Red-shift of the photoluminescent emission peaks of CdTe quantum dots due to the synergistic interaction with carbon quantum dot mixtures

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Abstract. We report the relatively large red-shift effect observed in down-shifting carbon quantum dots (CQDs) that is anticipated to have a positive impact on the power conversion efficiency of solar cells. Specifically, with an excitation wavelength of 390 nm, CQDs of different sizes, exhibited down-shifted emission peaks centered around 425 nm. However, a solution comprised of a mixture of CQDs of different sizes, was observed to have an emission peak red-shifted to 515 nm. The effect could arise when larger carbon quantum dots capture the photons emitted by their smaller counterparts followed by the subsequent re-emission at longer wavelengths. Furthermore, the red-shift effect was also observed in CdTe QDs when added to a solution with the aforementioned mixture of Carbon QDs. Thus, whereas a solution solely comprised of a collection of CdTe QDs of different sizes, exhibited a down-shifted photoluminescence centered around 555 nm, the peak was observed to be further red-shifted to 580 nm when combined with the solution of CQDs of different sizes. The quantum dot characterization included crystal structure analysis as well as photon absorption and photoluminescence wavelengths. Subsequently, the synthesized QDs were dispersed in a polymeric layer of poly-methyl-methacrylate (PMMA) and incorporated on functional and previously characterized solar cells, to quantify their influence in the electrical performance of the photovoltaic structures. We discuss the synthesis and characterization of the produced Carbon and CdTe QDs, as well as the observed improvement in the power conversion efficiency of the fabricated photovoltaic devices.

1. Introduction
Carbon, CdTe, Si, CdSe and ZnO quantum dots (QDs), among others, are frequently explored nanostructures that exhibit the property of capturing high energy photons and subsequently emitting...
lower energy ones that are more suitable for producing electron-hole pairs in silicon solar cells. The wavelength of the emitted photons is directly related to QD size, specifically, the larger the synthesized QD the longer the wavelength of said photons. The size of the produced Carbon quantum dots (CQDs) is controlled by the applied current during synthesis, while that of CdTe QDs is determined by the refluxing time. In addition to the aforementioned down-shifting effect, the colloidal mixtures of C and CdTe QDs of different sizes, exhibit significant differences. Specifically, the photoluminescent peak of a colloidal mixture of CdTe QDs (CdTeMS) is observed to be centered around the collection of the individual peaks, thus, there is no discernible red-shift or otherwise a deviation from what could be anticipated a priori. However, the CQD colloidal mixture (CMS) behaves differently since the peak is observed to be red-shifted respect to the position of the collection of the individual photoluminescent peaks. This additional red-shift should prove useful in boosting the power conversion efficiency of solar cells.

2. Experimental details

2.1. Synthesis of Carbon QDs

The Carbon nanostructures with a distribution of sizes (see Figure 1) were synthesized employing an alkali-assisted electrochemical fabrication method utilizing graphite rods for both the anode and the cathode [1][2], while varying the applied current between 10 and 60 mA in increments of 10 mA. The graphite rods employed had a diameter of 5 mm, a separation of anode to cathode of 25.4 mm, and were submerged 30 mm in an 100 ml electrolyte solution composed of ethanol and water with a volume ratio of 99.5/0.05 to which 0.3g of NaOH were added. The current was applied for one hour immediately upon the submersion of the graphite rods within the specified current range. Subsequently, the samples were stored for 48 hours at room temperature to stabilize them, and the produced solutions were allowed to evaporate until obtaining 5 ml for every 100 ml of quantum dot solution. Upon the completion of the evaporation step the samples were separated employing a silica-gel chromatography column with an 100 ml mixture of petroleum ether and diethyl ether with a volume ratio of 30/70. The final step was to evaporate the solvents thoroughly in each vial to increase the CQD concentration.

Figure 1.- Carbon quantum dots size distribution.

