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CdTe Quantum Dots Sensitized TiO_2 Electrodes for Photovoltaic Cells

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Abstract: The preparation and photovoltaic characterization of CdTe quantum dot-sensitized solar cells (QDSSCs) is presented. Fluorine doped Tin Oxide (FTO) substrates were coated with 20 nm-diameter TiO_2 nanoparticles (NPs). Presynthesized colloidal CdTe quantum dots of radius $R = 2.1$ nm were deposited on the TiO_2-coated substrates using direct adsorption (DA) method, by dipping for different times at ambient conditions. The FTO counter electrodes were coated with platinum, while the electrolyte containing I^-/ I^-_3 redox species was sandwiched between the two electrodes. The J-V characteristic curves of the assembled QDSSCs were measured at different simulated sunlight power. The short current density (J_{sc}) and efficiency (η) increase with dipping time. At 50 h dipping time, and AM 1.5 simulated sunlight, the open-circuit photovoltage V_{oc}, the short circuit photocurrent density J_{sc}, fill factor FF, and the efficiency for energy conversion η were 0.5 volts , 1,105 $\mu A/cm^2$, 0.43 and 0.19%, respectively. Furthermore, the J_{sc} increases linearly with increasing the intensities of the sun light which indicates the stability of the assembled cells.

Key words: CdTe, quantum dot, quantum dots sensitized solar cell, photovoltaic cells.

1. Introduction

Recently, sensitization of mesoporous metal oxides layers with various semiconducting quantum dots (QDs) or nanoparticles (NPs) have been under intensive investigations, particularly when these semiconductors are chalcoginides. This is due to their unique electronic, thermal and optical properties, especially when their size is below the corresponding exciton radius [1-3]. These photosensitizers, QD synthesized solar cells (QDSSCs) which are chalcoginides QDs deposited onto mesoporous TiO_2 NPs have easily tunable band gaps which leads to better light harvesting capability, stability, low cost photovoltaic cell [1]. In addition, QDSSCs have larger surface areas and provide a technically and economically credible alternative to conventional cells [4-6], silicon photovoltaic or dye-sensitized solar cells (DSSCs). The last cells have many limitations, such as difficulties in utilizing the infra-red regime of the solar spectrum, and instability for long-term uses [7]. CdTe has a high extinction coefficient (4.4×10^4 $M^{-1}\cdot cm^{-1}$) at 370 nm and valence band, conduction band, and band gap energies of -4.3, -5.7, and +1.475 eV, respectively [8]. These properties make it good sensitizer, capable of effectively injecting electrons into TiO_2 nanoparticles (NPs) (band gap: 3.4 eV). One of the many variables to be studied and improved are the synthetic routes for the QDs and the adsorption technique used to anchor these QDs onto the large band gap metal oxides. Normally, these adsorption methods are: (1) *in situ* growth of QDs by either chemical bath deposition (CBD) technique, containing both the cationic and anionic precursors, or successive ionic layer adsorption and reaction deposition (SILAR) method [9], (2) electrophoretic deposition (EPD) method [4], and (3) deposition of presynthesized

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colloidal QDs by either linker-assisted adsorption (LA), or direct adsorption (DA) for different dipping times.

In this work, we prepared CdTe QDs by chemical deposition (CD) technique [10] to be used as a sensitizer in QDSSCs. These colloidal QDs were adsorbed onto TiO_2 NPs by DA technique for different dipping times under ambient conditions. To the best of our knowledge, this is the first time that DA technique is used to deposit CdTe QDs onto TiO_2 NPs to assemble QDSSCs for photovoltaic applications.

2. Experiment

2.1 Preparation of CdTe Quantum Dots

Colloidal CdTe nano-crystals were synthesized by the method of Talapin et al [10] as follows: five grams of dodecylamine (DDA) were dissolved in 7 mL of tri-*n*-octylphosphine (TOP) at 50 °C in a 50 mL two-neck flask with a reflux condenser attached. Subsequently, 0.11 mL (1.47 mmol) of dimethylcadmium and 0.128 g (1 mmol) of tellurium powder were added under stirring. The temperature was slowly increased to 180 °C and after 30 min, the temperature was raised to 200 °C. The growth of the nano-crystals was allowed to proceed at this temperature for 20 h. Under these conditions, tellurium slowly dissolves in the reaction mixture, resulting in a very slow growth of CdTe nano-crystals at sufficiently high temperatures. Finally, toluene was added to the warm solution, and the mixture was left for 24 h at room temperature under stirring.

