Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Material

Planar Scattering from Hierarchical Anatase TiO_2 Nanoplates with Variable Shells to Improve Light Harvesting in Dye-Sensitized Solar Cells

Wei Shao, Feng Gu,* Lili Gai and Chunzhong Li *

Key Laboratory for Ultrafine Materials of Ministry of Education
School of Materials Science and Engineering
East China University of Science & Technology
Shanghai 200237, China
E-mail: gufeng@ecust.edu.cn and czli@ecust.edu.cn

Experimental Section

Preparation of the hierarchical hexagonal hollow anatase TiO_2 nanoplates

0.1 g $Cd(OH)_2$ nanoplates were added in 5 ml distilled water, followed by ultrasonic dispersion for 20 min. The above suspension was dropwise introduced to the aqueous solution consisting of 0.075 M ammonium fluotitanate ($(NH_4)_2TiF_6$, Sigma-Alorich Chemistry) and 0.2 M boric acid (H_3BO_3, Shanghai chemical Industrial Company) at room temperature under magnetic stirring for 2 h. The white precipitates were collected by filtration, washed several times with distilled water and absolute ethanol, dried at 80 ^oC for 6 h, and finally calcined in air at 450 ^oC for 30 min with the heating rate of 1 ^oC per minute to increase crystallinity. The single-shelled hexagonal hollow anatase TiO_2 nanoplates were obtained. If the white precipitates were not collected immediately, but left to stand for 18 h after stirred for 2 h, the products could be the double-shelled hexagonal hollow anatase TiO_2 nanoplates. For synthesis of the tri-shelled structure, the double-shelled nanoplates were used as the templates instead of $Cd(OH)_2$ nanoplates and the above experiment was repeated.

DSSCs fabrication

In the fabrication of DSSCs, the F-doped SnO_2 (FTO) conducting glass (Nippon Sheet Glass, SnO_2: F, 15 ohm/sq) was first cleaned in Triton X-100 aqueous solution, washed with acetone and ethanol, and treated with 50 mM $TiCl_4$ aqueous solution at 70 ^oC for 30 min, in order to make a good mechanical contact between the printed TiO_2 layer and FTO glass. An amount of 2.0 g of P25 TiO_2 was dispersed by adding 0.4 g PEG-20000, 10 ml terpineol, 0.4 g ethyl cellulose ethoce and 0.4 ml acetylacetone and grinded for 2 h. The result sol was printed onto the FTO glass with an active area of 0.25 cm^2 using the screen printing technique and then heated at 450 ^oC for 30 min. For the bi-layer structure, the sol of the scattering lay composed of the hexagonal hollow anatase TiO_2 nanoplates was prepared by the same method as that of P25 TiO_2 sol, followed by depositing by the screen printing technique on annealed P25 TiO_2 films and heated over the same heating profile as before. The resulting TiO_2 films were immersed in anhydrous ethanol containing 0.5mM of Ru-dye $(Bu_4N)_2[Ru(Hdcbpy)_2\text{-}(NCS)_2]$ (N719 dye, Solaronix), and kept for 24 h at room temperature. The dye-treated TiO_2 electrodes were rinsed with ethanol and dried under nitrogen flow. Pt counter electrodes were prepared on the FTO glasses using 0.7 mM H_2PtCl_6 solution, followed by heating at 380°C for 20 min in air. The redox electrolyte used was 0.1 M LiI, 0.05 M I_2, 0.6M 1, 2-dimethyl-3-propylimidazolium iodide, and 0.5 M 4-tertbutylpyridine in dried acetonitrile. The two electrodes were sealed together with a hot-melt polymer film (60 μm thick, Surlyn, DuPont).

Characterization

Scanning electron micrograph (SEM) images were taken with HITACHI S-4800 field-emission scanning electron microscopy, equipped with energy dispersive spectrometer (EDS Oxford).