2.2. Synthesis of CdTe QDs

CdTe QDs of measured sizes between 2 to 18 nm (see Figure 2) were obtained employing a chemical synthesis scheme. Specifically, 0.0533 g of cadmium acetate dihydrate (Cd(CH₃COO)₂ • 2H₂O, 99.5%) were dissolved in 50 ml of deionized (DI) water in an 125 ml Erlenmeyer flask, subsequently 18 µl of thioglycolic acid (TGA, 90%) were added, and the pH was adjusted with 1 M sodium hydroxide (NaOH) set solution until reaching a value between 10.5 to 11 in the pH scale, and stirred for 5 minutes. Separately, 0.0101 g of potassium tellurite (K₂TeO₃, 95%) were dissolved in 50 ml of DI water in an 125 ml Erlenmeyer flask, stirred for 5 minutes and 0.0101 g K₂TeO₃ were added to this second solution. Subsequently, the previously prepared solutions were mixed, 0.08 g of sodium borohydride (NaBH₄, 99.99%) were added to the mixture, and the reaction was allowed to proceed for 5 minutes. The mixed solution was then transferred to a single-neck, round-bottom flask that was attached to a Liebig condenser, which was stirred at 500 rpm while being refluxed. During the refluxing times of 15 min, 30
min, 1 h, 3 h, 5 h, 6 h, 8 h and 12 h, the flask remained submerged in laboratory oil whose temperature was maintained at 100°C. QD size and photoluminescent emission wavelengths were determined by the refluxing time [3] [4].

![Figure 2.- CdTe quantum dots size distribution](image)

3. Results and discussion

3.1. QD Colloidal Solution Characterization and Solar Cell Deployment

The colloidal mixture of Carbon QDs of different sizes (CMS) was observed to produce a spectrum with a red-shifted peak located at ~515 nm (see Figure 3 part (a.)) while the spectra of the previously synthesized CQDs with the selected current values, were observed to be centred around ~425 nm. As far as the CdTe QDs are concerned, their ultimate size can be adjusted by the refluxing time, and size is reflected in the emission wavelength of the synthesized nanostructures (see Figure 3 part (b.)). Specifically, with an excitation wavelength of 390 nm, CdTe QDs with a refluxing time of 1 h have a characteristic emission peak at ~548 nm, while the characteristic emission peak is located at ~570 nm for a refluxing time of 8 hours. When any single-sized colloidal CdTe solution is combined with the aforementioned CMS, the respective spectra is red-shifted (see Figure 4). In order to incorporate the synthesized QDs on functional solar cells, they had to be dispersed in a matrix layer [5]. For this purpose, we selected Polymethylmethacrylate (495 PMMA A2 from Microchem) as the matrix in which to disperse the CdTeMS + CMS. Upon nanostructure dispersion, the PMMA + QDs solutions were spin cast at 4,000 rpm on the window side of 52mm x 38mm, commercially available polysilicon solar cells (Eco-worthy Company) with a nominal thickness of 200µm. The resultant thin films had an average thickness of ~1050 nm. Solar cell performance was quantified using an Oriel Sol2A solar simulator under standard testing conditions. Specifically, measurements were collected before and after the deployment of the PMMA+QDs. The external quantum efficiency (EQE) was measured with an Oriel Quantum Efficiency Measurement kit (QE-PV-SI) using a spot size of approximately 2 mm². Solar cells performance improvement was corroborated in the measured values of the overall efficiency of the cells (see Figure 5) which improved from 12.43% to 13.03% upon QD deployment.

![Figure 3.- (a.) Carbon QDs have size-dependent, down-shifted photoluminescent emission peaks centered around 425 nm, however, the solution comprising all the carbon QDs previously synthesized, exhibits a red-shifted photoluminescent emission peak centered at ~515 nm (b.) Emission wavelength of CdTe QDs with different refluxing times under 390 nm excitation.](image)
Figure 4.- Emission spectra of colloidal solutions of CdTe QDs synthesized with different refluxing times of 1 h in (a) and 8 h in (b) and their shifted spectra when combined with CMS.

Figure 5.- A Comparison of the EQE before (Black line) and after the addition (Red line) of CMS + CdTeMS. The absorption and emission spectra are overlain.

4. Conclusions
The experimental observations of the interaction of the incorporation of PMMA thin films with downshifting CMS, CdTeMS and CdTeMS + CMS on the window side of solar cells indicate a relatively small but not negligible increase in the power conversion efficiency (PCE) of solar cells.

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