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PMMA Thin Film Including Semiconductor Quantum Dots for Frequency Conversion

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Abstract

Hybrid optical layers of PMMA containing different concentrations of CdSe/ZnS core/shell semiconductor quantum dots were fabricated. Their absorption and luminescence showing quantum confinement effects are given. A frequency down-conversion is then obtained. The external quantum efficiency measurement performed on silicon solar cell with and without the down-conversion layers shows that the luminescence induces new charge generation. In addition, Finite Difference Time Domain (FDTD) simulation of organic solar cell shows that, added to the frequency conversion effect, one can expect to have an increase in light confinement when quantum dots are embedded in the active layer.

Keywords: Semiconductor quantum dots, PMMA, photoluminescence, frequency down-conversion, FDTD

1) Introduction

The response of photovoltaic solar cells depends on the part of the solar spectrum efficiently collected. Generally a large part of the solar spectrum is lost both in the infrared and in the UV. It is estimated [1] that the efficiency of bulk silicon solar cells could be increased of 32% if the UV spectrum was used to create carriers. In the solar cell materials, UV photons generate hot electrons which are thermalized by phonon coupling and most of them do not give current. More than that, they induce a temperature increase that will again decrease the global solar cell efficiency. In the case of organic materials, the UV can also break the molecular bonds and can reduce the solar cell lifetime.

A lot of studies have been performed on up-conversion and down-conversion processes to change IR and UV photons in photons having energy in the useful spectrum range [2]. A particular attention has been held on lanthanides materials [3] and, more recently, on quantum dots (QDs).

In our study, we focus on the possibility of converting UV photons in visible photons by using PMMA layers including CdSe/ZnS QDs and we performed calculation of the electromagnetic field in organic solar cells including QDs.

It is well known that electron confinement occurs in semiconductor nanocrystals of a few nanometer sizes, i.e. sizes smaller than the de Broglie wavelength. The possible discrete energy levels of the electrons in such QDs depend on their size and so do their bandgap [4]. The optical properties of the quantum dots naturally depend on their electrical properties. So their absorption spectrum is modulated by confinement effects and, generally, they exhibit luminescence which can be excited with a wide range of wavelengths in their absorption spectrum. Therefore, the UV range of solar spectrum from wavelength of around 300nm is generally an efficient excitation source as shown on Fig 1. In [1] it is estimated that additional 1/3 of

the conventionally used solar energy spectrum may be collected if the UV fraction is utilized with a frequency down-conversion process.

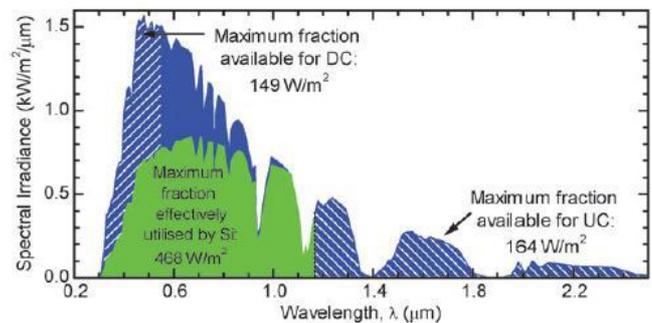


Figure 1: AM1.5G spectrum showing the fraction that is currently absorbed by a thick silicon device and the additional regions of the spectrum that can contribute towards up- and down-conversion [1].

2) Realization of PMMA thin films containing semiconductor quantum dots.

Poly(Methyl MethAcrylate) (PMMA) is known to be highly transparent in UV and in the visible spectrum. So it is an interesting material to host QDs having an absorption and a luminescent spectra in these wavelength ranges.

In this study, we utilized core shell type CdSe/ZnS QDs which have a diameter around 3nm. They have been bought from the company PlasmaChem GmbH. The advantage of the core/shell structure is that the shell prevents electron recombination and then helps to have a greater luminescence efficiency.

