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CdHgTe Quantum Dots Sensitized Solar Cell with Using of Titanium Dioxide Nanotubes

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ABSTRACT

The sensitization of TiO_2 nanotubes with CdHgTe quantum dots (QDs) was applied by using the direct dispersion technique. The CdHgTe-QDs were fabricated with different Hg% ratio in organic medium for controlling their particle size. While TiO_2 nanotubes (NTs) were fabricated by anodization technique. The QDs and NTs were characterized using SEM, TEM and UV-VIS spectrophotometer. In this work, the photovoltaic parameters of the quantum dots sensitized solar cell (QDSSC) depend mainly on the Hg% ratio in the QDs. The most efficient QDSSC was obtained at 25% of Hg ratio with J_{sc} of 4 mA/cm^2, V_{oc} of 0.63 V, FF of 0.32 and efficiency of 0.81%.

Keywords: Solar Cells; Quantum Dots; Nano-Tubes; TiO_2; Sensitization

1. Introduction

Quantum dots photovoltaic cells combine low-cost solution process-ability with quantum size-effect tunability to match absorption with the solar spectrum [1]. Relative to the dyes used in solar cells, QDs offer several advantages such as photo-stability, greater molar extinction coefficients, and size-dependent optical properties [2]. They also have the potential to increase the maximum attainable thermodynamic conversion efficiency of solar photon conversion up to 66% by utilizing hot photo-generated carriers to produce higher photo-voltages or higher photocurrents via multi-exciton generation capability. While the charge carriers are confined within an infinitesimal volume, thereby increasing their interactions and enhancing the probability for multiple exciton generation [3,4]. The calculations of the dependence of ideal solar cell conversion efficiency on band gap show that CdTe is an excellent match to our sun [5,6].

In order to control the CdTe QDs band gap, mercury was added to the preparation medium [2]. The key challenge with such cells, the quantum dot sensitized solar cells (QDSSCs), is the relatively low absorption cross section of the QDs [6]. Titania nanotubes (TNTs) present the key solution for carrier's recombination and low absorption issues via the highly ordered nano-structured matrix which provides continuous electron pathways to facilitate a good electrons collection with high surface area [7].

TiO_2 nanotubes arrays and particulate films were modified with CdS quantum dots with an aim to tune the response of the photo-electrochemical cell in the visible region via successive ionic layer adsorption and reaction (*SILAR*) [8].

The QDSSCs were fabricated by incorporating CdHgTe nanocrystals (NCs) and CdTe quantum dots, which prepared separately from aqueous mixtures of NaHTe, $Cd(NO_3)_2$, and 3-mercaptopropionic acid in the presence and absence of $HgCl_2$ respectively, then the sensitization of a modified TiO_2 nanoparticles was carried out to obtain an energy conversion efficiencies of 1.0% and 2.2% [2].

In this work, the sensitization of TiO_2 nanotubes-prepared with anodization method—with CdHgTe-QDs-prepared with organic method—was applied by direct dispersion. The aim of the present work is to enhance the QDSSCs efficiency by tuning the energy gab of the CdHgTe-QDs with changing Hg% ratio. The effect of Hg ratio in the QDs on the photovoltaic parameters of the QDSSC was investigated.

2. Experimental Work

2.1. Materials

Ti foil (99.7% B.D.H., England), Ethylene Glycol (Nice chemicals, India), Ammonium fluoride (oxford, India), Acetic Acid (99.9%, fluka, Germany), De-ionized water (DI), Cadmium acetate (MP Biomedicals), Tellurium powder (99%, Aldrich), Octadecene (Acros), Trioctylphosphine (TOP) (99%Acros), Oleic acid (99%, Aldrich), Mercury Chloride, Isopropanol (Aldrich) and n-hexane

(Aldrich) were used for fabricating the CdHgTe QDs-TiO_2 nanotubes solar cells.