2.2 Preparation of Solar Cell Electrodes

The TiO_2 colloidal paste was prepared by the method of G. Syrrokostas et al. [11]. Three grams of commercial TiO_2 nanopowder (20 nm) (Degussa P-25 Titanium dioxide consists of 80% anatase and 20% rutile) was ground in a porcelain mortar and mixed with a small amount of distilled water (1 mL) containing acetyl acetone (10% v/v) to create the paste. Acetyl acetone was used as a dispersing agent, since it prevents coagulation of TiO_2 nanoparticles and affects the porosity of the film. The paste was diluted further by slow addition of distilled water (4 mL) under continued grinding. The addition of water controls the viscosity and the final concentration of the paste. Finally, a few drops of a detergent (Triton X-100) were added to facilitate the spreading of the paste on the substrate, since this substance has the ability to reduce surface tension, resulting in even spreading and reducing the formation of cracks. The TiO_2 paste was deposited on a conducting glass substrate of SnO_2:F (FTO) with sheet resistance of 7 Ω/sq and > 80% transmittance in the visible region, using a simple doctor blade technique. This was followed by annealing at 450 °C for 30 min and the final thickness was 8 μm after the solvent evaporation. Then the TiO_2 films were dipped into a colloidal solution of presynthesized CdTe QDs, for different dipping times (3 h, 6 h, 24 h, 50 h) to form four working electrodes. The counter electrodes were prepared by coating another FTO substrate sheet of resistance of 7 Ω/sq with Pt.

2.3 Assembly of QDSSC

The CdTe QDs sensitized TiO_2 electrode and the Pt counter electrode were assembled as a sandwich type cell using clamps. Both electrodes were sealed by using a hot-melt polymer sheet (solaronix, SX1170-25PF) of 25 μm thickness in order to avoid evaporation of electrolyte. Finally, Iodide electrolyte solution was prepared by dissolving 0.127 g of 0.05 M Iodine (I_2) in 10 mL of water-free ethylene glycol, then adding 0.83 g of 0.5 M potassium iodide (KI). The electrolyte was inserted in the cell with a syringe, filling the space between the two electrodes.

2.4 Measurements

The average particles size of CdTe QDs was estimated using transmission electron microscope (TEM) and confirmed by The UV-Visible spectrum (JASCO V-670). The absorption spectra of the CdTe QDs sensitized TiO_2 electrodes were also recorded using a UV-Visible spectrophotometer. The CdTe QDSSCs were subjected to the illumination of a solar simulator (ABET technologies, Sun 2000 Solar Simulators, USA) operating at 100 mW/cm^2 (AM 1.5). The current density-voltage (J-V) characteristics for CdTe QDSSCs of different dipping time were recorded with a Keithley 2400 voltage source/ammeter. The intensity of the incident solar illumination was adjusted to 1 sun condition using a Leybold certified silicon reference solar cell (Model: [57863] Solar cell 2 V/0.3 A STE 4 /100). J-V characteristic curves of QDSSC were recorded at various illumination intensities using attenuators and calibrated by the previous Si reference solar cell. All experiments were carried out under ambient conditions.

3. Results and Discussion

3.1 Characterization of CdTe QDs

The UV-Visible spectrum of CdTe QDs in toluene shows absorption edge at 533 nm wavelength (2.32 eV) as shown in Fig. 1a. The size (R) of CdTe QDs was calculated using the effective mass approximation (EMA) model [12, 13].

$$E_{gn}(R) = E_{gb} + \frac{h^2}{8m^*R^2} - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 R} \quad (1)$$

where E_{gb} (=1.475 eV) is the bulk crystal band gap value of CdTe [14], E_{gn} is the nano crystal band gap value, R is the radius of the CdTe quantum dots, h is the Planck's constant, m^* is the reduced electron-hole mass (for CdTe, $m^* = 7.62 \times 10^{-32}$ kg [15]), e is the electron charge, ε_0 is the permittivity of vacuum and ε the relative dielectric constant of the semiconductor (for CdTe = 7.1 [14]). The calculated CdTe QDs size was found to be 2.1 nm, which is consistent with that determined using transmission electron microscope (TEM) image, shown in Fig. 1b.