In order to obtain a homogeneous layer, the spin coating method [5] is applied for fabricating different PMMA layers containing different weight ratio percentage of QDs. The rotation speed we used was in the range of 1000 to 2000 rpm

to have film thicknesses larger than 1 μm . A heat treatment at 80°C is required to evaporate the rest of chloroform solvent after the spinning process. The heat treatment has been performed at a temperature not too high to preserve the layers from being damaged.

Before depositing the layer, we used chloroform as a solvent for both PMMA and QDs. CdSe/ZnS QDs can be well dispersed in the chloroform solvent due to their hydrophobic properties. Magnet stirring and ultrasonic vibration are also used during the homogenizing procedures. The solution of QDs is then mixed with the PMMA solution. For our study we used 4.2%, 8.3%, and 16.6% weight ratio percentages of QDs in PMMA. A few drops of the mixed solutions are then sent on rotating silica substrates to make PMMA thin films including QDs.

3) Experimental Results and Discussions

3.1 Size distribution of the CdSe/ZnS QDs

We used transmission electron microscopy (TEM) measurement to observe the exact particle size and spatial distribution of CdSe/ZnS quantum dots. Before making the TEM measurement, the QDs were first homogeneously dispersed in CHCl_3 solution and a drop of the solution was deposited on a carbon coated grid for the TEM observation. As can be observed in Fig 2, the CdSe/ZnS QDs exhibit an average core diameter of around 3nm. The ZnS is an epitaxial layer of a few molecules thick. It is known that this size is small enough to have strong quantum confinement effects. It can also be seen that the QDs size distribution is homogeneous. In addition, the TEM image also reveals an electron diffraction pattern corresponding to the QDs crystalline phase.

In the PMMA layers, for the considered concentrations, as the QDs are well dispersed, the distances between the QDs should be large enough not to have QD coupling phenomena. Indeed the absorption spectra have the same shape for different concentrations (Fig. 3).

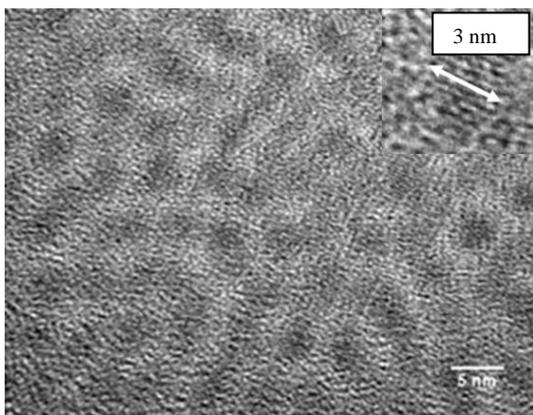


Figure 2: Transmission electron microscopy image of CdSe/ZnS quantum dots showing a size around 3nm.

3.2 Absorption and luminescence of PMMA layers containing CdSe/ZnS QDs

Reflectance (R) and transmittance (T) spectra of the layers with the different weight ratios have been measured. The losses $A = 1 - R - T$ are shown on Fig. 3 for the three considered concentrations. The thicknesses of the three QDs layers with different weight ratio are of 1.96 μm , 1.85 μm and 1.25 μm for 4.2%, 8.3% and 16.6% QDs concentrations, respectively.

