Tuning luminescence and reducing reabsorption of CdSe quantum disks for luminescent solar concentrators

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Abstract
Cadmium selenide (CdSe) quantum disks (QDs) have been synthesized for application in luminescent solar concentrators (LSCs). Luminescence tuning and reabsorption reduction of the QDs were achieved by controlling their size using a hot injection method. The overlap of the absorption and photoluminescence spectra of the as-prepared CdSe QDs was negligible. The as-prepared CdSe QDs were incorporated into polymethylmethacrylate without aggregation and luminescence quenching. The obtained highly transparent composites with non-affecting light-emitting properties were used as LSCs. The placement of a CdSe QDs doped LSC prototype (10 × 1 × 0.1 cm) on a Si-cell resulted in a 201% increase in the electrical power output of the Si-cell compared with that of the bare Si-cell.

Keywords: quantum disks, luminescence tuning, reabsorption reduction, luminescent solar concentrators

(Some figures may appear in colour only in the online journal)

1. Introduction
Solar concentration is an effective way of reducing the cost of photovoltaic (PV) energy, and allows the use of small cells operating at high efficiency. Although conventional solar concentrators such as mirrors and lenses enable the concentration of light upon a small cell, they have a range of requirements that increase their cost such as the inability to concentrate diffuse light and the need for solar cell cooling and solar tracking machinery [1, 2]. Luminescent solar concentrators (LSCs), proposed in the 1970s, offer an alternative approach to circumvent these drawbacks of conventional solar concentration technologies [3–5]. LSCs are composed of a thin glass or plastic substrate containing highly luminescent materials. Upon illumination with sunlight, the fluorophore emissions are concentrated towards the edge of the thin substrate by total internal reflection [6–8]. The emission energy is then collected by a PV cell at the thin-edge of the waveguide. Because the area of the LSC exposed to sunlight is much greater than the area of the PV cell, the radiation flux incident onto the device is greatly increased, thereby boosting both the photocurrent and the photovoltage [4, 6, 8]. Moreover, additional increases in power output can be obtained by matching the emission wavelength of the LSC emitters to the spectral peak of the PV efficiency of a given device. Based on such a design, spectral and spatial concentration of both specular and diffuse light can be achieved without the need for cooling or tracking [2, 8]. The simple configuration of LSCs facilitates the integration of PVs with urban environments, such as in windows and walls [6, 9].

Luminescent nanocrystals prepared via colloidal chemical methods are promising materials for application in LSCs [2, 10–14]. Compared with organic chromophores, luminescent nanocrystals present many advantages, such as large absorption cross-sections, tunable emission, near-unity
emission efficiency, enhanced photo-stability, and can be incorporated into organic or inorganic matrices via solution-based procedures [15–21]. However, an existing challenge plagues the use of luminescent nanocrystals in LSCs, namely that self-absorption losses result from the small energy separation between their emission and absorption spectra [2, 6, 8]. Therefore, a number of strategies for tuning the spectral profile of luminescent nanocrystals have been developed to overcome this problem, including size tuning, composition tuning, and surface tuning [2, 6, 22]. For instance, heterostructured nanocrystals (i.e., core/shell structures) and transition-metal ion doping have been conducted for surface tuning and composition tuning, respectively, to artificially reduce the reabsorption of the luminescent nanocrystals [8, 10, 22–24]. With knowledge of the size-dependent Stokes shift [2, 22, 25], tunable optical properties of luminescent nanocrystals could be achieved using size control processes. Also, a large surface/volume ratio makes it easier to tune the luminescence properties of such nanocrystals using size control [26]. A two-dimensional disk morphology may offer a better sunlight absorption cross-section than zero-dimensional dots and one-dimensional rods. Moreover, for the same number of molecules in the luminescent nanocrystals, quantum disks (QDs) may have a larger surface/volume ratio than those of quantum dots or quantum rods. Given these considerations, in this work we aimed to prepare QDs and tune their luminescence via size control to reduce their self-absorption, and fabricate a polymethylmethacrylate (PMMA)-based LSC containing the as-prepared QDs as luminescent materials.

