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Increased short-circuit current density and external quantum efficiency of silicon and dye sensitised solar cells through plasmonic luminescent down-shifting layers

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Abstract

Luminescent down-shifting (LDS) is a purely optical method to improve the short-wavelength response of photovoltaics by red-shifting the incident solar spectrum. This work is the first to investigate plasmonic LDS (pLDS) layers applied to c-Si and DSSC solar cells. The addition of pLDS composite layers containing core–shell quantum dots CdSe/ZnS was demonstrated to increase the short circuit current density (J_{sc}) of c-Si and DSSC devices between 300 and 500 nm, where the QDs is most absorbing. Up to ~22% (relative) increase has been achieved for both cells when compared with cells with no pLDS layers. External quantum efficiency measurements have shown significant enhancement where the solar cells have poor optical response, below 500 nm, while increased efficiency was confirmed with current–voltage (I–V) measurements.

Keywords: Spectral losses; Photovoltaics; Luminescent materials; Plasmonic luminescent down-shifting layers

1. Introduction

Luminescent down-shifting (LDS) is an optical approach to increase PV device efficiency using luminescent materials to convert short wavelength photons to longer wavelength photons where the solar cell is more efficient (Hovel et al., 1979; Strümpel et al., 2007; Klampaftis et al., 2009; McIntosh et al., 2009; Rothemund et al., 2011; Ross et al., 2014; Alonso-Álvarez et al., 2014; Bella et al., 2015; Griffini et al., 2015). A typical LDS consists of luminescent species such as quantum dots, organic dyes and rear-earth complexes doped in a transparent polymer sheets and deposited on top of PV cells (Klampaftis and Richards, 2011; Klampaftis et al., 2012; Ahmed et al., 2012b,a, 2013; Kennedy et al., 2015). Other techniques have recently been investigated where the luminescent species can be sprayed on top of the cells using a spray coating technique (Chander et al., 2015) or can be incorporated into a multifunctional coating system based on a photocurable fluoropolymer (Bella et al., 2015; Griffini et al., 2015). Such a coating system has allowed for significant improvement of the power conversion efficiency of uncoated DSSC devices and has also improved the cell stability and prevented photochemical and physical degradation.

A luminescent species such as core–shell type CdSe/ZnS QDs investigated in this study, which absorbs light below 465 nm and emits at 500 nm thus shifting the optical

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wavelength from where the cell has a poor optical response (at short wavelengths) to where the external quantum efficiency (EQE) of the cell is higher (at longer wavelengths). As a result of the luminescent process, more electron–hole pairs can be created in the solar cell for a given number of incident photons and a higher short-circuit current (I_{sc}) is generated. The optical process involves an LDS layer positioned on top of a PV cell and is illustrated in Fig. 1.

QDs exhibit broad absorption spectra, high absorption coefficients and emission wavelengths which can be tuned according to their size as a result of quantum confinement (Ethayaraja et al., 2007). They were proposed for the use in LSC instead of organic dyes (Gallagher et al., 2007; Reda, 2008; Kennedy et al., 2009; Meredith et al., 2009). The advantages of QDs with respect to organic dyes are their high brightness and stability (Bruchez Jr. et al., 1998; Meredith et al., 2009). However LDS devices using both QDs and organic dyes suffer from luminescence quenching at higher concentration (Chandra et al., 2015), known as "self-absorption" (Klampaftis et al., 2009; Debije et al., 2007) in which the downshifted photons are re-absorbed by the QDs/dye within the down shifting layer. This is a function of optical path length, particle concentration, and Stokes shift between absorption and emission peaks and results in low optical efficiency LDS devices. It has been shown (Wilson, 1987; Reisfeld et al., 1988; Chandra et al., 2010, 2012; Reisfeld, 2010; Chandra, 2013) that these losses can be offset by exploiting plasmonic interaction between metal nanoparticles (MNP) and the QD/dye emitters. The optical properties of luminescent species were shown to exhibit dramatic emission enhancement in the presence of metal nanoparticles (Reisfeld et al., 1988; Chandra et al., 2010, 2012; Reisfeld, 2010; Chandra, 2013; Noguez, 2006; Ghosh and Pal, 2007; Fort and Gŕesillon, 2008; Catchpole and Polman, 2008).

