

Improvement the optical properties of the P3HT:PC70BM film using CdSe QD

Jorge Cruz-Gómez
Posgrado en Energía
Universidad Autónoma de
Querétaro
Querétaro, Qro. México
jorge_jcg@icloud.com

Aruna Devi Rasu-Chettiar
Posgrado en Energía
Universidad Autónoma de
Querétaro
Querétaro, Qro. México
raranadevi89@gmail.com

Francisco javier de moure-Flores
Posgrado en Energía
Universidad Autónoma de
Querétaro
Querétaro, Qro. México
francisco.javier.demoure@uaq.edu
u.mx

Sandra Andrea Mayén-
Hernández
Posgrado en Energía
Universidad Autónoma de
Querétaro
Querétaro, Qro. México
sandra.mayen@uaq.edu.mx

Adrian Sosa-Domínguez
Posgrado en Energía
Universidad Autónoma de
querétaro
Querétaro, Qro. México
adrian.sosa@uaq.mx

José Santos-Cruz
Posgrado en Energía
Universidad Autónoma de
querétaro
Querétaro, Qro. México
jsantos@uaq.edu.mx

Abstract—Quantum dots have properties that make them useful in almost all areas of science and technology. The active layer of the organic solar cells is no exception; in this work cadmium selenium quantum dots are used to enhance the optical properties of the active layer P3HT:PC70BM. Cadmium selenium is a p-type semiconductor, just like PC70BM; so, its function in the active layer is the same as that of PC70BM. This work reports the synthesis of cadmium selenium quantum dots of three sizes 2.4, 3.0 and 5.6 nm. These materials were obtained by colloidal chemical synthesis at temperatures of 210, 240 and 280° C respectively. Using spin coating, thin films of the mixture of each size of quantum dots were grown in combination with P3HT; in addition, films of the commonly used mixture of P3HT:PC70BM were grown, as a reference to compare its operation. With cadmium selenium quantum dots an improvement in radiation absorption was found compared with the usual active layer.

Keywords— CdSe QD, colloidal chemical synthesis, organic solar cells.

I. INTRODUCTION

Quantum dots have received significant attention in the present century due to their many applications, including electronics, biology, medicine, electricity generation, paints, lubricants, personal care, and numerous projects [1][2]. The size of the quantum dots is less than the diameter of the Bohr exciton of the material in bulk, which opens numerous opportunities to be employed in different applications, as mentioned earlier. When materials have sizes of this magnitude,

resulting in excellent optical and electrical properties such as intense luminescence, narrow and symmetrical emission, high stability in the presence of photo and chemo radiation, adjustable bandgap according to their size, and possibility of generating multiple excitons with a photon [3]. In particular, cadmium selenide is an n-type semiconductor whose Bohr exciton radius is 5.7 nm [4]. Therefore, it is possible to synthesize cadmium selenide quantum dots with diameters less than 11.4 nm, which increases the bandwidth perched from 1.74 eV, exhibiting an upper wavelength limit for the absorption of solar radiation, 700 nm [3]. Therefore, adjusting the bandwidth in the interval of 700 nm corresponds to visible light, where the solar spectrum has greater power which is essential to be used in solar cells. Among the new solar cell technologies, organic and hybrid are highly studied due to their potential to obtain solar cells at low cost, where inexpensive solution processes are employed to prepare active layer thin films [5][6]. Most importantly, quantum dots need to be properly blended with organic polymers to make the active layer deposition in hybrid solar cells. For this purpose, quantum dots are synthesized by colloidal chemical synthesis, which involves organic solvents, and allows quantum dots to be properly mixed with polymers [7][8]. During the synthesis of cadmium selenide quantum dots (CdSe QD), high boiling point solvent and binding material are used, which forms a shell of aliphatic radicals around the quantum dots to prevent agglomeration and precipitation. Therefore, these binders need to be changed as they do not exhibit good electrical conduction properties: for instance, pyridine (PY) or ethanedithiol (EDT) are commonly used [9][10]. Besides, excessive recombination of charge carriers has been observed because these carriers have to jump between

quantum dots; to decrease this recombination m-phenylenediamine has been successfully used, which forms "bridges" between quantum dots [10]. In this work, CdSe quantum dots are synthesized and mixed with organic solvents to use as active layer in organic and hybrid solar cells; in which QD's displace or combine with the commonly used fullerene derivatives, PC70BM and PC60BM.