2. Experiment and results

Cadmium acetate dihydrate (Cd(OAc)$_2$•2H$_2$O), selenium powder (Se, 99%), myristic acid (98%), and 1-octadecene (ODE, 90%) were purchased from Sigma Aldrich. The solvents used in this work, including acetone, ethanol, toluene and hexane, were purchased from Sinapharm. All materials were used directly without further purification. The CdSe QDs were synthesized following a previously reported method with slight modification [27]. In a typical synthesis, 53.3 mg Cd(OAc)$_2$2H$_2$O, 5.7 mg myristic acid, and 5 mL ODE were added to a 100 mL two-necked round flask, and then degassed with vacuum pumping at room temperature for at least 30 min. The solution was then purged with argon gas using a standard Schlenk line. In another reaction flask, 4 mg Se powder was dissolved in 0.1 mL tricyclophosphine (TOP, 97%) with the assistance of a heat gun after the mixture had been degassed and protected with argon gas. 0.1 mL of the Se-TOP solution was then quickly injected into the Cd-precursor solution using a disposable syringe, and the reaction temperature was stabilized at 170 °C. The reaction solution was stirred vigorously throughout. The color of the solution changed from colorless to yellow with 30 min. Aliquots were taken to monitor the reaction by ultraviolet–visible (UV–vis) and photoluminescence spectroscopy in 10 min intervals. The reaction was stopped by removal of the heating mantle and cooling to room temperature in an ice-water bath. The synthesized CdSe QDs were washed by centrifugation using ethanol at 14 000 rpm, and then re-washed with hexane. The CdSe QDs were dispersed in hexane using an ultrasonic bath, for further characterization.

The absorption and emission spectra of the washed CdSe QDs were measured using a UV–vis spectrophotometer (UV-2550) and fluorescence spectrophotometer (F7000), respectively. The photoluminescence decays of the CdSe QDs were measured using a combined fluorescence lifetime and steady state spectrometer (FLSP920). The photoluminescence quantum yield of the as-prepared CdSe QDs was obtained by following the method reported in the literature. Both high and low magnification morphological characterizations were performed using a JEM-2100 transmission electron microscope (TEM).

2.1. CdSe QDs

To control the size and tune the luminescence of the CdSe QDs, the nucleation and growth processes of the CdSe QDs were temporally separated, as shown in figure 1. TOP was used to dissolve the Se powder to obtaining a better stoichiometric ratio between the cadmium and selenium. During their synthesis, the CdSe QDs were collected with a glass syringe in 10 min intervals and their photoluminescence under a 365 nm UV-lamp was measured. The emission colors of the different CdSe QD samples (sample I to III in figure 1) under the UV lamp varied from blue to yellow, attributed to the prolongation of their growth time.

To characterize their morphology, the as-prepared CdSe QDs were dispersed in hexane in an ultrasonic bath for 20 min, and the resulting solution was dripped onto a copper grid coated with 5 nm thick carbon film. The size and shape of the as-prepared CdSe QDs were measured using a JEM-2100 TEM. Figures 2(a)–(c) show the TEM images of samples I, II and III of the as-prepared CdSe QDs, respectively. The TEM images show that the prepared CdSe samples are in a planar and quasi-rectangular shape, which indicates that the samples can be considered as QDs. Note that image of the single QD is very close to the background due to the very small thickness of the disks (about 2 nm). The size of the as-prepared QDs typically increased from 36 × 24 nm to 58 × 38 nm as a result of the prolongation of the reaction duration. In addition, the increasing size of the QDs resulted in a red shift of the fluorescence from blue for sample I to yellow for sample III, owing to a reduction in quantum confinement. The EDS system of the JEM-2100 TEM was used to analyze the content of the as-prepared QDs. The results are presented in figures 2(d)–(f) for sample I, II, and III respectively, and confirm that the as-prepared QDs were composed of CdSe. The atomic ratio of cadmium to selenium of the as-prepared QDs was about 1.6 ± 0.1 for all of the QDs with different sizes.

