

Supporting Information

Combined plasmonic and upconversion rear reflectors for efficient dye-sensitized solar cells

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Experimental section

Materials

GdCl₃·6H₂O (99%), YbCl₃·6H₂O (99.9%), ErCl₃·6H₂O (99.9%), FeCl₃·6H₂O (≥98%), oleic acid (90%), 1-octadecene (90%), ammonium fluoride (NH₄F), AgNO₃ (99+%), polyvinylpyrrolidone (PVP) powder (avg.Mw #55,000), ascorbic acid (>99%) were purchased from Sigma-Aldrich. Ethylene glycol was purchased from J. T. Baker. Titanium(IV) chloride (TiCl₄) were purchased from Sigma Aldrich. Ruthenium dye (535-bisTBA, N719) was purchased from Solaronix. DSSC electrolyte LivionTM 10 was purchased from Merck, Germany. Sodium hydroxide (NaOH), and ethanol were purchased from Samchun chemicals, Korea. Ultra pure water (18 MΩ cm) was obtained from a μ pure HIQ water purifying system.

Synthesis of NaGdF₄:Yb/Er/Fe (UCNPs) nanoparticles

NaGdF₄ UCNPs doped with Yb³⁺,Er³⁺ (18, 2 mol%) and co-doped with 30 mol% Fe³⁺ ions were synthesized using oleic acid as coordinating ligand and 1-octadecene as non coordinating solvent. In the case of NaGdF₄:Yb,Er,Fe (18,2,30 mol%) nanocrystals, 0.50 mmol of GdCl₃·6H₂O, 0.18 mmol of YbCl₃·6H₂O, 0.02 mmol of ErCl₃·6H₂O and 0.30 mmol of FeCl₃·6H₂O were taken in a 100 ml 3-necked flask and 15 mL of octadecene and 8 mL of oleic acid were added. The flask was then heated to 150 °C under vacuum and held at this temperature for 60 min to get a homogenous solution. Subsequently, the flask was cooled down to room temperature and 10 mL methanol solution containing 4 mmol NH₄F and 2.5

mmol NaOH was added dropwise. The resulting solution was stirred at room temperature for 2 h and heated slowly to 70 °C until the entire methanol evaporated. The reaction vessel was then brought under a gentle flow of nitrogen and heated up to 300 °C and held at that temperature for 90 min. The flask was then cooled to room temperature and the nanoparticles were precipitated by adding ethanol (15 mL), centrifuged and washed with ethanol. The isolated oleate-stabilized nanoparticles were stored as 1 wt% dispersion in toluene.

Synthesis of silver particles (Ag-150)

A disposable glass vial containing 5 mL of ethylene glycol was heated to 160 °C. After 1 h a solution of silver nitrate in ethylene glycol (0.02 M, 3 mL) and a solution of PVP in ethylene glycol (0.2 M, 3 mL) were added simultaneously under vigorous stirring. The reaction continued at 160 °C for 2 h and allowed to cool to room temperature. The silver nanoparticles were purified by ultracentrifugation, washed with acetone and water and stored in ethanol (1 wt%) prior to use.

Synthesis of silver particles (Ag-1000)

In a typical synthesis, AgNO₃ (2 mmol) and a PVP (2mmol) were added to deionized water (100 mL) in a beaker with a magnetic stirrer at room temperature. An ascorbic acid (2mmol in 2 mL H₂O) solution was then quickly injected into the vigorously stirred mixture. The solution became grey immediately and then changed to dark grey a few minutes later, which indicated the appearance of a large quantity of colloidal silver particles. The product was obtained by centrifugation and was washed with water and ethanol in order to remove the excess surfactant.

Preparation of rear reflector films

Five different light reflection films were prepared and the compositions of the films are as follows: UCNP (RR-01), Ag-150 (RR-02), Ag-150+UCNP (RR-03), Ag-1000 (RR-04), Ag-1000+UCNP (RR-05). For the preparation of RR-05, a 1*1 cm pre-cleaned microscopic

slide was coated with 50 μL of silver particles (Ag-1000, 1 wt% in EtOH) by drop casting and dried at 70 $^{\circ}\text{C}$. Upconversion nanoparticles layer was coated by dropping 50 μL of UCNPs (1 wt% in toluene) and dried at 80 $^{\circ}\text{C}$ for 2 min.

Fabrication of DSSCs

TiO_2 paste was prepared according to reported literature procedures.¹ TiO_2 paste were coated on a conducting glass with F: SnO_2 film (FTO, 7 Ω/sq , Alrich) using a doctor-blade printing technique. After printing, the electrode was dried at 70 $^{\circ}\text{C}$ and then was sintered at 450 $^{\circ}\text{C}$ for 30 min in air. After sintering at 450 $^{\circ}\text{C}$, the TiO_2 films were treated with 40 mM TiCl_4 at 70 $^{\circ}\text{C}$ for 30 min, rinsed with water and ethanol and sintered at 450 $^{\circ}\text{C}$ for 30 min. At 80 $^{\circ}\text{C}$ in the cooling, the TiO_2 electrode was immersed into dye solution (N719, Solaronix, 0.5 mM in ethanol), and kept at the room temperature for 18 hrs. Then, the dye-adsorbed electrode was washed with ethanol and dried. Platinum counter electrodes were prepared by conventional thermal decomposition method using H_2PtCl_6 precursor. The dye-adsorbed TiO_2 electrode and counter electrode were stacked and sealed with a sealant (Surlyn, 60 μm -thick, Meltonix) at 100 $^{\circ}\text{C}$ for 15 s. The electrolyte solution of composition with 1.0 M 1,3-dimethyl-imidazolium iodide, 0.03 M I_2 , 0.1 M guanidinium thiocyanate, 0.5 M *tert.* Butylpyridine, 0.05 M LiI in acetonitrile and valeronitrile (85/15, v/v) was injected into the cell through a hole and end sealed. Rear reflector films were attached to the counter electrode using scotch tape or sealant (Surlyn, 60 μm -thick, Meltonix).