II. MATERIALS AND METHODS

A. Materials

The materials that we used to prepare QD's are as follows: tetradecyl phosphonic acid, $\text{CH}_3(\text{CH}_2)_{13}\text{P}(\text{OH})_2$ from Beantown Chemical (98% purity); cadmium oxide, Sigma-Aldrich CdO (99.5% purity); oleic acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$ from Meyer (reactive grade); 1-octadecene, $\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}$ from GFS chemicals (90% purity); Trioctylphine (TOP), $(\text{CH}_3(\text{CH}_2)_7)_3\text{P}$ of Sigma-Aldrich (97% purity); Octadecyl amine (ODA), Aldrich $\text{C}_{18}\text{H}_{39}\text{N}$ (90% purity); Meyer chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$ (99.5% purity); Poly(3-hexylthiophene-2,5 diyl) (P3HT), Aldrich (99.995% purity); pyridine, $\text{C}_5\text{H}_5\text{N}$ (99% purity); and n-octane, C_8H_{18} , Sigma-Aldrich (anhydrous with 99% purity). All reagents were used as received.

B. Methods

- Colloidal chemical synthesis The synthesis was carried out reported by Mohamed et al. [11]. The QD's was synthesized in a nitrogen atmosphere, using three-mouth flasks; in a flask, cadmium oxide was placed, and oleic acid and 1-octadecene were added, the temperature was increased to 240°C and stirred for 1 hour; in the other flask, selenium was added along with tetradecyl phosphonic acid, octadecyl amine and trioctylphosphine, the temperature was raised to 100°C and stirred for 1 hour. Then, the temperature of the cadmium mixture was adjusted to the synthesis temperature, in this work, the temperature was adjusted to 280°C , 240°C and 210°C . After stabilizing the temperature of the cadmium mixture, the selenium mixture was added, and allowed to react for 5 minutes. After the synthesis time, it was removed from the heating mantle and cooled quickly. When it reached 40°C , the nitrogen flow was stopped. Then, the reaction mixture was washed six times using acetone and methanol to get the pure CdSe quantum dots. Finally, they are redispersed in toluene and stored until the change of binder.
- Ligand change. For the change of binder, pyridine was added to the CdSe QD's solution and kept stirring for 12 hours at 60°C and 24 hours at room temperature. After this process, we washed the quantum dots using acetone and methanol by centrifuging [9]. They were dried at room temperature, then weighed and dissolved in a mixture of chlorobenzene and pyridine 9:1 by volume, at a 25 mg/mL concentration.
- CdSe QD:P3HT polymer films 25 mg of P3HT is mixed in 1 mL of chlorobenzene with 4 mL of the previously prepared CdSe QD's solution. Then, the mixture was

kept in a sonic bath for 8 hours and then used to deposit films on Corning glass by spin coating technique.

- Characterization of CdSe QD's and thin layers. The absorbance spectra were measured by UV-Vis spectrophotometer brand Thermo Scientific model Genesis 10S; the STEM images were acquired using a SEM microscope Hitachi model SU8230 equipment; the X-ray diffractograms were obtained using a Rigaku model Ultima IV equipment, with copper white using $\text{K}\alpha$ radiation with a wavelength of 0.15418 nm. The Raman spectra were obtained with Micro Raman equipment brand Thermo Scientific model DRX2, and the thickness of the samples was determined using a KLA Tencor profiler model D-100.

III. RESULTS AND DISCUSSION

A. Synthesis of CdSe QD

The synthesis of quantum dots was carried out at three different temperatures, such as 280°C , 240°C and 210°C , resulting in three different sizes; the samples were named according with their temperature of synthesis, S-210, S-240 and S-280. Figure 1 shows the absorption spectra of CdSe QD's dissolved in toluene and the corresponding bandgap obtained by the Tauc method. The diameter of the QD's was obtained by using the empirical relationship reported by Yu et al. [12]. This relationship is:

$$D = 1.6122 \times 10^{-9} \lambda^4 - 2.6575 \times 10^{-6} \lambda^3 + 1.6242 \times 10^{-3} \lambda^2 - 0.4277 \times \lambda + 41.57$$

where λ is the wavelength in nm, for the maximum of the first absorption edge, and D is the diameter in nm. The size of the quantum dots is greater at a higher temperature, as established by the theory of the growth of crystals and their relationship with relative saturation [13]

Other absorption edges are also observed due to discrete states that appear when the size decreases, and, as expected, they are more evident as the size of the QD's is smaller [14], [15]. Figure 1(a) shows some additional absorption edges due to energetic states within the conduction and valence bands. These absorption edges are originated by quantum confinement due to the size of the QD's, and being more defined for the smallest size [14–16]. Also, in Figure 1(a) differences are observed in the width of the first absorption edge; a narrow and sharp edge indicates little dispersion in size. Thus, the size distribution for S-210 is narrower qualitatively than the other samples [17].