2.2. Preparation of TiO_2 Nanotubes

Titania nanotubes were prepared by the electrochemical anodizing of Ti foil which was ultrasonically degreased with a mixture of Acetone, Methanol and Ethanol then rinsed with DI water and dried with nitrogen. The anodization process was carried out in an electrochemical cell with two electrodes model where the titanium is the anode and platinum wire is the counter electrode (the cathode). The anodization electrolyte was a mixture of Ethylene Glycol, Ammonium fluoride (0.5%wt), Acetic acid (for pH adjustment) and DI water (2% volume). All experiments were carried out at room temperature (25˚C) and the anodizing voltage was 40 V and applied for 3 hours. Once the process completed, the anodized sample removed from the cell and washed with a large amount of water then dried with nitrogen. The Ti electrode was annealed in air at 500˚C for 3 hours in order to improve Anatase phase. The morphology (*i.e.* length, diameter, and the shape) of the TiO_2 nanotubes was investigated by the scanning electron microscope (SEM: Joel Jsm 6360 LA, Japan).

2.3. Preparation of CdTe and CdHgTe QDs

Tellurium powder (0.127 gm) was added to triocytl-phosphine (TOP, 2 ml) and Octadecene (8 ml) with stirring at 60˚C for 30 min. till giving the greenish gray color with a complete dissolving. In a three neck rounded flask, Cadmium acetate (0.186 gm) was mixed with Oleic acid (2 ml) and Octadecene (5 ml) and then rising the temperature up to 80˚C. The tellurium precursor was added to the above cadmium solution at 80˚C. To synthesis CdHgTe QDs from organic medium, mercury chloride was added to above cadmium solution. The CdTe and CdHgTe QDs were separated in Isopropanol via centrifuge at 5000 rpm. These QDs were dissolved again in n-hexane to prepare the sensitization solution. UV-visible characterization of the CdHgTe QDs solution was carried out using Thermo-Evolution 600 spectrophotometer and the HRTEM images of the QDs were obtained using JEOL (JEM-2100 LaB6) TEM.

2.4. Preparation of Quantum Dot Sensitized Solar Cell (QDSSC)

The prepared nanotubes electrodes were immersed into the QDs/N-Hexane suspension. Then left for 3 days with sonication every 12 hours in airtight tubes to ensure a good QDs diffusion through the TNTs layer.

The QD sensitized solar cells with a structure of ITO/liquid electrolyte/CdHgTe-QDs/TiO_2 (NTs)/Ti were assembled as shown in **Figure 1**. The sensitized Ti-TNTs

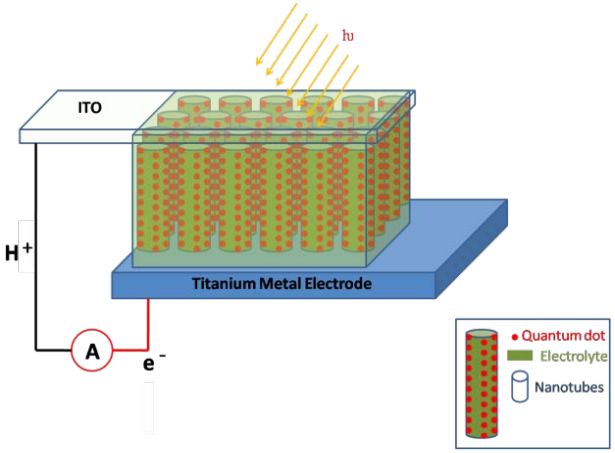

Figure 1. QDSSC assembly.

is the working electrode and a carbon activated indium tin oxide (ITO, R = 14 - 16 Ω) is the other electrode. The two electrodes were spaced by a polymeric spacer with 50 µm thickness. The Redox electrolyte was injected through the cell's sides.

All cells were illuminated by using Xenon lamp with an intensity of 100 m W/cm^2 (AM1.5). The lamp was calibrated with Solarex standard solar cell and the J-V measurements were obtained by using Keithley 2635A source-meter.

3. Results and Discussion

3.1. Characterization of TiO_2-NTs

Images of scanning electron microscope (SEM) for the anodized titanium show a highly ordered, smooth, and dense packed Titania nanotubes formed at 40 V for 3 h in Ethylene glycol/ammonium fluoride electrolyte. The obtained nanotubes having an average outer diameter of 75 nm and a wall thickness in the range of 10 - 14 nm while the tubular layer thickness was around 24 µm (as shown in **Figure 2**) which provides a naturally n-type semiconductor with a relatively high surface area with a 3.2 eV band gap (after annealing) referred to the anatase crystal structure [9].