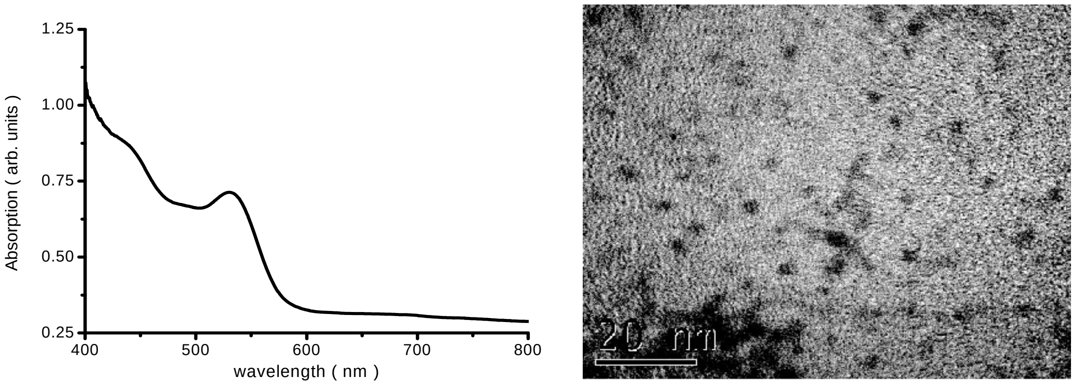
3.2 Characterization of CdTe QDs Sensitized TiO$_2$ Electrodes

Fig. 2 shows the absorption spectra of the working electrode for different dipping times as indicated. It is clear that the absorption increase with the increase of dipping times, up to 24 h, while there is no large difference between 24 and 50 h, especially in the region above 600 nm wavelength.

To ensure, that the adsorption of CdTe quantum dots onto the TiO$_2$ electrode takes place, EDX was performed and the results shown in Fig. 3 refers to the peaks due to Cd and Te, in addition to Ti.

3.3 Characterization of CdTe QDSSC

The J-V characteristics of the assembled CdTe QDSSCs for different deposition times (3 h, 6 h, 24 h, 50 h) using TiO$_2$ photoelectrodes and 100 mW/cm^2 from a solar simulator (ABET technologies, Sun 2000 Solar Simulators, USA) are shown in Fig. 4.



(a) (b)

Fig. 1 (a) UV-visible spectrum of CdTe QDs, (b) TEM image of CdTe QDs.

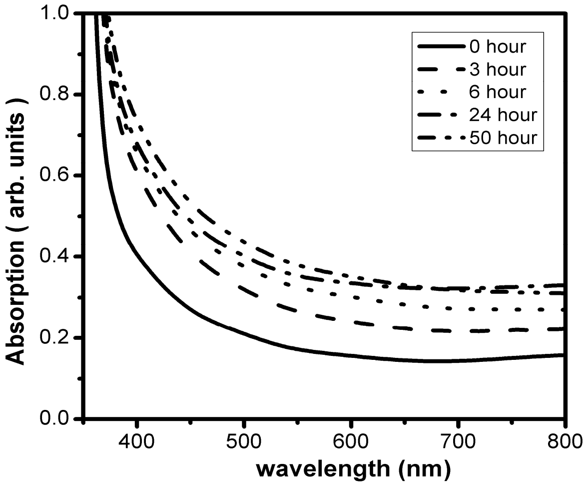


Fig. 2 UV-vis. absorption spectra of CdTe QDs (R = 2.10 nm) deposited on TiO_2 NPs at 0 h, 3 h, 6 h, 24 h and 50 h dipping times.

Table 1 gives the open circuit voltages (V_{oc}), short circuit current densities (J_{sc}), fill factor (FF), and efficiency for energy conversion (η) for CdTe QDSSCs at different dipping times (3 h-50 h). The values of V_{oc} ranged from 405 to 495 mVolt, while the values of J_{sc} varied from 987 to 1,105 μA/cm^2. The FF ranged from 0.40 to 0.35 and the values of η varied from 0.158 % to 0.190 %.