Figures 3(a)–(c) show the absorption and photoluminescence of sample I, II, and III of the as-prepared QDs in hexane solution, respectively, while the corresponding insets show photographs of the QD dispersions under a
For the smallest size of the as-prepared QDs (i.e., sample I), there was a significant overlap between the absorption spectrum and the photoluminescence spectrum. However, with the prolongation of the reaction duration, the fluorescence of the QDs was tuned from blue to yellow and the overlap of the absorption and photoluminescence spectra was reduced, as shown in figures 3(b) and (c). Moreover, the overlap of the spectra was negligible for the largest QDs (sample III). Therefore, it can be concluded that temporally separating the nucleation and growth processes of the CdSe QDs to control their size allowed us to tune their luminescence properties and reduce the overlap of their absorption and photoluminescence. In LSC applications, a significant overlap between absorption and photoluminescence spectra would result in significant reabsorption of the light emitted by the luminescent materials, which would become a serious problem for the long optical pathways expected in large-area LSCs. Although a certain fraction of the absorbed light would be re-emitted, the net result would still be an overall emission loss because of both the non-unity photoluminescence quantum yield and the isotropic character of the emitted radiation, which does not allow for the capture of all re-radiated photons by total internal reflection. For example, in typical glass or polymer waveguides, only about 75% of the emitted light is retained by total internal reflection. Thus, in comparison to sample I of the as-prepared CdSe QDs, sample III would be the more suitable for application in LSCs because of the negligible overlap of its absorption and photoluminescence spectra. Although a certain fraction of the absorbed light would be re-emitted, the net result would still be an overall emission loss because of both the non-unity photoluminescence quantum yield and the isotropic character of the emitted radiation, which does not allow for the capture of all re-radiated photons by total internal reflection. For example, in typical glass or polymer waveguides, only about 75% of the emitted light is retained by total internal reflection. Thus, in comparison to sample I of the as-prepared CdSe QDs, sample III would be the more suitable for application in LSCs because of the negligible overlap of its absorption and photoluminescence spectra. Therefore, in this work the as-prepared CdSe QDs of sample III were taken as the luminescence material to fabricate CdSe QD-doped luminescent solar concentrator (QD-LSC) prototype devices. Apart from low reabsorption, another key requisite property for the luminescent materials of LSCs is high photoluminescence quantum efficiency. The photoluminescence quantum efficiency of sample III of the as-prepared CdSe QDs was therefore measured, and was found to be 20±5% in hexane.

2.2. PMMA-based LSC containing CdSe QDs

Two of the main challenges in incorporating inorganic nanoparticles into a polymer matrix are the agglomeration and luminescence quenching of the inorganic nanoparticles. Thus, an effective method was required for incorporating the present as-prepared CdSe QDs in a high-optical-quality transparent matrix without causing degradation of their photoluminescence efficiency. In our studies we have focused on incorporating QDs into PMMA because of its excellent optical properties, high resistance to ultraviolet light exposure and various chemical treatments, and excellent performance in all-weather conditions. The procedure used to fabricate a PMMA-based LSC containing the CdSe QDs is summarized as follows.

About 20 mL MMA monomer solution and its radical initiator azobisisobutyronitrile (AIBN; 1000:1 w w⁻¹) were mixed well in advance, and then baked at 80 °C until a sticky solution was obtained. The reaction system was the cooled to room temperature to quench the polymerization process. Afterwards, about 3 mL of a 0.1 mM as-prepared CdSe QD toluene solution was mixed well with the prepared sticky solution, as shown in figure 4(a). The resulting mixture was then poured into a mold consisting of two glass slides separated by a silicone spacer, and baked in an oven at 40 °C until it became solid (about 12 h). Next, the temperature of the oven was increased to 100 °C for 1 h to carry out the final polymerization of the PMMA/QD nanocomposite. Finally, the edge of the prepared PMMA/QD nanocomposite was polished for use with the commercial solar cell.
Figure 2. Morphology and elemental analysis of the as-prepared QDs. (a)–(c) TEM images of samples I, II and III; (d)–(f) EDX analysis of samples I, II and III. Scale bar: 25 nm.
Figure 3. Absorption and photoluminescence spectra of the as-prepared CdSe QDs; (a) sample I, (b) II, (c) III.

Figure 4. (a) Colloidal solution of PMMA and as-prepared CdSe QDs under a UV-lamp; (b) QD-LSC illuminated by a solar simulator; (c) QD-LSC under ambient illumination.
As shown in figure 4, a CdSe QD-LSC with dimensions of $10 \times 1 \times 0.1$ cm was fabricated. Figure 4(b) displays a photograph of the QD-LSC under excitation with a solar simulator (Newport Oriel 91192), while figure 4(c) shows the device under ambient room light. As figure 4(b) shows, light was absorbed by the QDs, and the emission from the QDs propagated and was concentrated at the thin-edge of the substrate by total internal reflection.

2.3. Performance of the QD-LSC

To investigate whether the light-emitting properties of the as-prepared QDs were affected by their incorporation in the LSC, the absorption and photoluminescence spectra and the time-resolved photoluminescence of the QDs dispersed in hexane solution were compared with those of the QDs embedded in the PMMA matrix. The black and red curves in figures 5(a) and (b) represent the absorption and photoluminescence spectra of the QDs embedded in the PMMA matrix and those in hexane solution, respectively. It can be seen that there is little difference in the position and shape of the absorption and photoluminescence spectra between the QDs dispersed in hexane solution and those incorporated in the PMMA matrix, which implies that the light-emitting properties of the QDs were not affected by the incorporation. The red and black curves in figure 5(c) illustrate the time-resolved photoluminescence of the as-prepared CdSe QDs dispersed in hexane and embedded in PMMA matrix, respectively. Additional surface-defect-related non-radiative emission probably activated by initiator radicals of MMA would result in a faster photoluminescence decay of the QDs. However, the QDs embedded in the PMMA matrix exhibited an almost identical fluorescence lifetime to that exhibited by the QDs in hexane, which further confirms that the light-emitting properties of the QDs were not affected by their incorporation in the matrix. Insets I and II in figure 5 are photographs of the PMMA/QDs nanocomposite and QD hexane solution, respectively.