Transmission electron microscope (JEM-2100) and high-resolution transmission electron microscope (JEM-2010F) were used to characterize the samples. The X-ray diffraction (XRD) patterns of the samples were measured by using Japan Rigaku D/Max 2550, Cu Ka radiation. UV-vis measurements were made with a Cary 500 spectrophotometer, equipped with an integrating sphere assembly. The BET surface area was measured on an AUTOSORB-1 analyzer (Quantachrome Instruments). Photocurrent-voltage (I-V) measurement was performed with a Keithley model 2440 Source Meter and a Newport solar simulator system (equipped with a 1 kW xenon arc lamp, Oriel) at one sun (AM1.5, 100 $mW \cdot cm^{-2}$). Incident photon to current conversion efficiency (IPCE) was measured as a function of wavelength from 300 to 800 nm using an Oriel 300 W xenon arc lamp and a lock-in amplifier M 70104 (Oriel) under monochromator illumination, which was calibrated with a monocrystalline silicon diode.

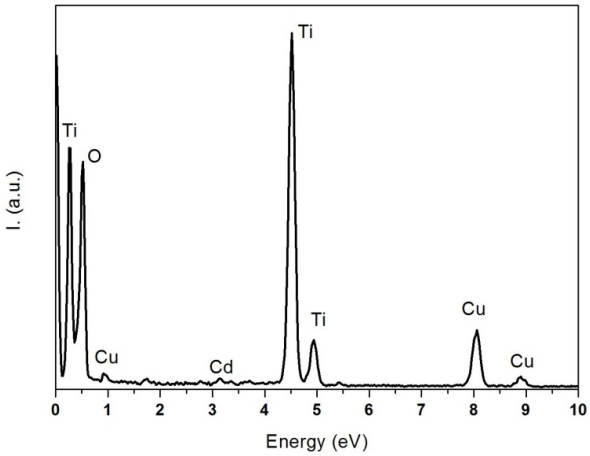

Fig. S1 EDS spectrum of the double-shelled hexagonal TiO_2 nanoplates.

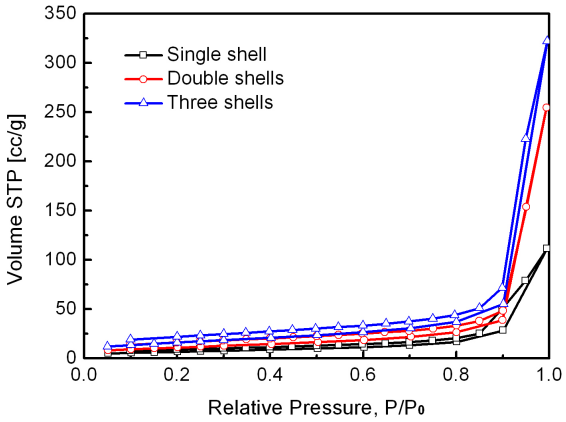

Fig. S1 N_2 Adsorption/desorption isotherms of the hierarchical TiO_2 nanoplates with different shell numbers.

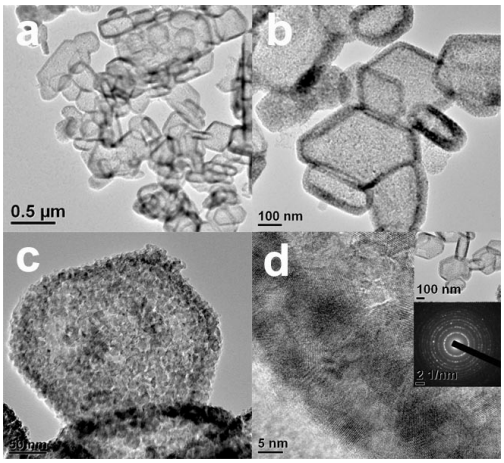

Fig. S3 (a, b) TEM images and (c, d) HRTEM images of the single-shelled TiO_2 nanoplates (inset showing the corresponding SAED pattern).

