



Application of a dual functional luminescent layer to enhance the light harvesting efficiency of dye sensitized solar cell



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ABSTRACT

A luminescent coating of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ particles applied on photoanode (TiO_2) layer of SQ1 sensitized solar cell by doctor blading the paste of phosphor particles. The luminescent layer acted as a dual functional layer and enhanced the short circuit current density (J_{SC}) by 64% via both scattering effect and downshifting of the photons in 400–600 nm spectral range to photons in 600–800 nm spectral range. Considerable relative enhancement in incident photon to current conversion efficiency (IPCE) up to 350% in 400–600 nm spectral range proves the down shifting effect as the dominant factor for the improved performance of dye sensitized solar cell (DSSC).

1. Introduction

Since the breakthrough work conducted by O'Regan and Gratzel in 1991 [1], dye sensitized solar cells have garnered much attention owing to relatively good efficiency and low fabrication cost [1,2]. The critical problems that limit the photon conversion efficiencies of a DSSC are low absorption cross-section and insensitivity of the dye molecule to the full solar spectrum. Therefore, the most straightforward way to increase the short circuit photocurrent of DSSC is to both intensify and broaden the absorption of incident light [3,4]. Light scattering is commonly applied in a DSSC to enhance the light harvesting (LH) by increasing the sunlight optical path length in photoanode [5]. Moreover, optical methods such as photon conversion by luminescent materials have been used to broaden LH by transforming un-absorbed photons into the absorption band by upconversion/downconversion/down shifting processes [6–10].

In our earlier report [11] we successfully demonstrated the potential of luminescent down shifting (LDS) technique by using NIR absorbing squaraine (SQ1) as a dye and visible light absorbing inorganic phosphor $\text{CaAlSiN}_3:\text{Eu}^{2+}$ as LDS material. The LDS layer was applied outside the DSSC in a reflective configuration, and it showed more than 50% increase in short circuit photocurrent of the device. Also, we made a detailed assessment of LDS layer outside DSSC [12] in which the light absorption by electrolyte has been found to be a major loss mechanism. Hence, bringing the LDS layer inside the DSSC could be advantageous bi-fold as it has the potential to minimize the

absorption loss caused by the electrolyte and can also act as a scattering layer (SL). Herein, we discuss the dual functional nature of the LDS layer used inside the DSSC and its role in the performance of the device.

2. Materials and methods

$\text{CaAlSiN}_3:\text{Eu}^{2+}$, acquired from Beijing Yuji Science & Technology Co., Ltd, was used as the down shifting material. Using an integrating sphere, the luminescence quantum efficiency of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor was measured to be about 50%. The LDS layer was coated on TiO_2 layer using doctor blade method. First, phosphor paste was prepared using Terpeneol (Merck), Ethyl Cellulose (Aldrich) and ethanol (Merck) according to the common method used to make TiO_2 paste for DSSC [13]. Concentration of phosphor powder, Terpeneol and Ethyl Cellulose in the final paste was 50%, 5% and 45% respectively. After fabrication of TiO_2 layer on FTO coated glass, phosphor paste was coated on the TiO_2 layer. Then heat treatment at 500 °C was done in order to have a porous layer of phosphor particles on TiO_2 layer with good adhesion. Thickness of LDS layer was measured with a digital micrometer to be $90 \pm 2 \mu\text{m}$ and $160 \pm 2 \mu\text{m}$ for LDS1 and LDS2 layers respectively. SL is a 4 μm thick layer of TiO_2 particles of 400 nm size. The details for SQ1 sensitized DSSCs assembly and characterizations are explained in SI.