The arrangement of the highly ordered Titania nanotubes array perpendicular to the surface permits a facile charge transfer along the length of the nanotubes to the conductive substrate [10]. The prepared nanotubes may resolve the problem of relatively low absorption cross section of the QDs by increasing the area of contacts in addition with the appropriate layer thickness which expected to increase the solar cell performance.

3.2. Characterization of CdHgTe QDs

3.2.1. UV-Vis. Spectroscopy

Figure 3 presents the UV-visible spectra of CdHgTe

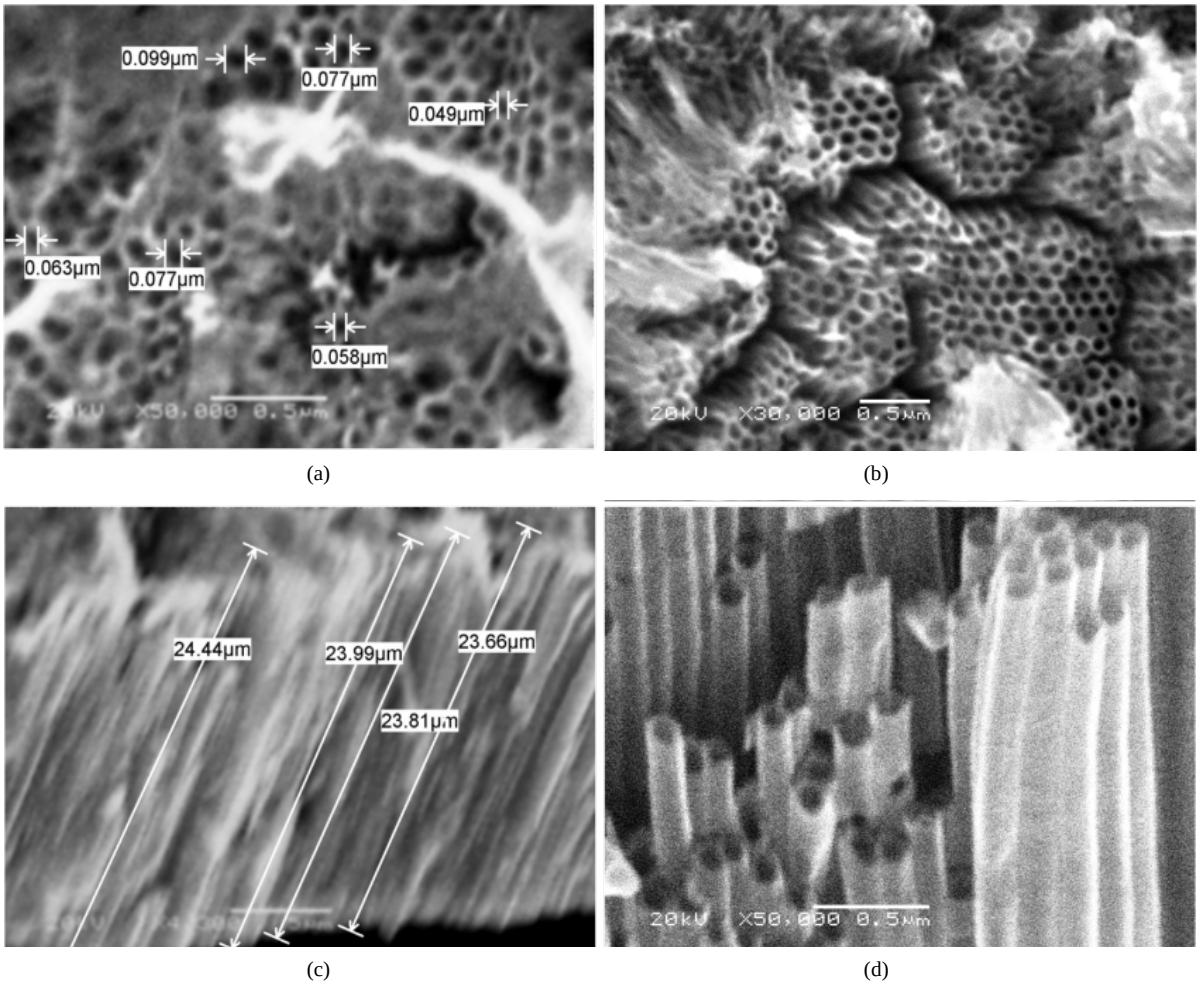

Figure 2. SEM images for a sample anodized at 40 V for 3 h in Ethylene Glycol: (a) and (b)Top views;(c) Side view; and (d) Side view at higher magnification.

