Design and performance of nanostructure-based luminescent solar concentrators

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ABSTRACT

A number of methods to reduce the cost of solar power generation have been developed over the last few decades. Recently, research and development in the area of Luminescent Solar Concentrators (LSCs) have shown that these devices are capable of significantly reducing the price of solar energy. We propose using near infra-red (NIR) quantum dots (QDs) as luminescent media in the LSC. Our results demonstrate that LSCs designed with NIR QDs can generate over twice the energy as the ones using their visible counterparts.

Keywords: Luminescent solar concentrators, quantum dots, solar energy.

1. INTRODUCTION

As of 2010, the biggest sources of electricity are still conventional power plants which use non-renewable coal and oil for energy production. Renewable energy generation is held back by the high costs (compared to coal and oil) and by the lack of availability of renewable energy sources at all times. While using a power grid can greatly alleviate the latter drawback, the cost of generation still makes it impractical from an economical standpoint to make a massive move towards renewable energy.

The price of harnessing solar energy is greatly influenced by the price of the device used to convert solar radiation into electricity – the photovoltaic (PV) cell. These devices typically consist of a semiconductor p-n junction, where solar radiation creates an electron-hole pair that is then separated by a built-in electric field from the depletion zone and transported to the external load. Since the time of their first use for energy generation in 1954 \cite{1}, the advances in design and manufacturing processes have reduced the expenses involved. However, even today, the price of generating solar energy remains greater than that of non-renewable power sources.

One way to drive down the price of solar energy is to use imaging devices, such as lenses or mirrors, to concentrate solar power onto a small area PV cell. This method, called concentrated photovoltaics (CPV), has the advantage of driving down the cost by reducing the amount of PV required, but due to the nature of the optics used it requires solar tracking and due to limitations of the PV cell’s efficiency, can cause overheating that leads to a drop in performance.

An alternate method of concentrating solar energy is a luminescent solar concentrator (LSC). Originally introduced in the late 1970's \cite{2,3}, an LSC consists of a planar sheet of transparent material, such as glass or plastic, doped with some luminescent species, as seen in Figure 1.

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In an LSC, the solar radiation is absorbed by the luminescent species which then re-emit the light at a longer wavelength. Due to the isotropic emission of these species (in most cases), 75% of the emitted light (for a transparent matrix with index of refraction $\sim 1.5$ [4]) is trapped by total internal reflection. The down-converted light is then guided along the concentrator to reach a PV cell attached to the edges of the LSC. To make the mean-free path of the emitted photon longer, the luminescent species are selected in such a way that their absorption and emission spectra overlap as little as possible so that the emitted light is less likely to get re-absorbed. The process of re-absorption by luminescent species is called self-absorption (SA) [5], and is one of the main limiting factors for creating large LSCs – N self absorption events results in a loss of $0.25 \times QY \times N$ photons, where quantum yield (QY) is defined as the ratio between the number of photons emitted by luminescent species to the number of photons absorbed.

The advantage of using LSCs is that like any concentrator it is designed to decrease the cost of generating solar energy by reducing the amount of PV material required. Additionally, when compared to a CPV, LSCs have advantages of not having heat dissipation problems and the ability to absorb indirect sunlight, which allows these devices to work without tracking [6,7].

In early research efforts, organic dyes were used as luminescent species. However, due to several notable drawbacks, mainly due to large self-absorption and a high rate of photo bleaching in dyes, the development and application of usable LSCs never materialized and interest waned in the 1980s. Some work with dyes continued as dyes with lower self-absorption and slower degradation were created, culminating in a 6.8% efficiency device created at MIT in 2008, but all of the dye-based devices, including the latest ones, have shown signs of degradation with time [8].

2. MOTIVATION

As of right now, there are no commercially viable LSCs. Top of the line dye-based concentrators still suffer from long-term degradation of performance under sunlight, whereas concentrators based on other luminescent species have an efficiency of about half when compared to what has been achieved with dyes [9]. The work on LSCs is therefore concentrated on stabilizing dyes or on seeking ways to bring up the efficiency of non-dye concentrators. The main goal of the latter branch is to find species with broad absorption spectra that emit light at near silicon band-gap (the reason for this will be explained later in the text) with as little overlap between the emission and the absorption spectra as possible (to limit SA) [10-12]. One type of the species that has been proposed are semiconductor nano-particles exhibiting quantum confinement properties – quantum dots (QDs) [13].