It is observed that both J_{sc} and η increase significantly as the dipping time increases. Fig. 5 shows the change in the case of η. It is evident that CdTe QDs deposited by DA method reported here, even for the least dipping time, gives values relatively higher than those reported in literatures [7, 8]. Using

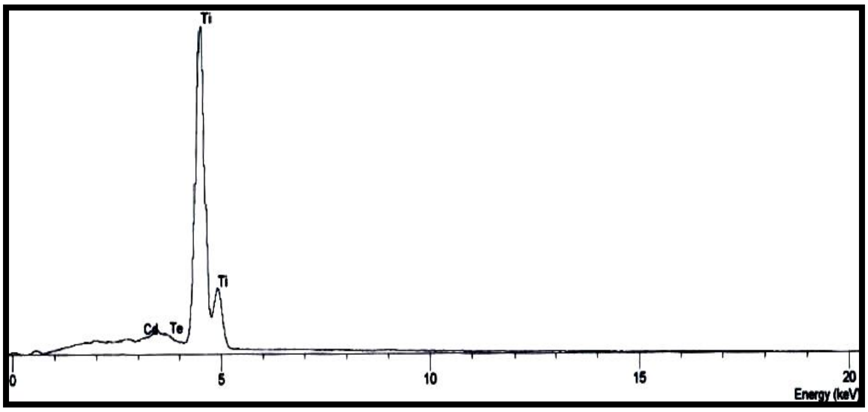


Fig. 3 EDX of CdTe quantum dots adsorbed onto TiO_2 film.

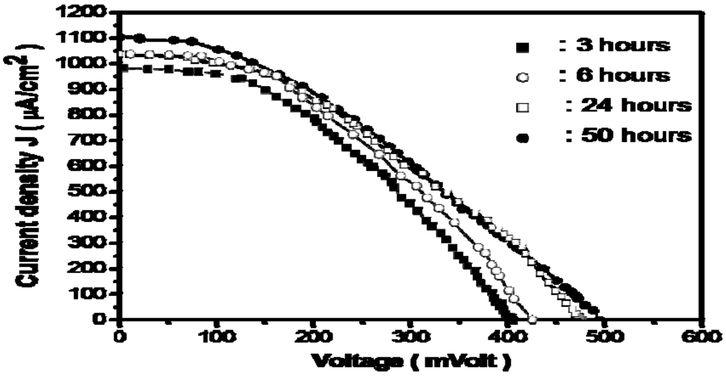


Fig. 4 J-V characteristics curve of a CdTe QDSSC for : 3 h, 6 h, 24 h and 50 h dipping time.

Table 1 J-V characteristics parameters of CdTe QDSSCs for different dipping times.

Dipping time (h)	V_{oc} (mVolt)	J_{sc} (μA/cm^2)	FF	η (%)
3	405	987	0.40	0.158
6	418	1035	0.38	0.167
24	472	1037	0.37	0.183
50	495	1105	0.35	0.190

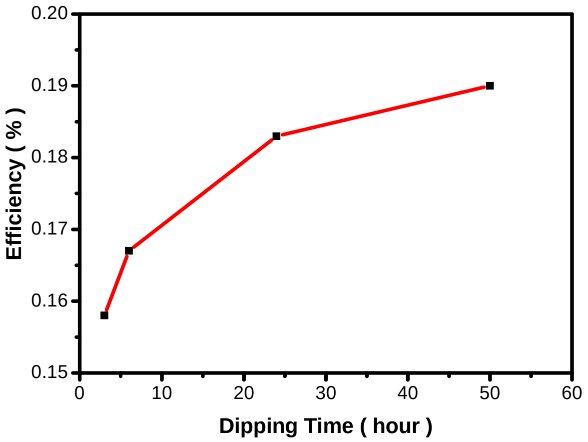
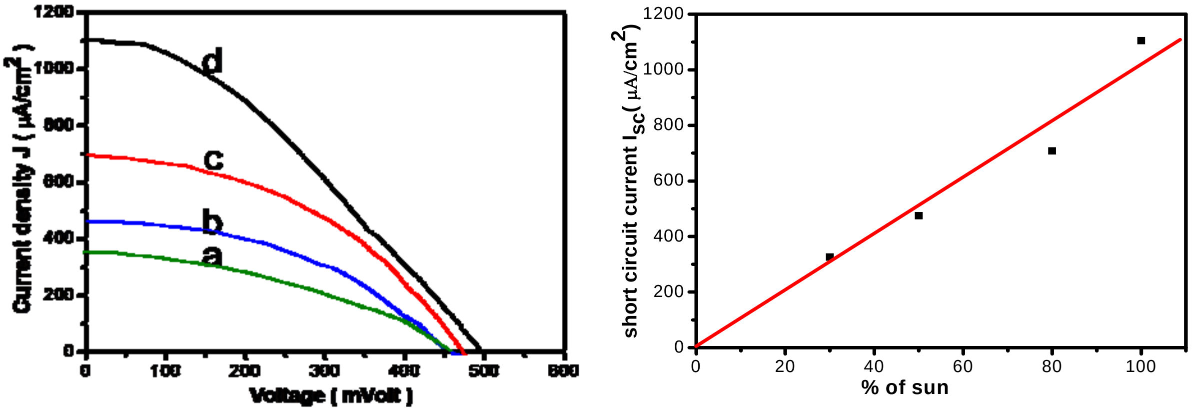