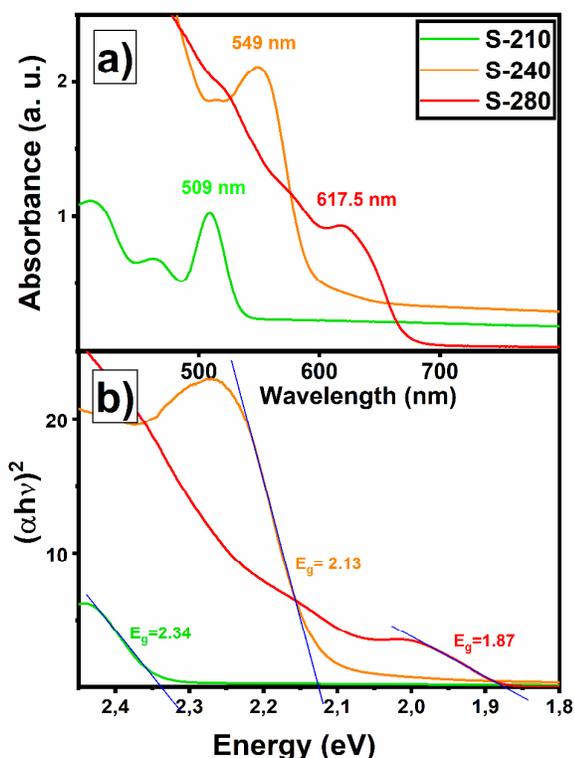


Fig. 1. Absorption spectra and calculated bandgaps for the three different sizes of CdSe QD's.

Figure 2 shows the images of the CdSe QD's samples dissolved in toluene; (a) sunlight and (b) UV; in 2b) the fluorescence of the QD's is clearly observed when excited with UV light. According to its bandwidth, the energy of the emitted photon has the corresponding color according to the visible light spectrum, green for 2.34 eV (531 nm), orange for 2.13 eV (583 nm) and red for 1.87 eV (664 nm). From Figure 2a), fluorescence did not observe because the energy of the solar spectrum is not enough to excite the QD's.

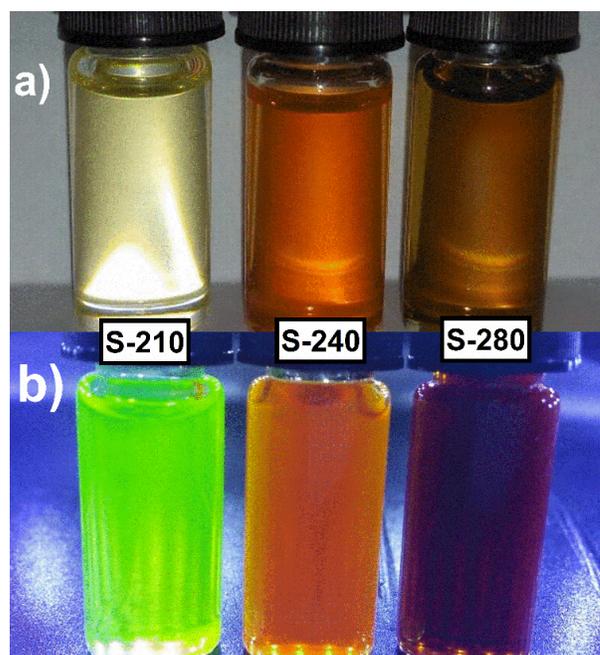


Fig. 2. Image of CdSe QD's solutions of different sizes. a) under visible light, and b) under UV light.

Figure 3 shows the histograms and STEM images of the three synthesized QD's sizes. Figures 3a and 3d correspond to S-210 with an estimated size of 2.4 nm; Figures 3b and 3e belong to the 3.0 nm QD's; and the 3c and 3f images refer to the 5.6 nm QD's. The three main sizes, obtained by histograms, have a good fit compared to the values estimated by the empirical relationship. A maximum difference of 0.06 nm was obtained when comparing the S-240. For all three QD's sizes, histograms show Gaussian behavior with a slight predominance of near-average and smaller sizes.