A PV cell (Si-cell) was placed against one of its two smallest faces of the QD-LSC to evaluate its practical performance, as shown schematically in figure 6(a). To compare the solar cell performances with and without the QD-LSC, an
illumination by the solar simulator (Newport Oriel 91192) under AM 1.5 conditions (100 mW cm\(^{-2}\)) was applied to the measurements. In addition, since the facet of the QD-LSC is 1 × 0.1 cm, the Si-cell was covered with a 1 × 0.1 cm diaphragm to maintain the same photosensitive area for each of the measurements. Figure 6(b) shows a bare PV cell which was directly illuminated by the solar simulator under AM 1.5 conditions. Inset I of figure 6(b) is the as-used Si-cell while inset II is the Si-cell covered with the diaphragm. The measurement of the Si-cell with the QD-LSC is performed under the same illumination condition, as shown in figure 6(c). Note that in the measurement, since the photosensitive area (1 × 0.1 cm) of the Si-cell is parallel to the illumination direction, the light absorption by the cell was outputted from the concentrator only. Through the extremely simple method (figures 6(b)–(c)), in which antireflection coatings to reduce optical losses were not employed, the photocurrent–voltage (I–V) curves of the Si-cell with and without the QD-LSC were measured with a source meter (Keithley 2400). Figure 7(a) shows the I–V curves of the Si-cell without and with the QD-LSC. The short-circuit current of the bare Si-cell without the QD-LSC was found to be 5.29 mA, while that of the QD-LSC was 6.47 mA. Multiplying the measured current by the measured voltage, the electrical power output of the Si-cell was obtained, and is shown as a function of voltage in figure 7(b). The maximum output power of the Si-cell with and without the QD-LSC was 1.69 and 0.84 mW, respectively. The concentration ratio (C) of a LSC is defined as the ratio between incoming and outgoing optical radiance, and can be given by

\[ C = G \times \eta_{\text{eff}}, \]

where \( G \) is the geometric gain, namely the ratio of the illuminated surface area of the QD-LSC to the area of the edge where the solar cell is attached, and \( \eta_{\text{eff}} \) is the optical efficiency, defined as the ratio between the incoming power coupled to the illuminated surface area of the QD-LSC and the outgoing power from the edge of the QD-LSC. Also, \( \eta_{\text{eff}} \)

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**Figure 6.** (a) Schematic of the photocurrent–voltage measurement setup for the QD-LSC; (b) photograph of the measurement of the photocurrent–voltage of the photovoltaic cell without the QD-LSC; (c) photograph of the measurement of the photocurrent–voltage of the photovoltaic cell with the QD-LSC.
can be given by
\[ \eta_{\text{eff}} = \frac{P_{\text{out}}}{P_{\text{in}} \eta_0}, \] (2)
where \( P_{\text{out}} \) is the electrical power output measured from the solar cell attached to the QD-LSC, \( P_{\text{in}} \) is the incident light power on the top surface of the QD-LSC, and \( \eta_0 \) is the conversion efficiency of the bare cell covered with the diaphragm. In our case, \( G = 100 \), \( (10 \times 1 \text{ cm})/(1 \times 0.1 \text{ cm}) \), \( \eta_0 = 8.4\% \), \( P_{\text{in}} = 1 \text{ W} \, (100 \text{ mW cm}^{-2} \times (10 \times 1 \text{ cm}^2)) \), and \( P_{\text{out}} = 1.69 \text{ mW} \). Thus, the optical efficiency of the QD-LSC calculated from formula (2) was 2.01\%, and the effective concentration ratio of the QD-LSC was 2.01. This corresponds to a 201\% increase in the electrical power output of the solar cell attached to the QD-LSC compared with that of the bare cell. Therefore, these test results provide an important proof of the feasibility of solar light concentration using LSCs doped with tuned CdSe QDs. However, it should be noted that the fluorescence quantum yield of the as-used CdSe QDs and the optical efficiency of the QD-LSC are still low, so there is also room for improvement in the quality of the QDs and the PMMA/QD nanocomposite, particularly for the fluorescence quantum yield of the QDs.