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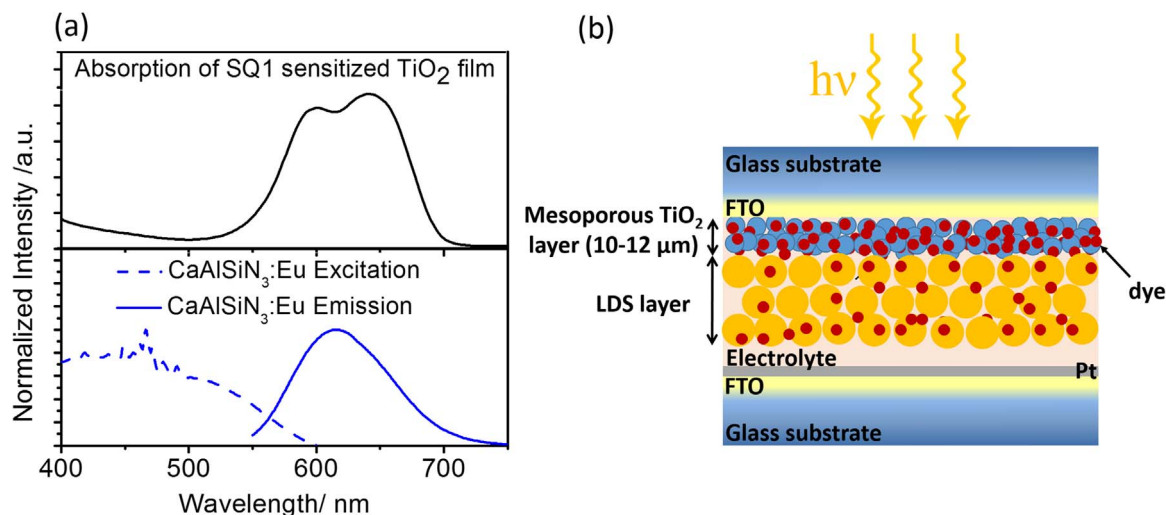


Fig. 1. (a) Absorption spectrum of SQ1 sensitized TiO_2 film together with the excitation ($\lambda_{\text{em}}/\text{nm}=615$) and emission ($\lambda_{\text{ex}}/\text{nm}=466$) spectra of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor. (b) Schematic demonstration of DSSC with LDS layer placed inside DSSC.

3. Results and discussions

The excitation and emission spectra of $\text{CaAlSiN}_3:\text{Eu}^{2+}$, together with the absorption spectrum of SQ1 sensitized TiO_2 film are shown in Fig. 1(a). The spectra demonstrate that $\text{CaAlSiN}_3:\text{Eu}^{2+}$ and SQ1 are ideal pairs in terms of LDS process, as it shows a full coverage of short wavelength region by the excitation band of the LDS layer and an excellent overlap between the emission band of down shifting material and absorption band of SQ1 sensitized TiO_2 film.

DSSC can take various configurations according to the position of LDS layer in the device architecture. Fig. 1(b) shows the structure of DSSC with LDS layer inside the cell used in this work. In this structure, luminescent layer coated on TiO_2 film works as a dual functional layer which acts as both SL and LDS layer.

Fig. 2 shows the photocurrent–voltage (J–V) characteristics of DSSC with and without the LDS layers and DSSC with SL. The photovoltaic parameters listed in Table 1 show current densities of 7.48 and 8.60 mA cm^{-2} for DSSCs with LDS1 and LDS2 layers respectively, compared to current density of 5.24 mA cm^{-2} for the reference cell. These current densities correspond to enhancements of 42% and 64% for DSSCs with LDS1 and LDS2 layers respectively, in

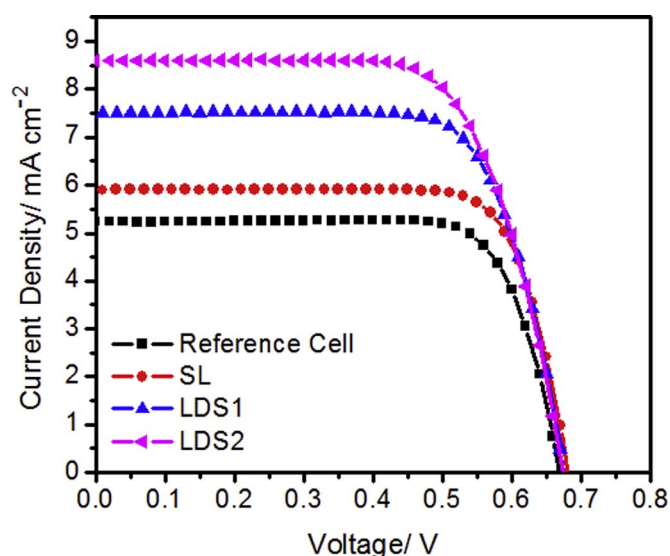


Fig. 2. Current–voltage characteristics of DSSC with SL and DSSCs with two different LDS layers compared to a reference DSSC without SL/LDS layer.