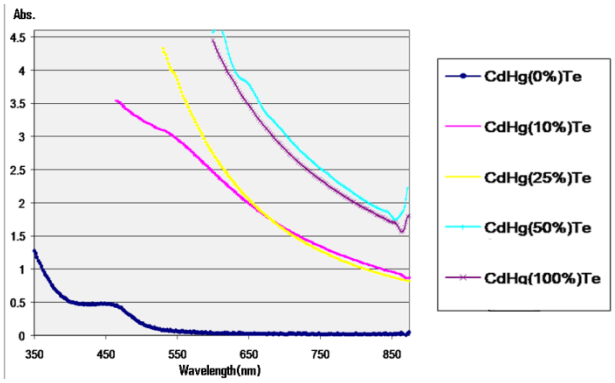

Figure 3. UV-visible absorption spectra of CdHgTe QDs prepared with different ratios of mercury. The obtained curves are similar to those reported in the previous work [12].

QDs prepared using organic medium at different ratios of Hg. For CdTe sample, the absorption peak is around 460 nm indicating the formation of CdTe QDs [11]. It was noted that as the relative concentration of mercury increases, the excitonic absorption peak of CdTe QDs shifts to the longer wavelengths from 460 nm (for 0% of Hg) to 855 nm(for 100% Hg) due to the quantum confinement effect as the QDs grow to larger size and this is a good evidence for the formation of CdHgTe QDs [12].

The Hg^{2+} ions substitute Cd^{2+} ions at the surface of the nanocrystals forming a CdHgTe alloy in the near-surface region, possibly with a concentration gradient decreasing towards the dot interior [11].

Using the absorption spectrum, the direct optical band gap energy of the QDs was calculated by simply plotting $(\alpha h\nu)^2$ versus (hν), obtained from the following relation [11]:

$$\alpha h\nu = A\,(h\nu - Eg)^{1/2} \quad (1)$$

Where α and A are the absorption coefficient and a constant respectively. The direct optical band energy gap of the CdHgTe QDs was calculated to be 2.3, 1.62, 1.5, 1.35 and 1.3 eV for 0, 10, 25, 50, and 100% ratio of Hg, respectively. The decrease in the optical band gap with increasing the Hg percentage is regarded to the formation

of a layer of HgTe on the QDs surface [12].

3.2.2. High Resolution Transmission Electron Microscope (HRTEM)

Figure 4 shows HRTEM images of CdHgTe QDs prepared using organic medium with different ratios of Hg. The existence of the lattice planes in the HRTEM images indicates that the QDs are highly crystalline as shown in the white circles mentioned in **Figure 4**. It was noted that the increase in Hg% ratio from 0 to 10, 25, 50 and 100 leads to an increase in the size of QDs from 2.8 to 8.6, 9, 9.5 and 10.8 nm respectively. This is due to the formation of a HgTe layer on the surface [12].

3.3. Characterization of TiO_2-NTs (TNTs)/CdHgTe Quantum Dots Solar Cells (QDSSCs)

The SEM images (**Figure 5**) showed fully covered TNTs with the sensitizer at the top and sides of the NT while there is no indication about the quantity of the QDs that decorate the TNTs from the inner. **Figure 6** shows the characteristic J-V curves for the QDSSCs prepared by using TNTs and CdHgTe QDs with different Hg% ratios. It is clear that the addition of mercury to the QDs core shell shifts the absorption of the QDs toward the red region as shown in **Figure 3** providing a wider absorption toward IR region and hence increases the short circuit current and the open circuit voltage as indicated in **Table 1**. As seen from the **Figure 6** that J_{sc} increased from 0.4 mA/cm^2 corresponding to 0% Hg to 3.1 and 4 m A/cm^2 for 10% Hg and 25% Hg respectively. The most efficient cell (regarded to 0.81% efficiency) with the highest current density value (4 m A/cm^2) was obtained when using 25% Hg corresponding to a band gap of 1.5 eV. While a noticeable decrease in the values of V_{oc} and J_{sc} were occurred when changing the energy band gap away from

