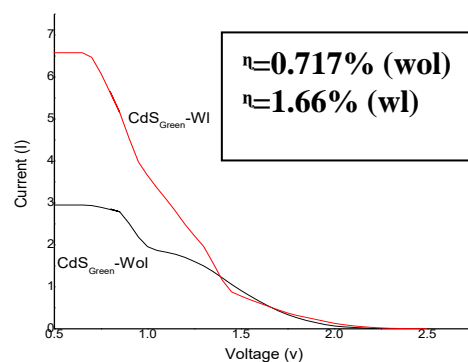


Fig. 7 I-V characteristics of CdS quantum dot solar cell by green method with light (wl) and without light (wol)

Under illumination, a large leakage current causes low open-circuit voltage V_{oc} . When light illuminates over the cell, the I_{sc} always increases slightly and V_{oc} decreased. Fig. 5 shows I-V characteristics of TiO₂ nanowires with light (wl) and without light (wol).



The efficiency of solar cell under non-illumination conditions without light (wl) is calculated as $\eta=1.42\%$, and with light (wl) illumination is calculated as $\eta=3.5\%$. Fig. 6 shows I-V characteristics of CdS quantum dot solar cell by chemical method with light (wl) and without light (wl). The efficiency of solar cell under non-illumination conditions without light (wl) is calculated as $\eta=1.42\%$, and with light (wl) illumination is calculated as $\eta=2.98\%$. Fig. 7 shows I-V characteristics of CdS quantum dot solar cell by green method with light (wl) and without light (wl). The efficiency of solar cell under non-illumination conditions without light (wl) is calculated as $\eta=0.717\%$, and with light (wl) illumination is calculated as $\eta=1.66\%$.

IV. CONCLUSION

It can be concluded that quantum dots are promising sensitizers for photo catalytic applications and it is obvious that CdS sensitized TiO₂ shows a better photo response than bare TiO₂. Electron transfer across the QD-TiO₂ junction, one of the first steps necessary to generate usable photocurrent from QDSSC was attained successfully. The physical and chemical characteristics of the produced TiO₂ and CdS were identified by means of XRD and UV-vis spectroscopy. The annealing process enhanced crystallization quality of the CdS quantum dots. A broad improvement range from 350 nm to 510 nm in the absorption spectrum was observed. The overall energy conversion efficiency of the fabricated cells was high up to 1.80%. The outcomes have demonstrated the applications of chemical bath deposited CdS quantum dots for sensitized solar cells. It is expected that the conversion efficiency can be enhanced further by optimizing the thickness of the TiO₂ electrode which is well suited for harvesting more light energy in solar cell applications.

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