Table 1

Photovoltaic parameters of DSSCs with SL/LDS layers compared to a reference DSSC.

Device Configuration	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Efficiency (%)	ΔJ_{sc} (%)
Reference cell	672	5.24	0.766	2.69	–
SL	684	5.90	0.771	3.11	12
LDS1	676	7.48	0.732	3.70	42
LDS2	676	8.60	0.692	4.02	64

comparison with that of the reference cell. Higher increase in current densities might be achieved by application of thicker LDS layers but thicker LDS films suffered from the poor adhesion between the LDS layer and the TiO_2 layer. Moreover, thicker LDS layers will disturb the ion transport in the electrolyte and thereby the operation of DSSC. Application of SL could also increase the current density of DSSC up to 12%, but the enhancement is much less than that achieved by application of LDS layers. This can be attributed to the dual functional nature of the LDS layer in DSSC which gives the effects of both light scattering and light conversion. SL can increase the light harvesting efficiency only by scattering back the transmitted light to the photoanode, which is an effective mechanism only for photons with wavelength in absorption band of dye molecules. However, photons outside the absorption band of the dye can contribute in current generation in the case of application of LDS layer as they will be converted to low energy photons and absorbed by the dye molecules. Open circuit voltage and fill factor of the devices with LDS layers will not considerably change compared to the reference cell since the LDS layers are sufficiently porous not to disturb ion transport in the electrolyte. In order to examine the reproducibility of these results, the photovoltaic measurements were performed with three to five identical devices. The highest efficiency is reported here while the average photovoltaic parameters of these devices with the calculated standard deviations are shown in Table S1. Small standard deviations indicate the good reproducibility in the cell preparation.

In order to determine the responsible mechanism for the enhancement of short circuit current density of DSSCs with LDS layers, incident photon-to-current conversion efficiency (IPCE) spectra for the reference cell and those with SL and LDS layers are shown in Fig. 3. The IPCE results exhibit significant enhancements in spectral range 400–600 nm coinciding with the excitation band of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor shown in Fig. 1(a). The values of IPCE reach around 25% and 30% at 500 nm for the DSSCs with LDS1 and LDS2 layers respectively; but this value cannot exceed 10% by using SL in DSSC, as the dye