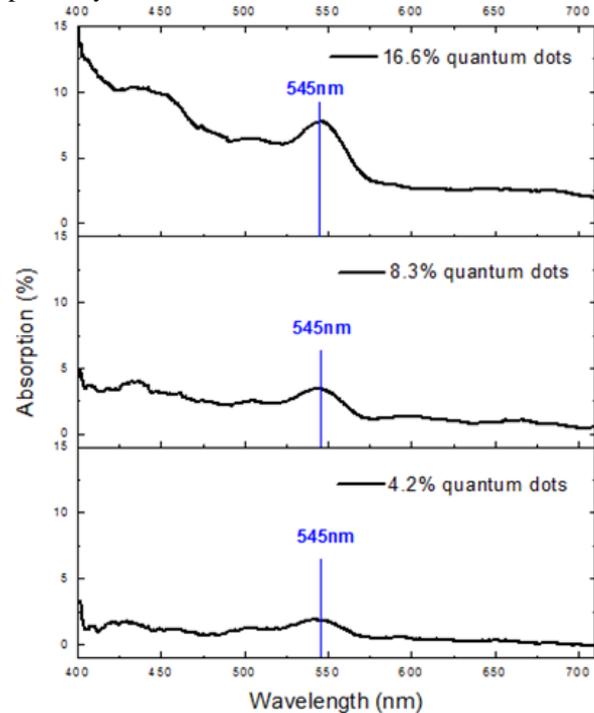


Figure 3: Absorption spectra of PMMA layers containing CdSe/ZnS QDs with weight ratio percentage of 4.2%, 8.3% and 16.6%.

In these three spectra, the position of the first main absorption peak, corresponding to the first excited energy level of the electrons, is located at around 545nm for the three different weight ratios. A bandgap shift phenomenon confirms the effect of quantum confinement. It can also be noticed that, as expected, the absorption increases with the concentration. In addition, other absorption peaks are also revealed not only at 545nm but also at around 500nm and 450nm. This shows that several different excitonic effects occur in the QDs embedded in the layers as predicted by quantum theory.

We also measured the photoluminescence of the layers with the different weight ratio percentages. The excitation source used for these measurements is an Ar^+ laser emitting at 514.53nm. A strong luminescence around 560nm in good agreement with the specifications from PlasmaChem GmbH was obtained for all the samples. The full width half maximum (FWHM) of the luminescent curves are around 23nm.

Because with increasing QDs concentration the viscosity is reducing, the sample with 16.6% QDs concentration for which the absorption is shown on Fig. 3 has a thinner thickness (1.25 μm) than the other two. We deposited a 16.6% QDs layer with a thickness of around 2.49 μm to obtain

a layer with a greater luminescence. Its absorption and luminescent spectra are shown on Fig. 4.

The difference between the maximum of the first main absorption peak and the maximum of the luminescent peak is around 15nm. This clearly shows that a down-conversion frequency effect is obtained with such a layer including CdSe/ZnS QDs. These frequency shift maybe attributed to a stoke effect [6] or induced by a dark exciton [7].

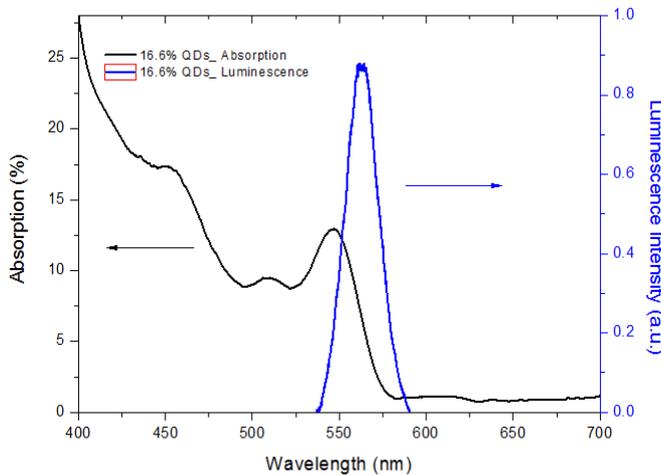


Figure 4: The absorption and photoluminescence spectra of a PMMA layer containing CdSe/ZnS QDs

3.3 Using PMMA thin films containing CdSe/ZnS QDs as down-conversion frequency layer

We consider a frequency conversion component made of a transparent PMMA thin film including QDs deposited on a silica substrate located in front of a solar cell. The aim is to collect the waste energy in the UV range which generally generates hot carriers [8]. The conversion layer collects the UV part of the solar spectrum to convert it into a wavelength range for which the active layer has its best efficiency.

It is necessary to have a homogeneous QDs distribution in order to avoid QDs coupling and to have an efficient and homogeneous photoluminescent source.

For verifying the frequency conversion effect we used a silicon solar cell.

We measured the external quantum efficiencies (EQE) of the silicon solar cell putting in front of it at first a substrate coated with a pure PMMA layer and then a substrate coated with the PMMA layer containing QDs considered in Fig. 4.