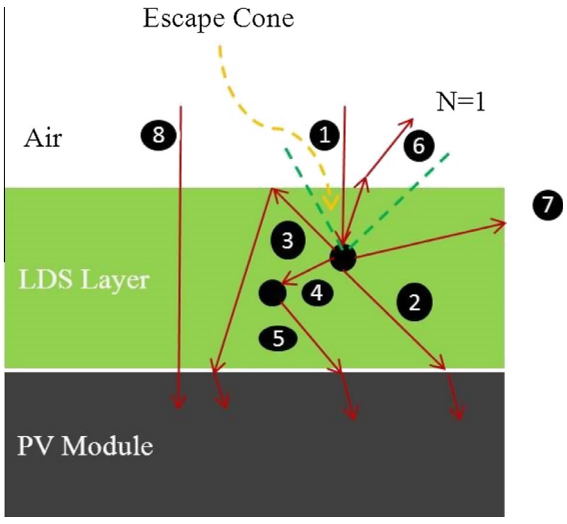

Fig. 1. Schematic diagram of PV modules with LDS layer on top (Klampaftis et al., 2009).

When light interacts with the surface plasmon resonance (SPR) at the surface of metals such as gold and silver (as presented in Fig. 2), it results in a surface plasmon polariton. In this state the electric field associated with the light is highly amplified in a small evanescent region near the surface of the MNP (Ghosh and Pal, 2007; Fort and Gŕesillon, 2008; Stranik et al., 2005; Ledwith et al., 2007). When a fluorescent species is placed in the range of the enhanced local electromagnetic (EM) field, plasmonic interaction takes place, which can enhance the light absorption and fluorescent emission rates (Chandra et al., 2010, 2012; Stranik et al., 2005; Stranik, 2007), hence the LDS layer efficiency.

2. Materials and experimental details

2.1. Plasmonic LDS layers fabrication

Core–shell type CdSe/ZnS quantum dots were used as the fluorescent material (Cytodiagnostics, Canada) which had a quantum yield of 0.71 ± 0.07 measured in solution. Silver nanoparticles (Ag NPs) were used for the pLDS composite layer. Ag NPs were synthesised in water and re-suspended in DFM solvent (the synthesis process followed the method reported by (Ledwith et al., 2007)). SEM analysis of Ag NP, as shown in Fig. 3, reveals that triangular and spherical shapes are present in the Ag NP structure with triangular shapes being dominant. The particles were quite uniform in size distribution with an average diameter of 45 ± 5 nm.

The fluorescent species/Ag NPs composites layers were prepared as follows. The QDs were mixed with the Ag NPs and sonicated in an ultrasonic bath for 25 min. The mixture was then added to poly(methyl methacrylate) (PMMA) (Carl Roth GmbH + Co.KG) solution, magnetically stirred for 20 min, and then placed in an ultra-sonic bath for another 15 min. Prepared solutions were drop cast on glass substrates (size $15.5 \times 15.5 \times 1$ mm) and cured for 72 h at 25 °C under a vacuum of 800 mbar. Uniform layers were obtained when removed from the glass substrate. The average thickness of the layers was measured by white light interferometer technique and found to be 0.95 ± 0.05 μm. The absorbance and photoluminescence (PL) spectra of the QDs in the PMMA film (at a concentration of 0.09 wt%) is shown in Fig. 4, showing that absorption mainly occurs in the wavelength range below 465 nm and the centering of the PL emission peak at 500 nm. The Ag NPs extinction spectra in DFM solvent and in PMMA film (at a concentration of 15 ppm) are shown in Fig. 5. The peaks at 410 nm and at 335 nm are attributed to the presence of the spherical particles in Ag NP. This result is consistent with what has been reported by (Ledwith et al., 2007).

2.2. Mono-crystalline silicon cells

Mono-crystalline silicon cells (2×2 cm, Sunrydz, Germany) were used for assessing the downshifting effect