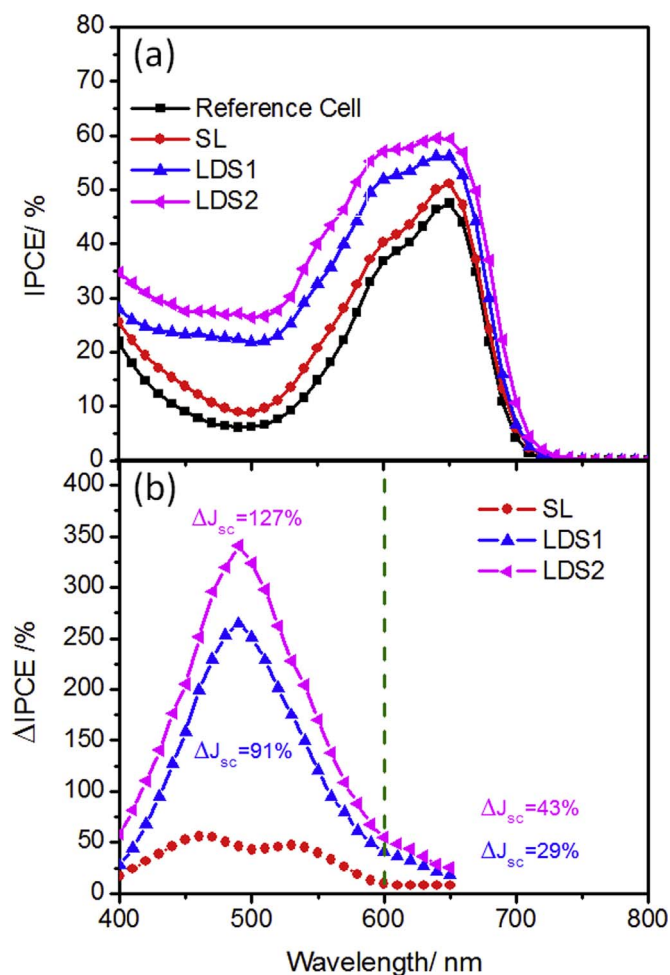


Fig. 3. (a) IPCE spectra of DSSC with SL and DSSCs with two different LDS layers and a reference DSSC without SL/LDS layer. (b) The percentage enhancement of IPCE with respect to the reference cell ($\Delta\text{IPCE}\%$) for devices with SL/LDS layers.

molecules do not show strong absorption in this spectral range. This proves that the IPCE enhancement in this range for the DSSCs with LDS layers is due to down shifting of the high-energy photons to the low-energy photons. Fig. 3(a) also shows a considerable change in IPCE of DSSCs with LDS layers in spectral range 600–800 nm. Since the phosphor particles will not be excited by the photons with wavelengths 600–800 nm (Fig. 1(a)), down shifting cannot happen for these photons and the LDS layer can cause the enhancement in IPCE in this spectral range only by scattering of the transmitted photons from the dye sensitized TiO_2 layer. SL also cause an enhancement in IPCE in spectral range 600–800 nm, but the enhancement is much lower than the increase caused by LDS layer. This can be attributed to the higher diffuse reflection of light caused by LDS layer in spectral range 600–800 nm compared to SL (Fig. S1). In fact, LDS layer caused the highest attainable increase in IPCE in spectral range 600–800 nm since the diffuse reflection of light in this region reaches about 100% for this layer.

The amount of increase in IPCE has been calculated for DSSCs with SL and LDS layers compared to the IPCE of the reference cell and it is plotted as a function of wavelength in Fig. 3(b). $\Delta\text{IPCE}\%$ reached 350%, 270% and 50% in 500 nm for the devices fabricated with LDS2, LDS1

and SL, respectively; while the $\Delta\text{IPCE}\%$ is calculated to be less than 25% in spectral range 600–800 nm. As the LDS effect and scattering effect independently work in 400–600 nm and 600–800 nm spectral ranges, the percentage of relative increase in J_{sc} for devices with LDS layers has been calculated from IPCE for these spectral ranges separately and it is shown on Fig. 3(b). The higher amount of $\Delta\text{IPCE}\%$ and $\Delta J_{\text{sc}}\%$ in 400–600 nm spectral range compared to 600–800 nm spectral range clearly confirms the LDS effect as the dominant factor for the increase in IPCE and thereby J_{sc} of the devices with LDS layers. The superior performance of LDS2 layer compared to LDS1 layer is related to the greater thickness for the LDS2 layer than for the LDS1 layer, so that conversion of larger number of high energy photons to low energy photons occurred for the former than for the latter layer.

4. Conclusion

We presented the application of a luminescent layer of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ particles inside DSSC sensitized with SQ1 dye as a dual functional layer. The LDS layer improved the LHE by both down shifting of the incident photons from the high-energy to the low-energy region and the effect of light scattering, whereas the former proved to be the dominant effect. Application of LDS2 layer with 50% luminescent quantum efficiency and $160 \pm 2 \mu\text{m}$ thickness caused a remarkable enhancement in IPCE, up to 350% relative increase in 500 nm. Accordingly, short circuit current density of DSSC increased by 64%. It is expected that this approach works with other phosphor/dye couples as excellent as with the phosphor/dye couple used here noting that the luminescent quantum efficiency and absorption coefficient of phosphor particles will be crucial parameters governing the performance of LDS layer.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2016.10.104>.

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