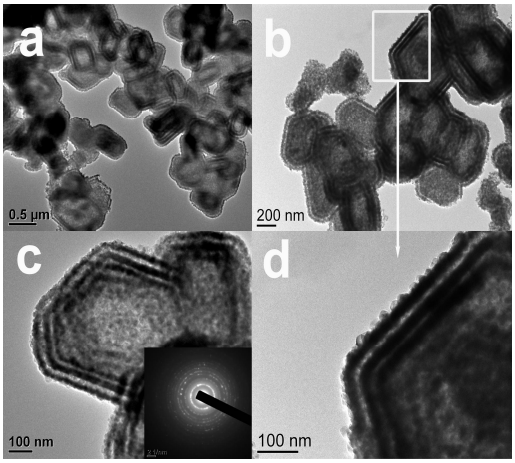

Fig. S4 TEM images of the three-shelled TiO_2 nanoplates.

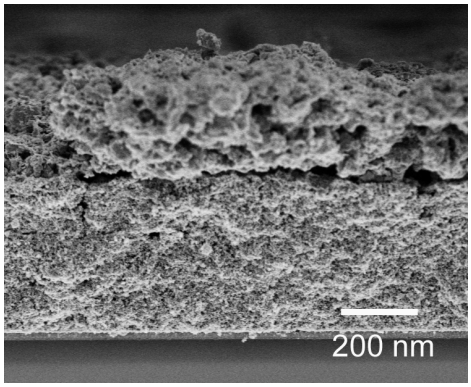

Fig. S5 Cross-sectional SEM image of the working photoanode.

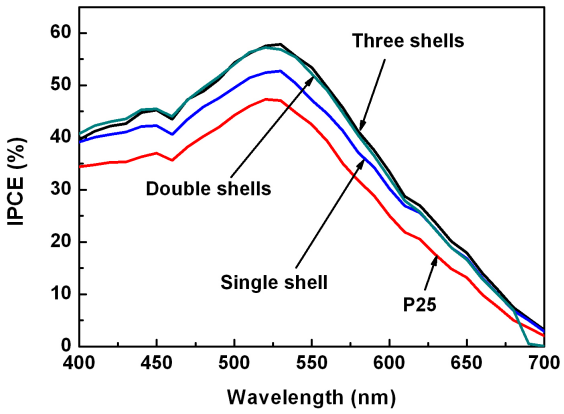

Fig. S6 IPCE curves of the photoanode composing of P25/ the hierarchical TiO_2 nanoplates with different shell numbers.

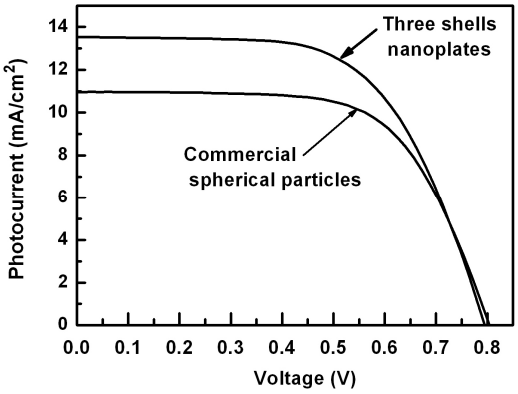

Fig. S7 I–V curves of the DSSCs

Table S1 BET results of the hierarchical TiO_2 nanoplates and the amount of adsorbed dye of the corresponding films.

The number of shell	BET area $m^2 \cdot g^{-1}$	Adsorbed dye $\times 10^{-7}$ mol·cm^{-2}
1	24.18	0.38
2	39.85	1.04
3	58.07	1.63

Table S2 Summarized cell performance results of the DSSCs prepared by the bilayer film with P25/ the hierarchical TiO_2 nanoplates with different shell numbers.

DSSC Photoanode		Voc V	Jsc $mA \cdot cm^{-2}$	FF	η %
P25 film		0.78	11.23	0.61	5.27
Bilayer film	P25 + S-TiO_2 nanoplates	0.80	11.95	0.55	5.33
	P25 + D-TiO_2 nanoplates	0.79	12.53	0.61	6.0
	P25 + T-TiO_2 nanoplates	0.79	13.52	0.61	6.53
	P25 + commercial T200 sphere	0.80	10.97	0.64	5.65