

Supplementary Material (ESI) for Chemical Communications
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Cubic CeO₂ Nanoparticles as Mirror-like Scattering Layer for Efficient Light Harvesting in Dye-Sensitized Solar Cells

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Experimental details

Nanoporous TiO₂ film preparation

TiO₂ films were screen-printed on pre-cleaned FTO glass with commercial TiO₂ paste (Dyesol Pty, Australia). The printing processes were repeated until a thickness of 12 µm was obtained. Subsequently the resultant films were sintered at 450°C for 30 min, designated as control films.

CeO₂ synthesis and CeO₂/TiO₂ bilayer and compound film preparation

Cerium hydroxide were synthesized by hydrothermal treatment of Ce₃(NO₃)₃·6H₂O in alkaline solution. Typically, 1g of Ce₃(NO₃)₃·6H₂O was added into 40 mL of 12M NaOH solution(demionized water:ethanol=3:1) with strong stirring. The homogenous solution was then transferred to a 125 mL Teflon-lined stainless-steel autoclave in the ambient environment. The sealed autoclave was transferred to a 180 °C electric oven and held there for 24 h, and then cooled to room temperature naturally. The crude solution containing Ce(OH)₃ was centrifugated to remove the solid impurities, and then the upper yellowish supernatant solution containing the nanoparticles was precipitated with the minimum volume of ethanol and further isolated by centrifugation. The purified nanoparticles were then treating with H₂O₂(37%) under ultrasonic conditions to partially oxidize the Ce(OH)₃. Finally the particles were washed with ethanol by repeating centrifugation (4750 rpm) and calcined at 450 °C for 1 h. To prepare the screen-printing paste, 4 g of ethyl cellulose and 15 ml of alpha-terpineol were mixed with the calcined nanoparticles in 40 mL of ethanol. Then the residual ethanol in the mixture was removed by using a rotary evaporator to produce a viscous paste.

The CeO₂ paste was deposited onto the TiO₂ film using a standard 43 mesh screen-printing machine then calcined at 450 °C for 1 h. This process was repeated for resulting in a double-layer CeO₂ film.

The photoanode composed of TiO₂/CeO₂ mixture were also prepared by mixing the TiO₂ paste with 5%(molar ratio) and 10%(molar ratio) of CeO₂ particles in ethanol

solution. The TiO₂/CeO₂ mixture pastes were deposited onto the FTO substrate using the standard 43 mesh screen-printing machine and then calcined at 450 °C for 1 h. This process is repeated until a thickness of ~12 μm in single layer fashion was obtained.

DSSCs Assembly and Characterization

The prepared films with a sensitized area of 0.15 cm² were immersed into N719 dye solution (3×10^{-4} M in butanol and acetonitrile, 1:1, v/v) for 24 h. The dye-sensitized films were washed with anhydrous acetonitrile after dye sensitization, and dried in N₂ flow before measurements. Platinum counter electrode on FTO substrate was prepared by spin-coating using 5 mM H₂PtCl₆ isopropanol solution and pyrolyzing the resulting film at 380 °C for 15 min. Liquid solution containing I⁻/I₃⁻ redox couple was used as the supporting electrolyte. Then the dye-sensitized TiO₂ film, electrolyte and platinum counter electrode were configured into a typical sandwich cell and sealed with thermoplastic sealant.

DSSCs Characterization

The morphology of the prepared films was characterized by using scanning electron microscope (JEOL 890). SEM images were taken under a high vacuum with platinum coating on the samples. X-ray diffraction (JEOL 890) was carried out in order to investigate the phase of each sample. Transmission electron microscopy (TEM, JEOL 4010) were employed for the crystalline analysis. The surface area were measured by using Tristar® II 3020 system. The Oriel solar simulator coupled with a Keithley 2400 model was employed for the photovoltaic measurement and the *I-V* curve was recorded using the UPTS software (Dyesol, Australia). The light intensity (AM1.5 G, 100 mW/cm², 25 °C) was adjusted with a NREL-calibrated silicon standard cell. The Quantum Efficiency (QE) values were recorded as a function of the wavelength from 350 nm to 850 nm (Newport, USA). A 300W Xenon lamp was used as a light source with a CS260 monochromator. The diffuse reflectance spectra were recorded using a UV-Vis spectrometer equipped with an integrating sphere accessory (UV-2450, Shimadzu). In details, the photoanode films prepared on FTO substrates were placed in the analysis chamber and scanned and the light reflectance in percentage (%) in the wavelength range of 800 nm to 300 nm was presented to indicate the light scattering

effect of the photoanodes. For estimation of the dye-loading amount, dye absorbed on the TiO₂ electrode was dissolved in a 0.1 M NaOH solution of water and ethanol (50/50, v/v), and its absorption property was measured by the UV-vis spectrometer (UV-2450, Shimadzu).