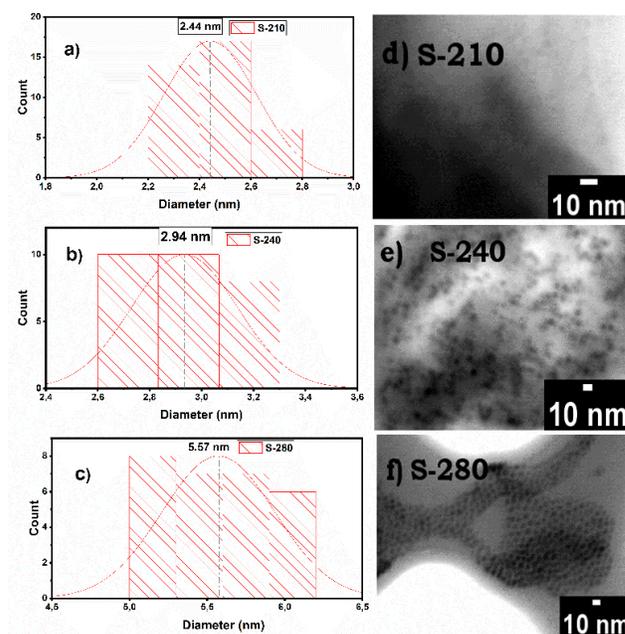


Fig. 3. Histograms and STEM images of CdSe QD's. (a) and (d) correspond to S-210; (b) and (e) to S-240; and (c) and (f) to S-280.

Figure 4 shows the Raman spectra of the CdSe QD's synthesized at three different sizes. From the Figure, the CdSe QD's signals are observed in a dashed grey line; 146 cm^{-1} correspond to the transverse optical mode (TO); 188.7 cm^{-1} related to the optical surface phonon mode (SO); 210 cm^{-1} ascribed to the first-order longitudinal phonon (1LO) mode, and overtone mode (2LO) was obtained at 415 cm^{-1} and even a very weak mode corresponding to a second overtone is reported in 622 cm^{-1} (3LO) [18–20]. The Raman peaks were greatly shifted to lower wavenumber for smaller particle size compared to a larger one (the observed signals with respect to those reported for bulk material). Thus, 1LO mode has a displacement of 9 cm^{-1} for S-210 and S-240 and 7.5 cm^{-1} for S-280. The 2LO mode of S-280 have a displacement of 9 cm^{-1} . These shifts are explained by the confinement of phonons due to the reduction in size [20].

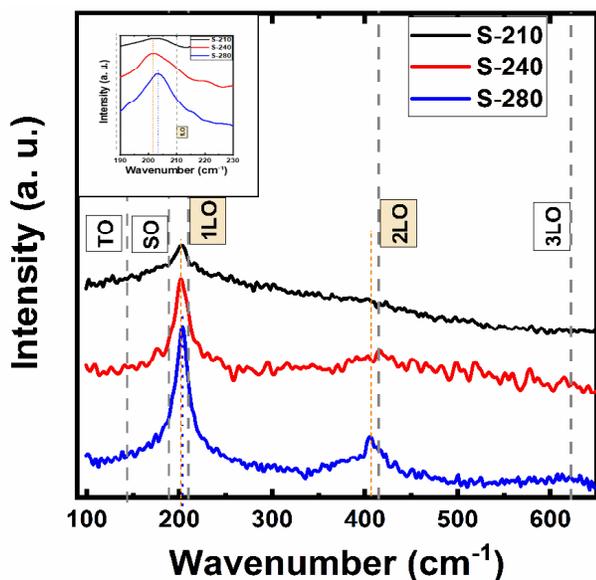


Fig. 4. Raman spectra of CdSe QD's using laser with $\lambda=532$ nm, and in the insert, a zoom view of the zone from 190 to 230 cm^{-1} .

The XRD pattern (Figure 5) depicts the main reflections, (1 1 1), (2 2 0) and (3 1 1), corresponding to the cubic crystal structure of CdSe. These reflections are compared with those reported in PDF #19-0191 of the X-ray analysis with wavelength 1.5406 Å, radiation $\alpha 1$ of copper, of the CdSe with cubic phase in powder. The observation of the signals is a large width, according to the general condition of a large width of the XRD signals for nanometer-sized materials. For S-210 the calculated average crystallite size using Scherrer's equation [21], was 1.8 nm. The observed differences in the size are explained as follows: in Scherrer's model, the width at the average height is attributed only to the size of crystallite, resulting in the lowest possible value. Furthermore, (2 0 0) and (2 1 0) planes corresponding to selenium dioxide (SeO_2) were observed by deconvoluting in the range from 18 to 30 degrees in 2 Theta (Figure 5b). The reflections corresponding to the planes (1 1 1) and (2 0 0) of the CdO (Figure 4a) were also identified.