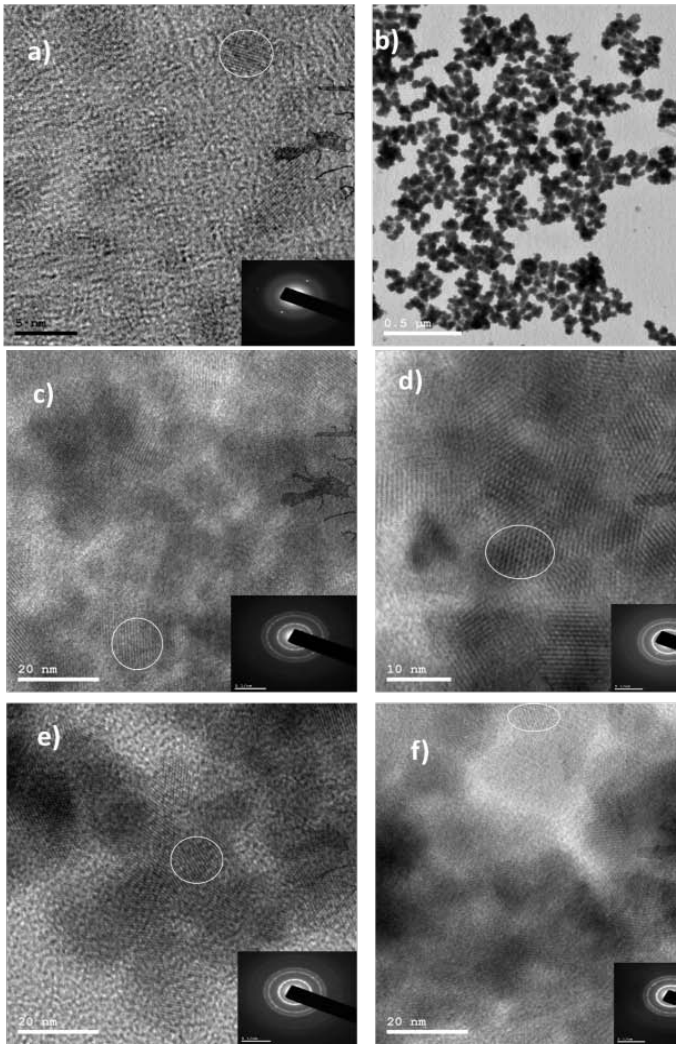

Figure 4. HRTEM images of colloidal CdHgTe solution prepared using organic method. (a) 0% of Hg, (b) 10% of Hg at low magnification, (c) 10% of Hg at higher magnification, (d) 25% of Hg, (e) 50% Hg, and (f) 100% Hg.

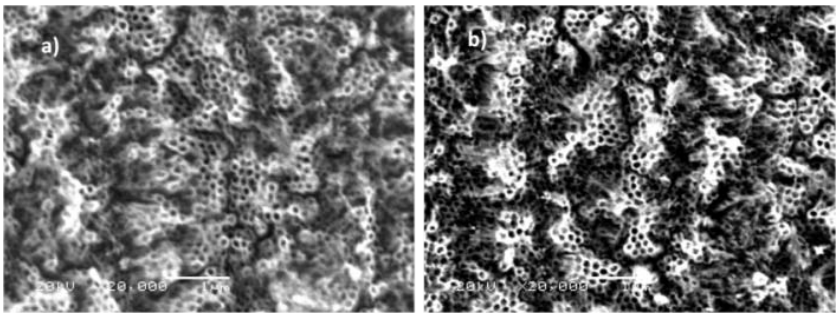

Figure 5. SEM images of Titania nanotubes after sensitization: a) Top view for a sample sensitized with CdHgTe QDs, b) Top view of a sample sensitized with CdTe QDs.