The EQE of the solar cell having the PMMA layer containing QDs is divided by $1-T(\lambda)$ which is the light spectrum collected by the Si solar cell with $T(\lambda)$ the QDs layer transmission. If the layer was not luminescent we should find the EQE of the Si Solar cell alone. As can be seen on Fig. 5, the luminescence increases the response in the wavelength range under 560nm. This shows that new photons are obtained from this wavelength range and that these photons produce charges.

At the total the cell efficiency has not increased because the absorption is stronger than the luminescence but this lets

expect an increase in efficiency if the absorption band is shifted down to the near UV. This should be achieved by using QDs of other size and composition. This work is under progress.

Another interesting configuration is to embed the QDs directly in the active layer so that the down-conversion takes place inside the cell. It is well known that the inclusion of metallic nanoparticles in the active layer has strong consequences on the electromagnetic field distribution [9]. It is then interesting to calculate the electromagnetic field distribution in the case of QDs inclusion.

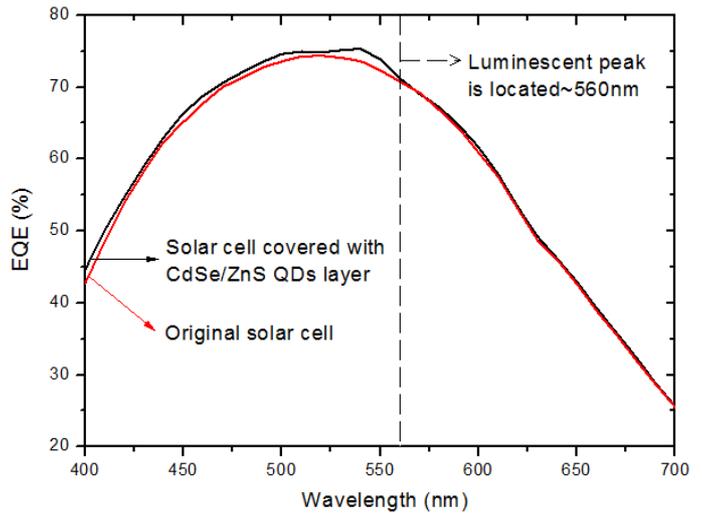


Figure 5: External quantum efficiencies measured on a silicon solar cell covered with a glass coated with a pure PMMA layer and with a glass coated with a PMMA layer containing CdSe/ZnS QDs. In this last case the EQE has been divided by $1-T(\lambda)$ of the QDs layer.

4 Toward the inclusion of quantum dots in the active layer of organic solar cells: simulation by Finite Difference Time Domain calculation

As for our QDs, P3HT/PCBM blend used in organic solar cells (OSC) is well soluble in chloroform [10].

In order to model the effect of QDs inclusion into the P3HT/PCBM active layer of an OSC, we used the Finite Difference Time Domain (FDTD) method [11] to calculate the electromagnetic field distribution.

For these calculations, we assumed a periodical distribution of CdSe nanoparticles (NPs). The model used is shown on Fig 6. The source is polychromatic plane wave polarised along the x-axis. The selected space-mesh size was 1 \AA and the time-mesh size was $1.9 \times 10^{-18} \text{ s}$. The NPs diameter is of 3nm and the distances considered between them are of 1nm or 3nm. As the shell layer thickness is of only a few angstroms it is neglected in these calculations.