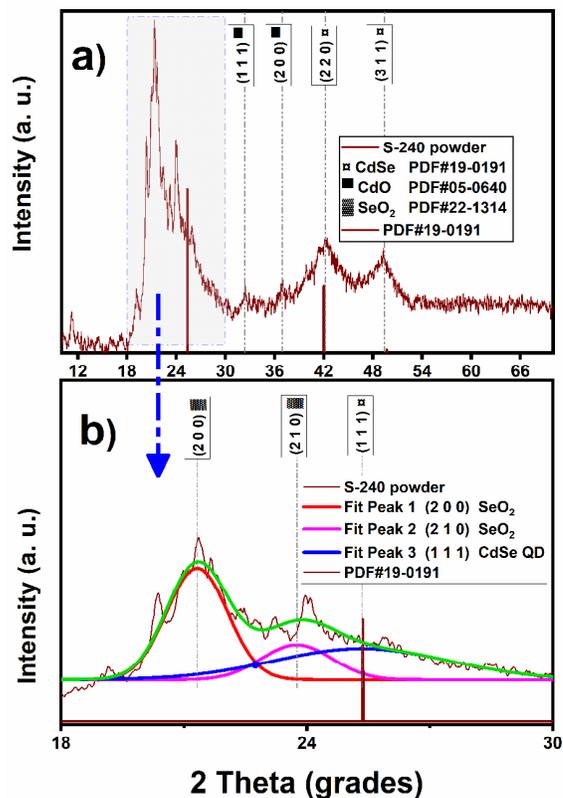


Fig. 5. a) Diffractogram of sample S-240 of CdSe QD's and b) Magnified view from 18 to 30 degrees in 2 theta.

B. CdSe QD's and P3HT layers

Figure 6 shows the UV-Vis absorbance spectrum of the P3HT polymer solution and the fullerene-derived PC70BM molecule; the solution is 1:1 by weight with 25 mg/mL of chlorobenzene with 3% by volume of diiodo octane (DIO) and P3HT spectra with three different sizes of CdSe QD's. The highest absorption of solar radiation for the former was observed at 500 and 300 nm. This absorption spectrum is greatly improved when the polymer is mixed with CdSe QD's in a weight ratio of 1:4 using the same solvent, especially with those of S-280. As can be seen in Figure 6 the absorption in the wavelength interval from 510 to 670 nm is improved.

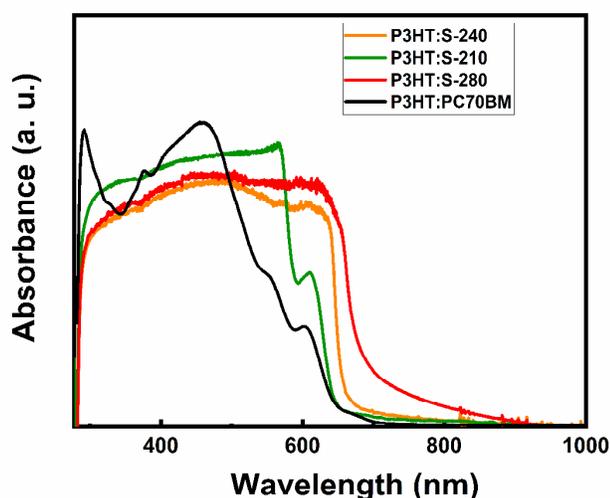


Fig. 6. UV-Vis absorbance spectra of P3HT:CdSe QD's (1:4) and P3HT:PC70BM (1:1).

In this way, the change of PC70BM by CdSe QD's improved the absorption of radiation in intervals where the solar spectrum has an important power. Then acceptable results can be expected from solar cells using CdSe QD's instead of PC70BM for the active layer. The additional positive effect is that CdSe QD's are less likely to degrade than the PC70BM; the cells can even be manufactured without the need for nitrogen atmosphere, with the consequent savings.

IV. CONCLUSIONS

CdSe quantum dots were synthesized with three different sizes such as 2.4, 3.0 and 5.6 nm. The obtained quantum dots were blended well with the organic solvents, revealing their potential in organic solar cells. Specifically, quantum dots synthesized with a size of 5.6 nm showed the absorption in the range between 510 and 670 nm, where P3HT and PC70BM polymers did not reveal the proper absorption in this range. When the CdSe QD's ligand changed from the TOP to the EDT, the QD's remained soluble and mixed with the polymer solution. Then, the mixture of the polymer and QD's were used to deposit the active layer by spin coating. Moreover, the optical properties were enhanced by replacing PC70BM with CdSe QD's.

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