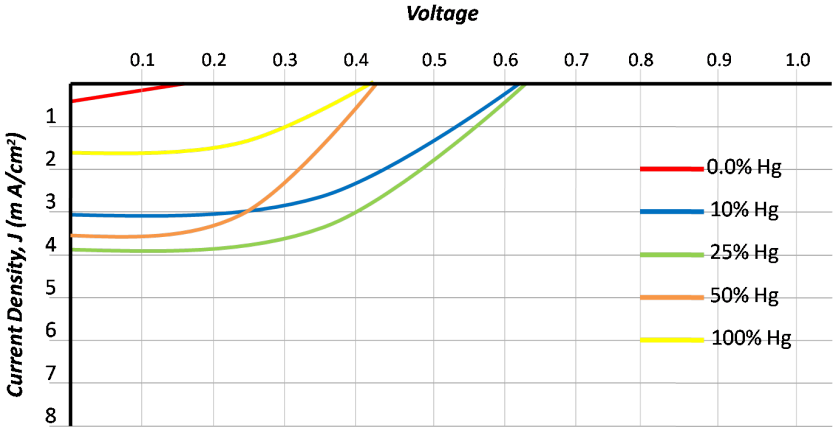

Figure 6. J-V characteristic curves of TiO_2-NTs/CdHgTe-QDs sensitized solar cell with different Hg % ratios.

Table 1. Photovoltaic parameters of the prepared QDSSCs.

	CdHgTe (0% Hg)	CdHgTe(10% Hg)	CdHgTe (25% Hg)	CdHgTe (50% Hg)	CdHgTe (100% Hg)
Particle size (nm)	3.5	8.5	9	9.5	10.5
E_g(eV)	2.3	1.62	1.5	1.35	1.3
J_{sc}(mA/cm^2)	0.4	3.1	4	3.6	1.7
V_{oc}(V)	0.15	0.61	0.63	0.43	0.41
FF	0.18	0.23	0.32	0.34	0.2
Efficiency%	0.012	0.435	0.81	0.53	0.14

this value (*i.e.* 1.5 eV). This result up to 1.5 eV is due to the excited state of the QD lies well above the TiO_2 conduction band level and photo-excited electrons injection into TiO_2 would be energetically favorable[1]. While, by increasing the band gap (>1.5 eV), the hole level exhibits a large discontinuity with the TiO_2 valence band, providing a very large barrier to the undesired passage of majority holes from the p-type QD layer into the n-type TiO_2 electrode [1].

Additionally, V_{oc} and J_{sc} values were dramatically dropping by increasing the Hg% ratio from 25% to 100%. This behavior can be explained by another cause which is regarded to the distorted QDs structure with an access of mercury concentrations. When the Hg% ratio increased, Hg^{2+} ions should be substituted at the surface of the nanocrystals, and in theory, if complete surface exchange occurs, a core/single-monolayer-shell structure will result [12]. The substitution reaction then completes either due to an exhaustion of Hg ions in solution or because of the formation of a complete "locking" layer of HgTe on the surface. And finally the outer layer forms an almost perfectly passivated quantum dot [12].

From another point of view, the obtained J-V curves suffering from a bad fill factor due to the high series resistance of cell and moreover the spacer issue which is a strong factor that may reduce the cell efficiency. On the other hand, the performance of the prepared solar cell in this work can be enhanced in further work using a better sensitization technique, better sealing conditions and by the usage of a linker.

4. Conclusions

The direct dispersion technique was used for fabricating CdHgTe-QDs sensitized TiO_2-NTs solar cells with different Hg% ratios in QDs. The obtained highly ordered and dense packed Titania nanotubes were having an average outer diameter of 75 nm and a layer thickness of 24 µm. In addition, the direct energy gap of the highly crystalline CdHgTe QDs was calculated to be 2.3, 1.62, 1.5, 1.35 and 1.3 eV for 0%, 10%, 25%, 50%, and 100% ratio of Hg respectively.

The increase in V_{oc} and J_{sc} values corresponding to a change in Hg% ratio from 0% to 25% was due to the absorption enhancement in IR region while the decrease in V_{oc} and J_{sc} values corresponding to a change in Hg ratio from 25% to 100% was due to either the discontinuity in the energy level or the formation of locking layer of HgTe on the QDs surface. The most efficient QDSSC was obtained at 25% of Hg ratio with J_{sc} of 4 mA/cm^2, V_{oc} of 0.63 V, FF of 0.32 and efficiency of 0.81%.

The performance of the QDSSC mentioned in this work can be enhanced using a better sensitization technique, better sealing conditions and by the usage of a linker.

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