In order to compare the performance of different LSCs it is useful to be able to quantify their efficiency, which can be done in two ways. The first, referred to as the power conversion efficiency, is to take the ratio of power generated by the PV cell, coupled to the device, to the total solar flux incident on the LSC. Alternatively one could calculate the integrated optical efficiency of the LSC, that is defined as $\eta_{opt} = \frac{I_{LSC} \times A_{PV}}{I_{PV} \times A_{LSC}}$ [12], where $I_{PV}$ is the photocurrent generated in the PV cell without the concentrator, $A_{LSC}$ the area of the top of the LSC and $A_{PV}$ the active area of the PV cell. The ratio $A_{LSC} / A_{PV}$ is known as the geometric factor and gives the measure of how big the concentrator is when compared to
the PV cells coupled to it. Thus, while $I_{LSC}$ should increase as the area of the concentrator increases, the geometric factor weights it in such a way so as to have optical efficiency display the overall performance of the LSC.

3. PERFORMED EXPERIMENTS

In order to confirm our thesis that NIR QDs are better suited for the use in LSCs, a comparative study of CdSe/ZnS QDs (emission 620nm) and PbS QDs (emission 850nm) has been carried out. Both types of QDs were purchased from Evident Technologies. For our experiment, liquid solutions were sealed in quartz panels of dimensions $45 \times 12 \times 4$ mm$^3$ (optical path length of 2 mm) as seen on Figure 2. At the short edge of the panel, a high efficiency silicon PV cell was attached (as seen on Figure 1) with an active area of $12 \times 4$ mm$^2$. The absorption/emission spectra were taken with a Perkin Elmer UV-VIS spectrometer, and the spatially-resolved spectra with a 300mm Acton spectrometer with a thermoelectrically cooled CCD (resolution 0.14 nm).

![Figure 2](image)

Figure 2 a) Sample cuvette used in the experiments b) Sample cuvette with Rhodamine B sample excited by a 407nm laser c) Dimensions of the sample cuvette used.

The results for absorption measurement are shown in Figure 3a. As expected, PbS QDs absorb larger wavelength range of photons. However, to achieve the same absorbance ($A=\epsilon c$) with smaller molar extinction coefficient of PbS QDs $\epsilon = 2 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ versus $3 \times 10^5$ L mol$^{-1}$ cm$^{-1}$ for CdSe/ZnS, we had to use 15 times greater concentration of PbS QD. Overlaying absorption and emission curves for PbS and CdSe QDs on same graph (Figure 3b) one can see that due to larger band gap and bigger energy splitting (produced by stronger quantum confinement) PbS QDs have a smaller overlap between emission and absorption curves and higher Stokes shift [14].

![Figure 3](image)

Figure 3 a) Absorption spectra for PbS and CdSe quantum dots b) Overlaid emission and absorption curves for PbS and CdSe QDs with Stokes Shift shown. (Reprinted with permission from [15] Copyright [2010], American Institute of Physics).
To verify smaller SA in PbS QDs, the red-shift measurement was carried out as described above. The results for this measurement are presented in Figure 4. Figure 4a shows normalized spectra for the 50 μM solution of PbS at d= 0, 10 and 20 mm. Regardless of the excitation-collection separation, the emission spectrum appears to have a bimodal distribution with peaks at λ₁ = 896 nm and λ₂ = 928 nm, which can arise from two fractions of differently sized dots in the ensemble [16]. With increasing excitation-collection separation, the spectral weight shifts from λ₁ to λ₂ as the emission from the smaller dots are increasingly absorbed and re-emitted by the larger ones. Individually the peak at λ₁ shifts by ~ 4 nm and the one at λ₂ by ~ 2 nm between d = 0 and 20 mm. CdSe/ZnS QD emission with equivalent absorbance shows a red-shift of almost 20 nm by d = 20 mm. Since the 50 μM sample shows relatively small SA, the measurement is repeated with a 193 μM (stock concentration) solution of PbS. This sample shows very high absorption (fig. 3a, black) and its emission spectrum shows a single peak at 928 nm at d = 0 (fig. 4b, black). The decimation of the previously observed λ₁ implies that in the 193 μM solution the luminescence from the smaller dots is quenched. As d is increased, the spectrum red-shifts and this shift in the peak of emission from the d = 0 value is plotted in the inset (solid circles), along with the observed red-shift in the 3 μM CdSe/ZnS solution (open circles). The former saturates around Δλ = 20 nm but the latter keeps increasing up to the limits of the measurement capability.