3. Conclusion

We have demonstrated experimentally that prolonging the reaction duration increases the size of CdSe QDs synthesized using a hot injection method. The increase in size causes a red shift in the photoluminescence of the QDs, which further results in a reduction of the reabsorption of the QDs. CdSe QDs with negligible reabsorption were synthesized, and the as-prepared CdSe QDs (typical size of \( 38 \times 58 \text{ nm} \)) were used as dopants in QD-LSC prototype devices (\( 10 \times 1 \times 0.1 \text{ cm} \)). The absorption spectrum, photoluminescence spectrum, and time-resolved photoluminescence of the QDs in hexane solution and in the QD-LSC prototype device showed that the light-emitting properties of the QDs were not affected by their incorporation into a PMMA matrix. Comparison between the electrical power output of a Si-cell with and without the QD-LSC indicated that the effective concentration ratio of the present QD-LSC is 2.01. This indicates that the QD-LSC can increase the electrical power output of a solar cell by 201\%, a result that implies the feasibility of solar light concentration using LSC doped with tuned CdSe QDs.

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Reference

[1] Currie M J, Mapel J K, Heidel T D, Goffri S and Baldo M A 2008 Science 321 226
[2] Purcell-Milton F and Gun’ko Y K 2012 J. Mater. Chem. 22 16687.
[3] Weber W H and Lambe J 1976 Appl. Opt. 15 2299
[4] Goetzberger A and Greube W 1977 Appl. Phys. 14 123
[5] Reisfeld R and Neuman S 1978 Nature 274 144
[6] Debye M G and Verbunt P P C 2012 Adv. Energy Mater. 2 12
[7] Van Sark W G, Barnham K W, Slooff L H, Chatten A J, Büchtemann A, Meyer A and Vannackelbergh D 2008 Opt. Express 16 21773
[8] Meinardi F, Colombo A, Velizhanin K A, Simonutti R, Lorenzon M, Beverina L, Viswanatha R, Klimov V I and Brovelli S 2014 Nat. Photonics 8 392
[9] Banal J L, White J M, Ghiggino K P and Wong W W 2014 Sci. Rep. 4 4635
[10] Coropceanu I and Bawendi M G 2014 Nano Lett. 14 4097
[11] Erickson C S, Bradshaw L R, McDowall S, Gilbertson J D, Gamelin D R and Patrick D L 2014 ACS Nano 8 3461
[12] Bronstein N D, Li L, Xu L, Yao Y, Ferry V E, Alivisatos A P and Nuzzo R G 2013 ACS Nano 8 44
[13] Bradshaw L R, Knowles K, McDowall S and Gamelin D R 2015 Nano Lett. 15 1315
[14] Zhao Y M and Lunt R R 2013 Adv. Energy Mater. 3 1143
[15] Bomm J, Büchtemann A, Chatten A J, Bose R, Farrell D J, Chan N L and Koole R 2011 Sol. Energy Mater. Sol. Cells 95 2087
[16] Shcherbatyuk G V, Inman R H, Wang C, Winston R and Ghosh S 2010 Appl. Phys. Lett. 96 191901
[17] Hyldahl M G, Bailey S T and Wittmershaus B P 2009 Sol. Energy 83 566
[18] Petruska M Z, Malko A V, Voyles P M and Klimov V I 2003 Adv. Mater. 15 610
[19] Wood V, Panzer M J, Chen J, Bradley M S, Halpert J E, Bawendi M G and Bulović V 2009 Adv. Mater. 21 2151
[20] Tamborra M, Striccoli M, Comparelli R, Curri M L, Petrella A and Agostiano A 2004 Nanotechnology 15 S240
[21] Otto T, Müller M, Mundra P, Lesnyak V, Demir H V, Gaponik N and Eychmüller A 2012 Nano Lett. 12 5348
[22] Zhong H, Bai Z and Zou B 2012 J. Phys. Chem. Lett. 3 3167
[23] Krumer Z, Perla S J, van Dijk-Moes R J A, Zhao Y, de Brouwer A F, Groeneveld E and de Mello Donegá C 2013 Sol. Energy Mat. Sol. Cells 111 57
[24] Barnham K, Marques J L, Hassard J and O’Brien P 2000 Appl. Phys. Lett. 76 1197
[25] Omata T, Nose K and Otsuka-Yao-Matsuo S 2009 J. Appl. Phys. 105 073106
[26] Baker Dr and Kamat P V 2010 Langmuir 26 11272
[27] Li Z and Peng X 2011 J. Am. Chem. Soc. 133 6578