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Scattering enhanced quantum dots based luminescent solar concentrators by silica microparticles

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ABSTRACT

Luminescent solar concentrator (LSC) integrated with c-Si photovoltaic cells (PV cells) in building integrated photovoltaics (BIPV) could grow up to be an important element of our life for energy harvest in the future. Heavy metal free quantum dots (QDs) are promising for LSC applications, which can be controlled to possess effective large Stokes Shift and low reabsorption of emission that benefit their applications in BIPV. In our work, different amount and size of SiO_2 particles were added to $CuInS_2$/ZnS QDs based LSCs to realize highly efficient scattering enhanced LSC (S-LSC) devices. Since SiO_2 particles induced scattering effect, we achieved a power conversion efficiencies (PCE) of 4.20%, which showed an improvement of 60.3% compared with the pure QDs based LSC without SiO_2 particles. This study suggests a new method of scattering enhancement to realize better performance for LSC.

1. Introduction

Recent years, luminophores based luminescent solar concentrator (LSC), as a promising energy harvester, can be widely used with c-Si photovoltaic cells (PV cells) in building integrated photovoltaics (BIPV) [1–6]. For energy harvest, luminophores based LSC could guide incident light to PV cells, which is supposed to be installed at the LSC edges and can convert light into electricity, through total internal reflection. This technique benefits the applications in future self-sustaining buildings. However, the widely utilization of LSCs so far has been hindered by the lack of suitable luminophores. Organic fluorescent dyes based LSC were investigated in recent decades [7,8], but it provided limited coverage of the solar spectrum, and suffered from significant optical loss associated with serious reabsorption. These disadvantages of the material not only reduced the light-harvesting efficiency of LSC, but also led to intense coloring of devices, which made a limitation on their applications in practical architectures.

To overcome these limitations and improve the performance of LSC, nanocrystals (NCs), such as quantum dots (QDs) [9–12], quantum rods (QRs) [13,14], and luminescent perovskites, were investigated as luminophores in LSC [15–20]. Compared to traditional organic fluorescent dyes based LSC, NCs based LSC possessed many priorities, such as broader absorption range because of the intrinsic properties of luminescent NCs, and lower reabsorption normally due to the core-shell architecture or doped energy state engineering of NCs [21–24]. For ameliorating the performance of LSC, many efforts were made to improve the efficiency of LSC by using NCs as luminophores. For instance, Meinardi *et al.* developed large effective Stokes-shift engineered CdSe/CdS QDs with core-thick-shell structure [25], which made the overlap between optical absorption and emission greatly reduced, and further realized high efficient LSC with suppressed reabsorption losses. Erickson *et al.* developed Mn-doped ZnSe QDs to decrease the reabsorption as well by fabricating NCs based LSC with near-zero reabsorption behavior [2]. Cirloganu *et al.* developed thick-shell PbSe/CdSe QDs [26], which featured a lower absorption onset (~1.75 eV) than CdS (2.6 eV) and ZnSe (2.7 eV), and then can extended the coverage of solar spectrum due to the suitable energy gap of the absorber material. However, all of these materials contained hazardous heavy metal elements, such as Cd and Pb, thus, expensive disposal/recycling cost was required [10,27–30], which imposed certain constraints on

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their use in practical. Heavy metal free QDs will be the development trends for the LSC applications [31–35], which can avoid utilization of heavy metal in BIPV. Our group developed $CuInS_2$/ZnS QDs with visible emission and $AgInS_2$/ZnS NCs with near infrared (NIR) emission and introduced them to LSC, respectively [1,36]. Meinardi et al. used $CuInSe_xS_{2-x}$ QDs coated with ZnS to realize highly efficient NIR QDs-LSC, which reduced reabsorption losses and extended coverage of the solar spectrum [31]. They focused on $CuInSe_xS_{2-x}$ NIR QDs with broad absorption range, large Stokes shift, and colorless LSC devices incorporated with these QDs. In these efforts, high efficient NCs with Cd-free or Pb-free were frequently and successfully employed in LSC demonstrating well light converting, low reabsorption, and high energy harvesting properties. However, LSC devices would also suffer from low efficiency due to other loss mechanisms, such as surface losses and energy dissipation [37-41].

To enhance the efficiency and cut down the cost of LSC, we should further increase the sunlight utilization. Scattering materials being integrated into LSC devices is an effective way to boost up the availability ratio of sunlight [42]. They mainly offer two functions for LSC devices. On one hand, the direction of incident sunlight will be changed when it collides the scattering particles and the probability of light captured and absorbed by QDs will be raised. On the other hand, the longer wavelength emission that re-emitted from QDs will be redirected by the scattering particles, which will be more likely guided to the PV cells installed at the edge of LSC. Some previous papers exemplified scattering effect was helpful to improve the efficiency of LSC [43]. Chou et al. studied the strong scattering effect induced by segregated dyes in the polydimethylsiloxane (PDMS) waveguides and achieved a PCE as high as 5.23% with the dimension of 5.0 cm × 5.0 cm × 0.5 cm [42]. Haines et al. studied the effect of dye concentration on the efficiency of the perylene diimide derivative LSC, and demonstrated that dye aggregation play an important role on the LSC performance [44]. Debije et al. researched the effect of adding white scattering layers to the LSC waveguides, and obtained a large enhancement of energy output from the waveguides [43].