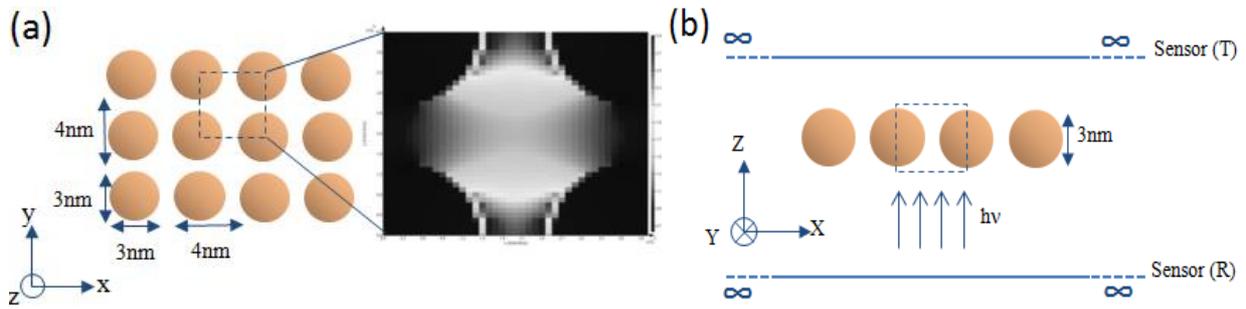


Figure 6: Model used for FDTD calculations. CdSe nanoparticles of 3nm in diameter are embedded into a P3HT/PCBM layer: (a) top view and (b) side view

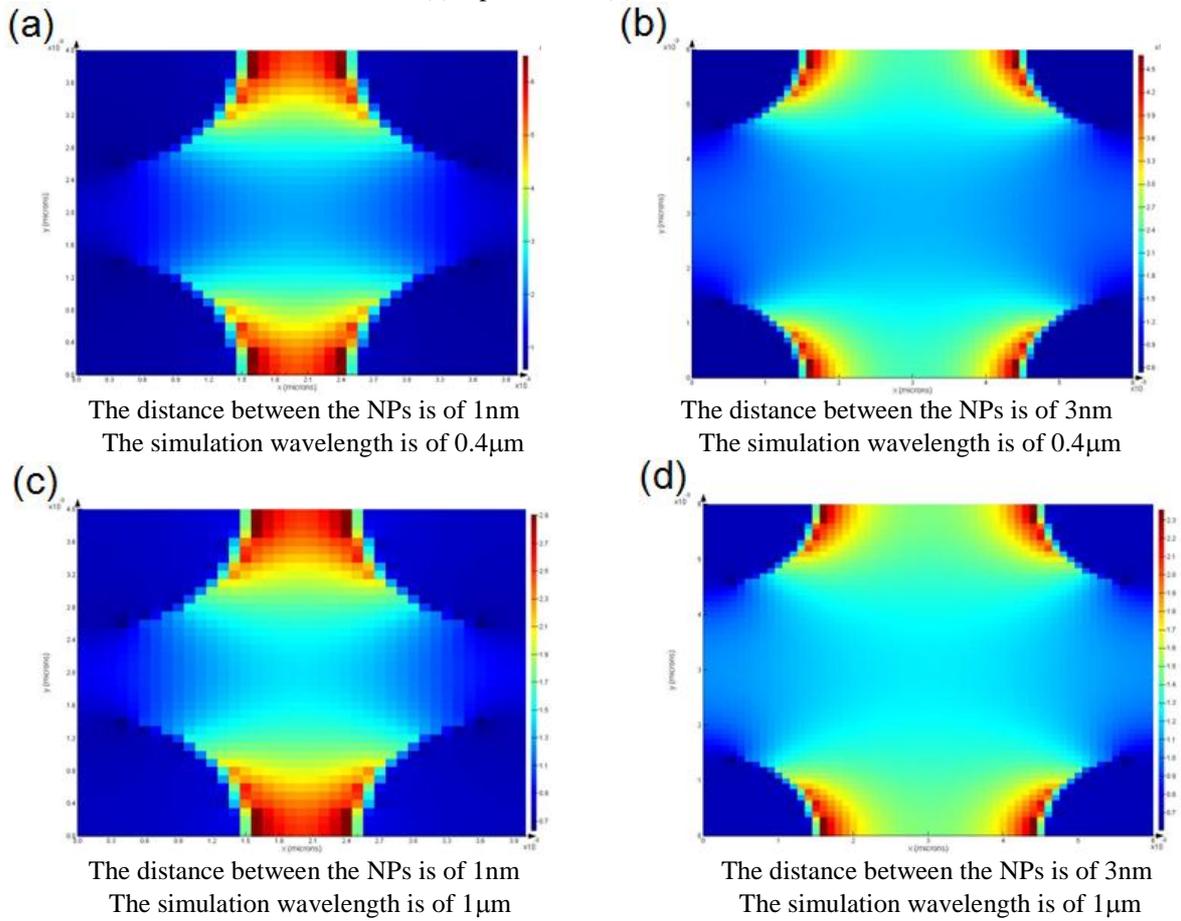


Figure 7: Electric field distribution in the X-Y plane for two wavelengths and two different distances between the NPs.