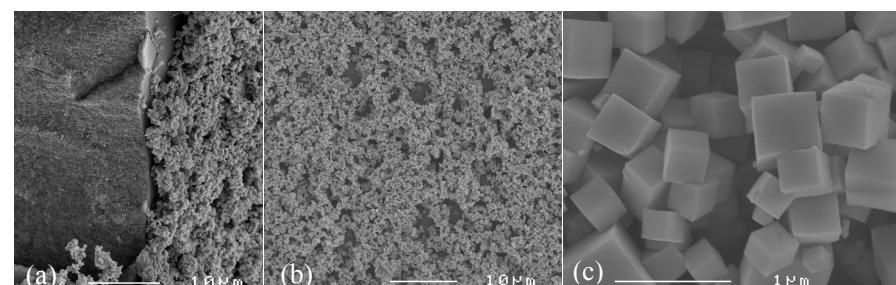


Fig.S1 SEM images of (a) cross-section of cubic CeO₂ thin layer, (b) surface morphology of CeO₂ thin layer and (c) high magnification CeO₂ nanoparticles.

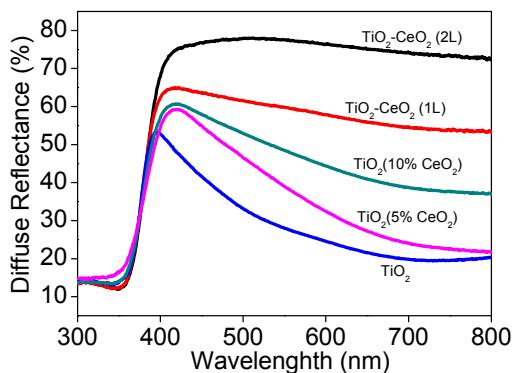


Fig.S2 UV-vis diffuse reflectance of the control and modified films

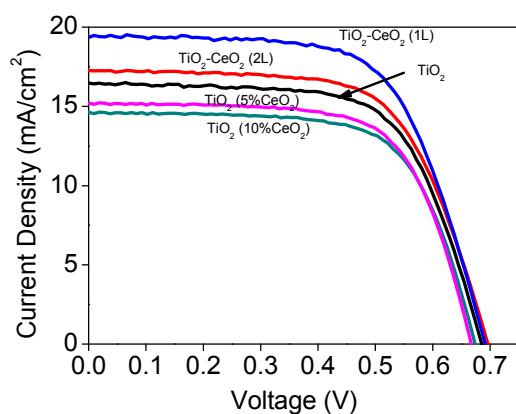


Fig.S3 Photocurrent as a function of photovoltage for DSSCs with control and modified films

Brief Discussion:

Additional experiments by mixing TiO₂ nanoparticles with 5 mol% and 10 mol% of CeO₂ scattering crystals as photoanodes was conducted for comparison. The light scattering effect and DSSC performance were measured (supporting S-Fig. 2 and S-Fig. 3). It was clear that the photoanodes composed of mixed TiO₂ and CeO₂ in a single layer structure had improved light scattering efficiency compared with that of pure TiO₂ photoanodes, while the improvement was still lower than that with a bilayer design. The overall conversion efficiency of TiO₂/CeO₂ mixture photoanodes were 6.6% (10 mol% CeO₂) and 6.9% (5 mol% CeO₂) respectively, which were lower than those of bi-layered photoanodes and even the control pure TiO₂ films. The exact reason for such reduced efficiency is not clear yet, while we speculate that the interfacial contact of large sized CeO₂ and TiO₂ nanoparticles in the mixture might play an important role in altering the charge carrier transport. Nevertheless, these experimental evidences confirmed the beneficial bilayer structure design for efficient light scattering and QE improvement of DSSC [*Adv. Funct. Mater.* 2010, **20**, 1301–1305, *Coordination Chemistry Reviews*, 248, 13, 2004, 1381 – 1389].