As our previous research, we synthesized heavy metal free $CuInS_2$/ZnS QDs as luminophores embedded into pure polymethylmethacrylate (PMMA) for LSC devices [36]. And in this work, micron sized SiO_2 particles were further introduced into LSC waveguides as scattering materials to achieve scattering enhanced LSC (S-LSC). The schematic for S-LSC is shown in Fig. 1. SiO_2 particles could change the direction of incident sunlight, which would increase the probability of light captured and absorbed by QDs. Moreover, the emission of longer wavelength that re-emitted from QDs will also be redirected by the SiO_2 particles, which will be more likely guided to the PV cells installed at the edge of LSC. We studied the effect of LSC devices performance when adding different size or concentration of SiO_2 particles, which could scatter light well. The results demonstrated that SiO_2 particles would largely increase in PCE of QDs based LSC devices. The highest PCE of S-LSC with 5 μm SiO_2 particles reached as high as 4.20%, with an increment of 60.3% compared with those normal pure QDs based LSC devices. Thereby, S-LSC is an effective new method to realize better performance for LSC.

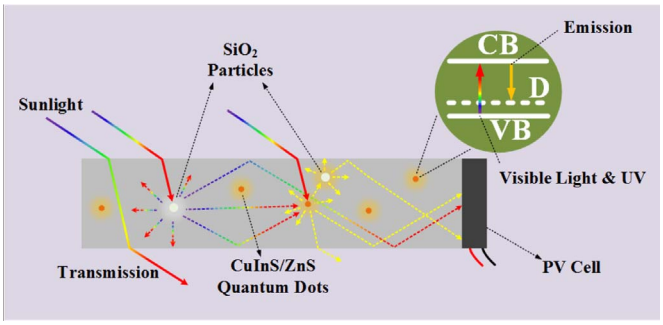

Fig. 1. Schematic for scattering enhanced LSC (S-LSC).

2. Materials and methods

2.1. Materials

Most chemicals used in the experiments including Copper (I) iodide (CuI, 99.999%), indium (III) acetate ($In[OAc]_3$, 99.99%), zinc stearate ($Zn[St]_2$, 10–12% Zn basis), 1-dodecanethiol (DDT, 98%), methyl methacrylate (MMA, 99%), 2, 2'-azobis(2-methylpropionitrile) (AIBN, 99%), SiO_2 (99%), liquid paraffin, *n*-hexane, chloroform and absolute ethanol were purchased from Aladdin. All solvents and reagents were of analytical grade and directly used without further purification.

2.2. Characterization techniques

X-ray diffraction (XRD) measurements were carried out on an X-ray diffractometer (Bruker Advance D8 Ew, Germany) with Cu Kα radiation (λ = 1.54178 Å). The operation voltage and current was 40 kV and 25 mA, respectively. The 2θ range was from 23° to 82° in steps of 0.02°. The transmission electron microscopy (TEM) images were taken by a FEI Tecnai G2 F30 transmission electron microscope operating at an acceleration voltage of 300 kV. The ultraviolet-visible (UV–Vis) transmittance spectra were measured by using dual-beam spectrometer Lambda 950 (PerkinElmer) with a 150 mm diameter Spectralon integrating sphere. The excitation and emission spectra were carried out through a FluoroSENS-9000 spectrophotometer with a static xenon lamp (150 W) as an excitation source. Solar simulator with an air mass 1.5 global (AM1.5 G, 100 mW·cm^{-2}) illumination and a Keithley 2400 sourcemeter were used for the J-V characterization. Optical microscopy images were performed on INSIZE ISM-PM 100.

2.3. Synthesis and fabrications

The $CuInS_2$/ZnS QDs were simply synthesized by two steps, which was preparing $CuInS_2$ QDs firstly and then growing of ZnS shell [36]. The optical-grade PMMA was typically produced by the bulk polymerization of MMA in the presence of thermal radical initiators. To generate some homogeneous and transparent nanocomposites, it was necessary to transfer the QDs and SiO_2 into the MMA monomer solution uniformly before the process of polymerization. Finally, the resulting composites after thermal polymerization of QDs-PMMA were cut into squares and polished for optical measurement so that LSC devices was obtained. And the dimensions of our investigated LSC is 2.0 cm × 2.0 cm × 0.8 cm with the geometry factor was about 2.5 according to G = L/H, where L was the length and H stands for height.

3. Results and discussion

The core-shell structured $CuInS_2$/ZnS QDs were synthesized as our previous method. The PL QY was approximate around 65% due to the inorganic surface passivation by ZnS. And the emission peak of final QDs was measured as 588 nm with broad emission band-gap (FWHM = 115 nm). The TEM image was also given as Fig. 1(a). The as prepared $CuInS_2$/ZnS revealed uniformed size distribution with average size around 4.0 nm. The XRD pattern in Fig. 2(b) confirmed the chalcopyrite structure for both $CuInS_2$ core and $CuInS_2$/ZnS core-shell QDs, which inferred that the surface passivation well maintained the chalcopyrite structure and successfully prevented the independent ZnS forming [45]. The passivation of ZnS on $CuInS_2$ was also inferred from the slight peak shifts toward to larger scattering angles, for phase (112) (inset data) and (220) respectively. The PL and Absorption spectra were also illustrated in Fig. 2(c) indicating as prepared core-shell structured QDs revealed effective large stocks-shift and consequent low re-absorption, which be beneficial for applying them in LSC techniques. The