

Notes and references

Key Laboratory of Artificial Micro/Nano-Structures of Ministry of Education

School of Physical Science and Technology, Wuhan University
Wuhan 430072, Hubei, PR China

Fax: +86 27 8764-2569; Tel: +86 27 8764-2784;

E-mail: xzzhao@whu.edu.cn

† Electronic Supplementary Information (ESI) available. See

DOI: 10.1039/b000000x/

Experimental section

Preparation of double shell β -NaYF₄:Yb³⁺, Er³⁺/SiO₂/TiO₂ submicroplates: β -NaYF₄:Yb³⁺, Er³⁺ submicroplates were prepared by a one-step hydrothermal treatment method¹. In a typical synthesis, an aqueous solution (5 mL, 0.2 M) of Y(NO₃)₃, Yb(NO₃)₃, and Er(NO₃)₃ (lanthanide ion molar ratio, Y/Yb/Er = 78:20:2) was mixed with an aqueous solution of sodium citrate (45 mL, 2.08 M) under stirring for 30 min to form a white solution. Subsequently, aqueous solution (20 mL) of NaF (20 mL, 0.625 M) was added and stirred for 1 h, resulting in a complex with the lanthanide/sodium citrate/NaF molar ratio being 1/90/12. Then, HNO₃ was added to adjust the pH of the solution to 3. The as-obtained solution was then transferred into a 100 mL autoclave and hydrothermally treated at 180 °C for 2 h. After cooling to room temperature, products obtained were separated by centrifugation and washed with deionized water and ethanol and then dried at 80 °C in vacuum.

For coating with SiO₂ and then the TiO₂ shell, as-obtained β -NaYF₄:Yb³⁺, Er³⁺ plates (0.2 g) were dispersed into isopropanol (100 mL) under sonication for 10 min. Deionized water (20 mL), Polyvinylpyrrolidone-K30 (PVP-K30, 0.01g), tetraethyl orthosilicate (TEOS, 0.4 mL), and then ammonia (2 mL) were added into the solution simultaneously. After stirring for 1 h, the obtained product was washed several times with water and ethanol and redispersed in a mixed solution containing ethanol (70 mL) and PVP-K30 (0.02 g). After stirring for 30 min, Tetrabutyl titanate (TBOT, 0.1 mL) was added to the above solution. After the solution was stirred for 1 h, 0.5g deionized water was added and then transferred in to a 100 mL autoclave and maintained at 200 °C for 1 h. The resulting white precipitates were separated by centrifugation, washed with ethanol and deionized water in sequence, and then dried in vacuum at 80 °C for later use. For comparison, bare and only SiO₂ coated samples were also prepared.

Device fabrication: TiO₂ (20-40 nm) paste for transparent layer was prepared by hydrolysis of titanium tetraisopropoxide *via* the reported procedure.² To obtain the paste for scattering layer, previously obtained bare, only SiO₂ coated, and double shell coated submicroplates were added into the solution contain ethanol (4 mL), water (1 mL) and acetylacetone (0.16 mL) and the string for 1 h. Doctor blade method was used to prepare photoelectrodes followed by sintering at 500 °C for 30 min. For dye adsorption, films were immersed in ethanol solution of N719 dye (0.5 mM) for 24 h at room temperature. The liquid electrolyte was comprised of LiI (0.1 M), I₂ (0.05 M) and 4-tert-butylpyridine (TBP, 0.5 M) in acetonitrile. The platinum counter electrode was prepared by spin-coating H₂PtCl₆ (in isopropanol, 15 mM) onto the FTO glass followed by heating at 410 °C for 30 min.

Characterizations: X-ray diffraction (XRD) characterization was performed on a D8 Focus diffractometer. Field emission scanning electron microscopy, FE-SEM (JEOL, 6700F, Japan) was applied to study the morphology and composition of the samples. Transmission electron microscope equipped with energy dispersive X-ray analysis and high-resolution transmission electron microscope system investigations were carried out on a JEOL 2010. To obtain the dye loading amount adsorbed on different photoanodes, NaOH anques solution (0.1 M) was used for desorption and UV-vis spectrometer (Varian Carry 5000) was used to measure the absorption spectra. Diffuse reflection spectrums of pure and modified films were observed on Carry 5000. For PL

measurements, the excitation source was a CW Ti: sapphire laser (Mira 900, Coherent). The PL spectra were recorded by a spectrometer (Spectrapro 2500 i, Acton). To study the NIR response of the DSSC device, a 980 nm laser (300 mW) was used as a NIR source. The incident photon conversion efficiency (IPCE) was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source. IPCE photocurrents were recorded under short-circuit conditions using a Newport 2931-C power meter. Photocurrent-voltage measurement of cells were performed on a Keithley 2400 source meter (Keithly Instruments Inc., USA) by applying external potential bias to the device under simulated illumination (Newport, 91192) with a power density of 100 mW cm⁻² (AM 1.5, global) which was calibrated with a Si photodiode. The irradiated area of each cell was kept at 0.25 cm² by using a light-tight metal mask.

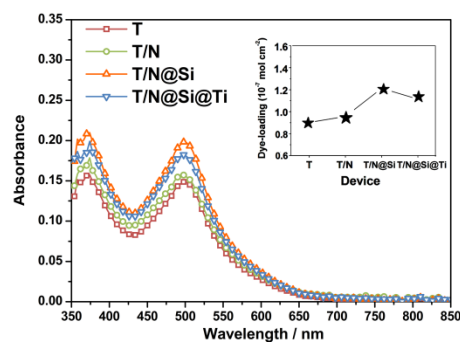


Figure S1 Absorption spectra of N 719 dye in 0.1 M NaOH aqueous solution, desorbed from the photoanodes based on T, T/N, T/N@Si, and T/N@Si@Ti.

1. C. Li, Z. Quan, J. Yang, P. Yang and J. Lin, Inorg Chem, 2007, **46**, 6329-6337.
2. R. L. Willis, C. Olson, B. O'Regan, T. Lutz, J. Nelson and J. R. Durrant, The Journal of Physical Chemistry B, 2002, **106**, 7605-7613.