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Downshifting maximization procedure applied to [Eu(bphen)(tta)$_3$] at different concentrations applied to a photovoltaic device and covered with a hemispherical reflector

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ABSTRACT

In this work we propose the determination of the maximum downshifting efficiency of any new downshifter applied to photovoltaic (PV) devices in terms of downshifter concentration and the description of the optics applied as the standard procedure if increases in EQE, conversion efficiency and/or I_{sc} are being reported. A standard procedure is defined for determining the maximum downshifting efficiency, firstly in by reaching the solubility limit of the downshifting precursors and, subsequently, by reaching the maximum luminescent intensity of the downshifter. Also, we consider that a description of the optics applied to the experiment should be included to guarantee the reproducibility of the results. This procedure is successfully applied to poly(methylmethacrilate) (PMMA) films containing the active species [Eu(bphen)(tta)$_3$] (bphen = 4,7-biphenyl-1,10-phenantroline and Htta = thenoltrifluoroacetone). Finally, a hemispherical reflector is applied on the PV device in order to modify the optics applied in the experimental setup and for increasing the EQE of the PV device. This scheme is proposed to be integrated in PV devices for its use in niche applications where concentrator photovoltaics (CPV) offers some advantages in relation to non-concentrator configurations.

1. Introduction

It is commonly considered that the evaluation of the downshifting properties applied to a PV device should be completed by comparing the device with the downshifting layer to a similar device with a non-luminescent layer of the same material and using the established AM1.5G spectrum [1]. However, in works where downshifters are integrated in PV devices the increase in EQE reported is not explicitly referred to a downshifter concentration where the increase in EQE reaches the maximum value [1–7] or only for some of the compounds studied [8]. In some cases (i) the studies are related to the concentration of the downshifter constituents for maximizing its photoluminescent intensity [9]; or (ii) the deposition temperature of the downshifting film for optimizing dopant insertions and activations in the downshifter [10], but not the concentration of the downshifter itself once the best synthesis procedure and stoichiometry has been defined. In other works (i) the solubility limit is experimentally selected, but not the maximum luminescent of the downshifter [11]; (ii) the quantum dots concentration are expected to be maximized by defining a quality factor as the absorption/reabsorption coefficient, but it is difficult to obtain experimentally in comparison to the direct photoluminescent characterization of the downshifter embedded in the host material [12]; (iii) the experimental results shown are for a short set of samples in terms of downshifter concentrations and simply select the sample with the best results [13,14]; or (iv) an optimum optical density (OD) is simulated at the absorption maximum, and suggesting that increasing the absorbance would require unnecessary material consumption for a limited or no improvement in current density [15].

As it will be exposed in this work, this EQE maximum depends on the concentration of the downshifters on the PV device, but also

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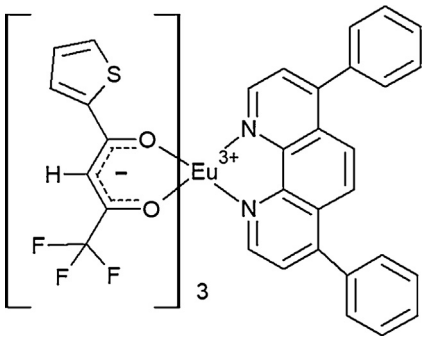

Fig. 1. Schematic view of the molecular structure of [Eu(bphen)(tta)$_3$].

on the optics applied to increase the collection of photons by the solar cell. The direct relation between increase in EQE and the photoluminescent (PL) intensity of the downshifter [16] offers a simple procedure to reach the maximum increase in EQE by integrating the downshifter on the PV device. Then, we consider that previous to any EQE measurement, the downshifter concentration for reaching the maximum PL intensity should be determined.

In this work we prepare PMMA films with different ratios of the [Eu(bphen)(tta)$_3$] downshifter to determine its optimal concentration for a maximum increase in EQE for a PV mini module. Also a hemispherical reflector is placed on the downshifter-PMMA layer to avoid most photon losses due to the isotropic nature of the downshifting emission and for increasing the EQE of a PV device placed below. This active species has been selected for absorbing UV light, helping to increase the EQE of the PV device used in this work. Moreover, downshifting in the UV range can reduce the expected yellowing of the PV module encapsulant under ambient conditions [17] and the degradation in performance for some types of solar cells (e.g. based on perovskites) [18].

