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Toward cadmium-free spectral down-shifting converters for photovoltaic applications

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ABSTRACT

Spectrum down-shifting converters based on Cd-free Zn–Cu–In–S(ZCIS)/ZnS core/shell quantum dots are modeled and simulated for applications in photovoltaics using the Monte-Carlo approach. The set of physical characteristics required for the successful implementation of this type of material in spectral converters have been identified. The advantage of using ZCIS/ZnS quantum dots in such converters is highlighted through a comparison with the conventional CdSe/ZnS quantum dots. The simulation model has been evaluated experimentally using ZCIS/ZnS quantum dots dispersed in polydimethylsiloxane (PDMS) as a spectrally converting top layer. In addition to validating the utility and precision of the simulation, it is shown that the polymerization of polydimethylsiloxane does not significantly impede the photoluminescent quantum yield of the ZCIS/ZnS quantum dots.

1. Introduction

Among the variety of approaches aimed at raising the efficiency of the conventional photovoltaic (PV) cells (p–n junction, bulk heterojunction), there is a specific approach for improving light energy harvesting by matching the solar spectrum and the spectral characteristic of the PV cell not through active layer modification, but through an appropriate modification of the solar spectrum. This idea is well grounded for both down- and up- energy conversion. It has been shown that there is the potential to raise the efficiency of an ideal single-junction cell equipped with a down-converter up to 39% [1] thus overcoming the inherited efficiency limits of the PV cells. Another strategy in the sun-spectrum modification would be a down-shifting approach that improves the spectral response of photovoltaic cells in certain spectral regions and helps to avoid thermalization in the active layer [2]. However, to the best of our knowledge, no commercial modules with spectral converters are available today due to the lack of demonstrated significant improvement in quantum efficiency.

Nevertheless, a significant research effort is focused on the development of a range of up- and down-converters (or down-shifters). In an attempt to solve the problem of poor blue spectral response in CdTe/CdS cells, Maryuama et al. [3] presented a down-shifting layer based on a fluorescent coloring agent (FCA) and showed the positive effect of the latter on the maximum power of a CdTe cell. However, the stability of such an FCA is considered insufficient for solar irradiation applications. Richards et al. [4] studied the same type of solar cell by ray-tracing modeling and experiment [5]. The authors used, *inter alia*, a mix of two organic dyes (violet and yellow) dispersed in ethylene-vinyl acetate (EVA) and built a prototype CdTe/CdS-module with a down-shifting film on top of it, demonstrating a 7% improvement in the short circuit current. Abderrezek et al. [6] simulated a converter based on dye-in-poly(methyl methacrylate) (PMMA), placed on top of GaAs, GaInP, AlInP, AlGaAs solar cells. The authors reported a gain in the power conversion efficiency up to 8.4%. A notable quality of many organic dyes is their very high quantum yield (up to 95%) and a

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small overlap between emission and absorption spectra, but most of them suffer from a narrow (molecular) absorption range and degradation of luminescent properties [7]. A study carried out by Le Donne and co-workers [8] focused on the down-shifting effect in a silicon cell using organolanthanide complex synthesis. The experimental results showed almost 2.9% relative gain of the power conversion efficiency under 1 Sun (AM1.5 spectrum). In such compounds, the organic groups work as receptors while the rare-earth ions (Eu^{3+}, Tb^{3+}, Ir^{3+}) emit the shifted light.

There are also materials that have much broader absorption spectra and possess better stability. In 2004 van Sark et al. [9] studied CdSe quantum dots (QDs) as spectral shifting components for photovoltaic applications and have shown that QDs can be used as an alternative material for down-shifting converters on top of multi-crystalline and amorphous silicon solar cells. Later, Hogson et al. [10] reported the application of CdSe/ZnS QD/PMMA luminescent down-shifting films to CdTe solar cells. QDs are not prone to the photobleaching effects typical of the organic dyes and they are very well suited for solution-based deposition procedures such as printing, especially if they are synthesized as a colloid. In particular, CdSe/ZnS core/shell QDs, rods, and plates have been widely studied and appear to be an attractive material for display, solar concentrator, and spectral converter applications, but the small Stokes-shift inherent to CdSe and CdSe/ZnS QDs (15–30 nm) results in a high level of re-absorption losses. An interesting method of Stokes-shift engineering was proposed in Ref. [11] for a precise specific shelling of the QD core to increase the applicability of CdSe QDs for solar concentrators.