Fig. 5 Efficiency of CdTe QDSSCs vs. dipping time.

LA method to anchor CdTe QDs onto TiO_2 mesoporous layer by 4-mercaptobenzoic acid (MBA) as a linker, Lee et al. [7] obtained $J_{sc} = 216$ μA/cm^2 and an efficiency 0.065%, much less than above results. Furthermore, it was even reported by Kniprath et al. [8] using CdTe QDs as sensitizer and a conjugated polymer as hole transport layer, that there were no photocurrent observed. They attributed this result to the energy barrier introduced by the CdS shell of the stabilizing thiol capping. The improvement in our assembled cell is due to the direct attachment of the CdTe QDs to the surfaces of TiO_2 NPs, which enhances the electronic injection. In addition, such mode of attachment was inferred to, by Gimenez et al. [16] where partial removal of capping TOP layer at the contact points with the oxide particles occur, that consequently the distance between the QD (electron donor) and the TiO_2 particles (acceptor) is reduced, leading to increase of J_{sc}. The relatively long adsorption time, helps in reducing the limiting effect of other parameters such as surface and solution cleanliness, QD concentration in the dispersion of TiO_2, type of TiO_2 paste etc, in QD loadings.

To investigate the performance of the assembled CdTe QDSSCs with various intensities of solar illumination (from 30%-100% sun), the J-V characteristics curves were recorded for the 50 h dipping time assembly, and is shown in Fig. 6a for the indicated intensities. Table 2 shows measured parameters of CdTe QDSSCs for different percentage of sun. It is seen that as the intensity of the incident light increases, the measured J_{sc} increases linearly as shown in Fig. 6b due to increased injected electrons. The approximately constant values of V_{oc} and η,



(a) (b)

Fig. 6 (a): J-V characteristics curve of a CdTe QDSSC for 50 h dipping time at: (a) 30%, (b) 50%, (c) 80%, and (d) 100% of sun. (b): short circuit current J_{sc} vs. percentage of sun.

Table 2 J-V characteristics parameters of CdTe QDSSCs for different percents of sun.

Sun (%)	V_{oc} (mVolt)	J_{sc} (μA/cm^2)	FF	η (%)
30	466	326	0.39	0.195
50	468	475	0.43	0.190
80	470	708	0.44	0.181
100	495	1,105	0.35	0.190

indicate the relative stability of CdTe QDSSCs that is prepared by DA method, in contrast to the dye sensitized solar cells, where bleaching may occur.

4. Conclusions

CdTe QDs of radius 2.1 nm were adsorbed onto TiO_2 NPs using the direct adsorption (DA) method, for different dipping times up to 50 h, as a sensitizer for photovoltaic cell. Our results show that J_{sc} and η increase as the dipping time increase, and are of much higher values than others. Furthermore, as the intensity of the incident solar light increases, J_{sc} increases linearly, indicating greater stability of CdTe QDSSCs, in contrast to dye sensitized solar cells. The performance of such QDSSCs can further be enhanced by tuning the QDs size to harvest more solar spectra.

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