Next, a concentration study has been carried out. With a high-performance Si PV cell coupled to the edge of our panel, cell was filled with different concentration of luminescent species. Figure 5 is a comparison of the photocurrent I_{LSC} generated by PbS and CdSe QDs as a function of the concentration. We believe that the shape of these curves is determined by the interplay between number of photons absorbed by the material, and self-absorption. Due to the larger part of CdSe QDs emission spectrum being subject to self-absorption, the interplay between self-absorption and absorption is far more pronounced in these dots. Currently it is believed that the red-shift and self-absorption are proportional to each other, therefore the exponential fit A+Be^{-Cx} (as obtained from insert of figure 4b) can be used to model self-absorption at distance x, and 1-e^{-Dy} can be used to model amount of light absorbed at concentration y (as per Beer-Lambert law).

From the standpoint of current generated by the different LSCs, one can see that the 193 μM PbS QD solution produces 250 μA (red curve) with a PV cell attached along one edge. This current drops slightly after photo-exposure (blue curve). Figure 5 compares the performance of PbS QDs to CdSe/ZnS QDs and Rhodamine B, a high quantum yield organic dye.
traditionally used in LSCs. While PbS demonstrates superior performance, it also exhibits a photo-instability that is inherent in these QDs [17]. There is a fast decay of the photocurrent over a period of a few minutes that is known to be caused by photo-darkening (or collective ‘blinking’) and is reversible when the illumination of the sample is interrupted (seen in the inset). The rate of photocurrent reduction due to this effect is independent of the concentration of the QD solution, as is shown by the comparison of the two curves at 5 and 20 minutes in figure 5. In addition, there is also a slower, gradual and permanent decay due to photo-oxidation, denoted by the dotted line in figure 6 (inset) which decreases $I_{LSC}$ at the rate of 0.1% per minute.

Figure 5 - Concentration study for PbS and CdSe QDs with concentration of PbS QDs on top scale vs. photocurrent on right. Similarly for CdSe QDs concentration is on the bottom with current on the left scales. (Reprinted with permission from [15] Copyright [2010], American Institute of Physics).

Figure 6 – Comparison between samples of PbS and CdSe QDs with Rhodamine B dye. Insert shows photo response for 193 μM PbS QD sample as a function of time. (Reprinted with permission from [15] Copyright [2010], American Institute of Physics).
An attempt to arrest the decay in PbS QDs has been made by immersing them in a PMMA matrix. The preliminary results of this experiment are shown on Figure 7. It is worth noting that, as described above, inserting QDs in a polymer holds an entirely new set of challenges that will be explored in future studies.

![Figure 7 – Long and short term stability of PbS QDs in PMMA matrix.](image)

4. CONCLUSION

To summarize our findings to date, we have supported our original thesis of superiority of NIR QDs for use in LSCs by showing that NIR QDs with lower emission/absorption spectrum overlap produce better results when used as light emitting species when compared to their visible counterparts. However, since only a single size of PbS QDs have been examined, more experiments need to be performed to test the dependence of LSC efficiency on size (which is linked to overlap in absorption and emission spectra as well as the emission wavelength) of QDs. Furthermore, we have demonstrated that PbS QDs have poor photo-stability in presence of oxygen, which coupled with their low quantum yield leads to the conclusion that there are several avenues that need to be explored and improved upon before a perfectly optimal QD species is designed for use in LSCs.

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REFERENCES