Characterization

X-ray diffraction measurements were carried out on Rigaku Miniflex II. Transmission electron microscopy (TEM) images were obtained using Tecnai (G2F30) TEM at an accelerating voltage of 300 kV. The upconversion photoluminescence (PL) spectra were recorded on Horiba Jobin Yvon spectrometer equipped with a 980 nm IR laser as excitation source. Diffuse reflectance spectra were recorded on a UV-3600 shimadzu UV-vis-NIR

spectrophotometer. UV-vis absorption spectra were recorded on Scinco (S-4100) UV-vis spectrophotometer. Solar energy conversion efficiency was measured using solar simulator (Oriel Sol 3A Solar Simulator, 94063A, Newport Stratford Inc.) under a simulated standard solar light, *i.e.*, 100 mW cm^{-2} ; AM1.5G checked with an NREL-calibrated Si-solar cell.

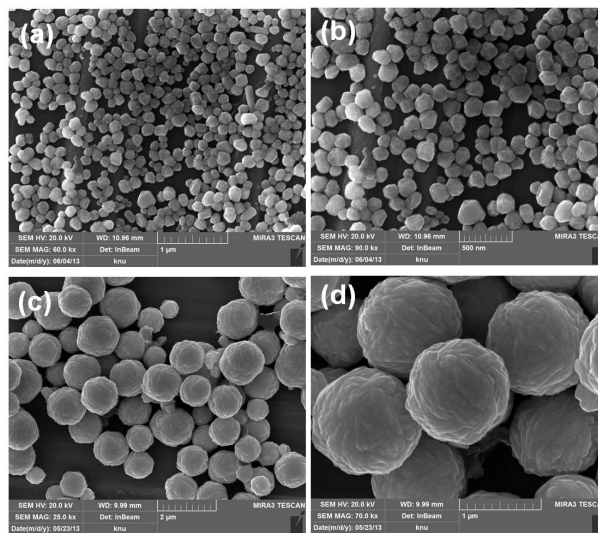


Fig. S1. SEM images of Ag-150 (a,b) and Ag-1000 (c,d).

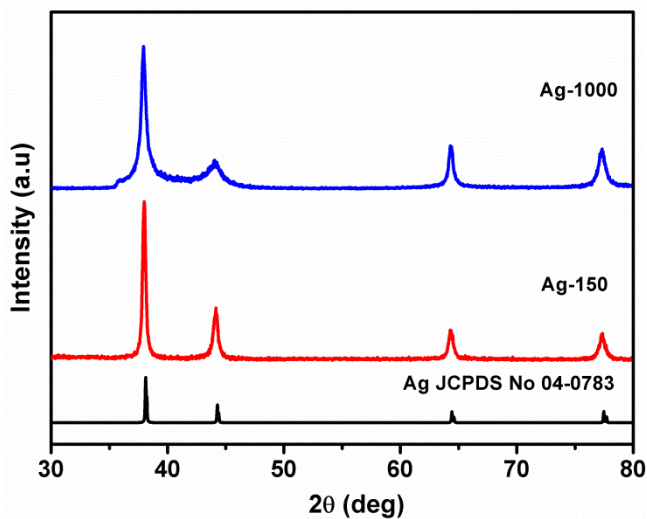


Fig. S2. XRD patterns of Ag-150 and Ag-1000.

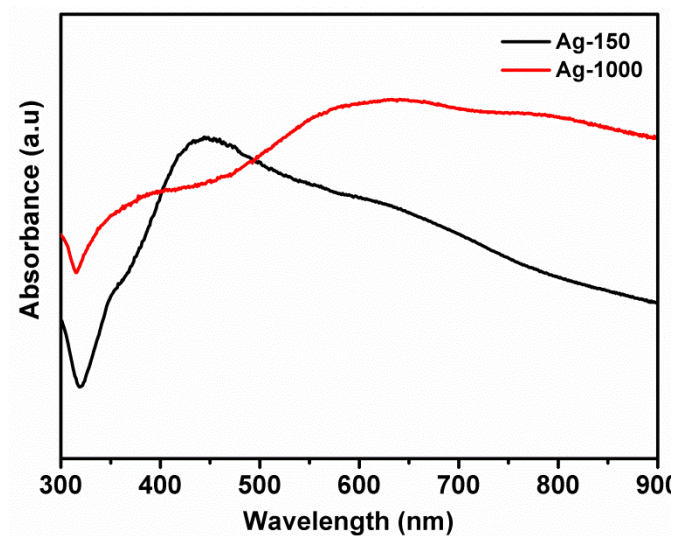


Fig. S3. UV-visible absorption spectra of Ag-150 and Ag-1000.

Reference

1. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovolt: Res. Appl.*, 2007, **15**, 603-612.