2. Experimental

The downshifter [Eu(bphen)(tta)$_3$] active species (Fig. 1) was obtained by the reaction of stoichiometric quantities of europium (III) nitrate pentahydrate (99.99%), 4,7-biphenyl-1,10-phenantroline (bphen, 97%), 2-thenoltrifluoroacetone (Htta, 99%), and triethylamine (99%), following a procedure similar to that previously described [19]. 2-thenoyltrifluoroacetone (668 mg, 3 mmol) was dissolved in 40 ml of ethanol and the solution was heated at 65 °C under stirring in an erlenmeyer flask. Triethylamine (416 μl, 3 mmol) was added under stirring. Subsequently, a solution of bphen (332 mg, 1 mmol) in ethanol (40 ml) was added. In a different beaker, Eu(NO$_3$)$_3$ (425 mg, 1 mmol) was dissolved in ethanol (10 ml). Finally, both solution were mixed and stirred for 2 h. After that time, 50 ml of water were added and a white product was obtained that was filtered, washed with water and dried in an oven at 60 °C overnight (yield 1.059 g, 92%). Elemental analysis calculated (in %) for $C_{48}H_{28}N_2Eu_1O_6F_9S_3$: C, 50.23; H, 2.46; N, 2.44; S, 8.38. obtained: C, 50.47; H, 2.47; N, 2.69; S, 8.51.

PPMA films were prepared by spin coating following a procedure similar to that described previously [20]. In a typical experiment for the preparation of the films, a 20 × 20 × 2 mm bare glass is washed with a solution of soap and deionized water, dried with a dinitrogen current and placed in the holder of a spin-coater. The desired amount of sample (in our experiments in the 0.26–7.90 mg range) is dissolved in 1500 μL of CH_2Cl_2 and then 26.25 mg of PMMA are added. Then, the solution is poured on the glass and spin-coated at 800 rpm for 10 s. The solvent is allowed to evaporate at room temperature. We have found that this solvent amount is enough to obtain a film that completely covers the glass and the PPMA/CH_2Cl_2 ratio and spin coating conditions gives film thicknesses in the 300–470 nm range which are optimum for the EQE experiments. Finally, the glass is directly placed on a PV mini module, and illuminated for measuring the EQE (Fig. 2a). With this configuration an air gap exists between the glass and the PV device, introducing an additional optical loss. However, this configuration with an air gap has been selected because it eases placing alternative glasses on the PV mini module and, then, the EQE characterization with different downshifters. Consequently, this setup guarantees the comparison and reproducibility of results. Other authors add a refractive index matching oil carefully chosen to prevent reflection losses between the downshifter and the solar cell [15]. However, this procedure can also produce some inconveniences (e.g., poor polymer adherence to the solar cell despite the application of the matching oil) and, as our experiments are carried out only for comparative purposes, avoiding the matching oil eases the experimental procedure.

Also, a hemispherical reflector has been placed above the downshifter for collecting to the solar cell most of the downshifted photons isotropically directed out of the device (Fig. 2b). As the reflector is made of aluminum with a reflectance almost constant in the 280–1200 nm spectral range [21], no corrections to the initial EQE results have been introduced when the hemispherical reflector is used. Optimal alignment of the hemispherical reflector to the light source is needed to avoid any loss of light reaching the solar cell and, thus, obtaining the highest increase in EQE.

Luminescent spectra were obtained exciting the samples using a 400 W Xe arc lamp passed through a 0.25 m Spex 1680 double monochromator. Fluorescence was detected using a 0.25 m Spex 1681 monochromator with photomultiplier. The active specie was selected showing a large Stokes shift, avoiding overlap of emission and absorption spectra and, consequently, reemission processes in the downshifter.

The PV device is a PV mini module based on a single p-type mc-Si solar cell (non-textured and with a SiN_x antireflection coating optimized at 600 nm) encapsulated in a standard solar glass and showing a 16% conversion efficiency. A standard EQE setup based on a 100 W Xe arc lamp, double monochromator and a digital lock-in amplifier, integrated in the SPECLAB commercial setup at Fraunhofer ISE Lab (Germany) has been used. The PV mini

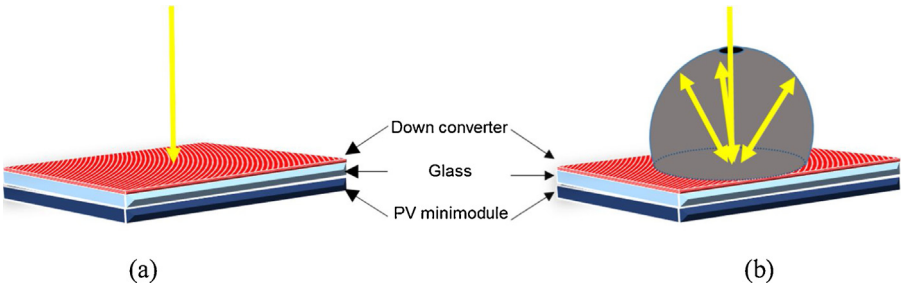

Fig. 2. Scheme of (a) the downshifter deposited on glass and placed on the PV mini module; and (b) the same configuration but also a hemispherical reflector placed on the downshifter for collecting to the solar cell most of the downshifted photons previously emitted isotropically out of the device.