However, the presence of a heavy metal (Cd) in such QDs has motivated further research on the application of non-toxic materials for display and photovoltaic technologies. Most of the research in this area involves the use of Zn- and Si- based compounds [12–14]. The application of ZnO QDs demonstrated a slight improvement in the spectral response characteristics of silicon solar cells [15,16]. Also, the wide-bandgap semiconductor ZnS is a well-known and promising luminescent material that is frequently doped with Mn, Cu or other transition metals. The use of this material in the form of QDs embedded in poly(methyl methacrylate) (PMMA) for photovoltaic applications was described in Ref. [12]. The authors reported a relative efficiency increase of around 2% in a silicon solar cell with respect to the same cell covered with an undoped PMMA layer. The ZnS:Mn nanoparticles used in that work were synthesized without a capping agent and were embedded into the PMMA matrix through radical polymerization with thermal initiation.

Motivated by this previous work and the clear need for way to numerically screen materials for this particular application, we present an analysis of the distribution of losses inside a QD-based spectral down-shifting converter. The required physical parameters for the successful realization of a commercially viable cover-film material with down-shifting capabilities are also discussed. Proposed for such applications is another Cd-free material with well-suited spectral characteristics – the ZnCuInS/ZnS core/shell nanoparticles. In the literature, such multi-component QDs are referred to as alloyed QDs. The chalcopyrite nanocrystals, $CuInS_2$ (CIS) in particular, have attracted the attention of many researchers because of their user-friendly synthesis technology and heavy metal-free material composition, as well as photoluminescence (PL) spectra that are well suited to display and *in-vivo* imaging needs [17]. The CIS bandgap (1.45 eV) is considered very promising for VIS–NIR applications. To broaden the potential of this compound, Zn atoms are incorporated into the CIS lattice to form a solid of CIS and ZnS commonly referred to as ZCIS. This approach provides the opportunity for tuning the band gap while keeping the particle size unchanged. Nose et al. [18] found Zn doping to be a critical factor in the PL intensity. Consequently, ZCIS QDs have been extensively studied for use in solid-state lighting and QD-LEDs [19,20], photocatalysis applications [21], *in-vivo* imaging [22], *etc*. The PL spectra, dynamics, and the role of ZnS shelling were described by several authors [18,23]. Due to the more complex crystalline structure, the PL mechanism involves a donor-acceptor recombination that produces the high Stokes-shift (Table 1) required for a luminescent spectrum-shifting layer. The next section discuss the impact of a ZCIS/ZnS-based spectral converter on different types of solar cells as modeled using our Monte Carlo approach. Finally, we also present an experimental verification of the simulation model.

Table 1
Spectral parameters of core-shell CdSe and ZCIS QDs.

Material	First excitation maximum, (nm)	Emission, λ, (nm)	Stokes shift, (nm)	Emission, FWHM, (nm)
CdSe/ZnS [29]	532	562	30	35
CdSe/ZnS [30]	550–560	575	15–25	30
ZCIS/ZnS [18]	437	562	130	100
ZCIS/ZnS (present study)	465 (*smoothed*)	585	> 100	98

2. Monte Carlo modeling

The modeling study was performed with a custom code written in the MatLab environment based on the ray-tracing concept [4,24]. The input parameters are the spectral characteristics of the luminescent moieties (emission and absorption spectra); their emission ability is expressed in terms of the quantum yield and the physical parameters of the transparent matrix in which the luminescent particles are dispersed. Within the simulation, photons are moving inside a 3-D plate of host material located on top of the solar cell and undergoing the processes of absorption, reemission, reabsorption, reflection, and refraction.

According to the Beer–Bouguer–Lambert law, the probability of photon absorption in the composite can be expressed as an exponential relationship that includes the optical path traveled by the photon. In the present Monte-Carlo approach, the determination of the photon optical path Δs inside the composite includes both a random component and an exponential dependence on the extinction coefficient τ (mm^{-1}). Thus, the following relationship for Δs is used:

$$\Delta s = \frac{\ln(1-\epsilon)}{\tau},$$

where ε is a random number uniformly distributed from 0 to 1 [24]. The simulation is run with N photons at each wavelength from 285 to 1600 nm ($N = 10^5$). The sum of the AM1.5 spectrum altered by absorption and the light emitted by the QDs gives the resulting spectrum in the model (Fig. 1). The down shifting layer on the top of the solar cell can introduce additional losses through reflection from additional surfaces and/or matrix absorption over a broad spectral range. However, the modeled plate can be deposited as a cover-film during the wafer processing of the solar cell such that no additional capping is needed, and therefore no additional reflection interfaces or material absorption effects arise.

It was shown in Ref. [9] that spectral changes in the blue region and the concentration of QDs influence the device's short-circuit current, maximal power and efficiency in comparable extent, while the open-circuit voltage and fill factor are only slightly affected. Thus, in Ref. [6] the mean ratio of the efficiency change to the short circuit current change was established to be 0.91 for a single junction GaAs solar cell with dye-based luminescent