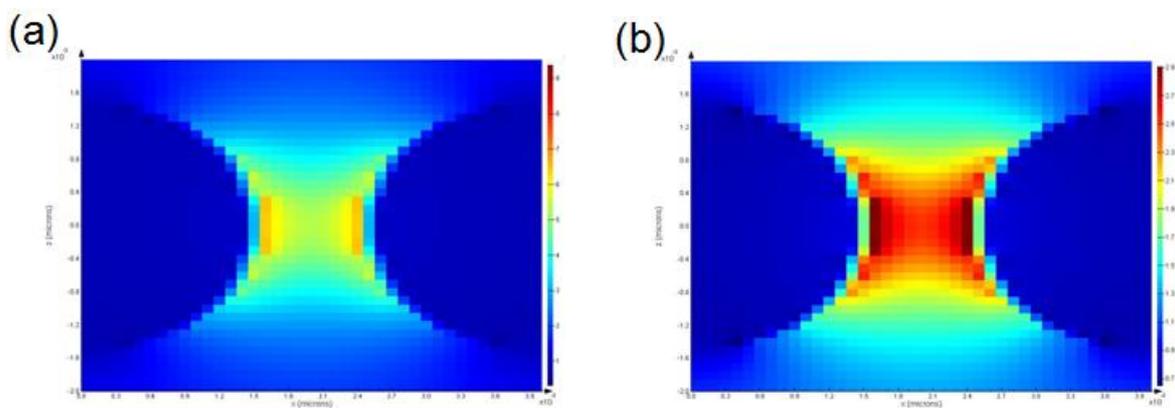


Figure 8: Electric field distribution in the X-Z plane for distances between the NPs of 1nm and two wavelengths: (a) 0.4 μ m (b) 1 μ m

A comparison of the electric field distribution in the X-Y plane is shown on Fig. 7 for two wavelengths and two different distances between the NPs. It can be seen that a field enhancement is obtained in the surrounding of the NPs. This enhancement is stronger for a distance of 1nm than for 3nm. It is also stronger for a wavelength of 1 μ m than for 0.4 μ m. The electric field distribution is also shown in the X-Z plane for the two wavelengths and a distance of 1nm between the NPs on Fig. 8. The field is 45 times greater for 1 μ m than for 0.4 μ m.

It is important to note that the geometrical dimensions considered here are much smaller than the calculation wavelengths and also much smaller than in [12] and [13]. However, strong field enhancements are obtained.

In these calculations, we used the bulk refractive index for the CdSe NPs. This does not take into account the electron confinement effect. The complex refractive index of QDs can be strongly different from bulk. We now implement optical methods to determine the effective refractive index to be attributed to QDs [14]. At wavelength of 1 μ m, P3HT/PCBM is transparent and it would be more interesting to have a field enhancement around 600nm for which this material weakly absorbs.

Conclusion

We have successfully fabricated hybrid layers of PMMA containing semiconductor quantum dots of CdSe/ZnS. The quantum confinement effect has evident consequences on the absorption and luminescence of these layers. A frequency down-conversion was obtained. Through external quantum efficiency measurement with a silicon solar cell, we verified that this leads to an increase in charge generation. In order to simulate the effect of QDs in OSC we used the Finite Difference Time Domain (FDTD) method and we show that another improvement can come from an optical electric field intensity enhancement between each of QDs. This result is obtained for structures much smaller than the wavelength.

Taking into account the effective refractive index of QDs and looking for an optimum QDs arrangement and size we should be able to obtain an increase of OSC efficiency because of both a light trapping effect and, in the case of core/shell QDs, a down-conversion frequency to collect UV light. We will develop now new simulations and will make QDs OSC in the near future.

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