

Fabrication and Photovoltaic Performance of Hierarchically Titanate Tubular Structures Self-assembled by Nanotubes and Nanosheets

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Experimental

Preparation of tubular structures: All chemicals used in this study were analytical-grade and were used as received from Shanghai Chemical Reagent Factory of China without further purification. Distilled water was used in all experiments. Titanium glycolate rods, served as precursor for the fabrication of tubular structures, were prepared from tetrabutyl titanate ($\text{Ti}(\text{C}_4\text{H}_9)_4$, TBOT) according to the previous reported method [S1,S2]. In a typical synthesis, TBOT (5 ml) and ethylene glycol (500 ml) were heated at 170 °C in an oil bath with magnetic stirring for 2 h under atmospheric pressure conditions. After the solution was cooled to room temperature, the white precipitates were centrifuged and washed with distilled water for five times and then dried in a vacuum oven at 80 °C for 6 h. Subsequently, the dried titanium glycolate rods were collected and used as the precursor for the preparation of TiO_2 tubular structures. Typically, 0.4 g of titanium glycolate precursor and 0.12 ml of H_2O_2 (30 wt%) were added into 80 ml of a 0.1 M NaOH aqueous solution under vigorous stirring for 30 min. Afterwards, the solution with light-yellow color was transferred to a 100 ml Teflon-lined autoclave. The autoclave was sealed and kept at 180 °C for 24 h and then air cooled to room temperature. The white precipitates were centrifuged and washed with 0.1 M HCl and distilled water to pH 7. Finally, the precipitates were dried in a vacuum oven at 80 °C for 6 h and sintered at 450 °C for 30 min for further characterization.

Fabrication of DSSCs: To prepare a screen-printable paste of HTT, 0.5 g of as-prepared sample, 0.5 ml of acetylacetone and 0.5 ml of Triton X-100 were added into 5.0 ml of anhydrous ethanol in an agate mortar and then ground for 30 min. Screen-printable paste of commercial P25

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nanoparticles (NP) was also prepared by the same method. The fluorine-doped tin oxide (FTO) glasses (Nippon sheet glass, 14-20 Ω sq⁻¹) used as the substrates for dye-sensitized solar cells were cleaned ultrasonically with acetone, ethanol and distilled water for 15 min, respectively, and then dried in air. Tubular TiO₂ film was deposited on FTO glasses by the doctor blade method. For the preparation of NP/HTT bilayered film, after the NP layer was first deposited on FTO glass by the same method, the film was dried at room temperature and annealed at 450 °C for 30 min in an oven. Then, the HTT overlayer was deposited on annealed NP film and heated by the same heating method as previously. The film thickness was controlled by adhesive tapes that were covered on the edges of FTO glasses. After annealing, the film electrodes were immersed in anhydrous ethanol containing 0.3 mM of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis-tetrabutylammonium (N719, Solaronix S.A., Switzerland), and kept for 24 h at 50 °C in a sealed beaker. The extent of sensitization was estimated by comparing the colors at the top and bottom of the film. The sensitization was completed after the colors at the top and bottom of the film were the same. The sensitized film electrodes were washed with anhydrous alcohol one time, and then dried in an oven at 80 °C for 2 h. The typical dye-sensitized solar cells were assembled in a sandwich type by placing a platinum-coated conducting glass on the dye-sensitized electrodes separated by a ca. 50 μ m polymer spacer. The assembled cell was then injected into one drop of electrolyte which was made with 0.3 M LiI (Aldrich), 0.05 M I₂ (Aldrich), 0.6 M 1-propyl-3-methylimidazolium iodide (Suzhou, China), and 0.5 M tert-butylpyridine (Aldrich) in dry acetonitrile (Shanghai, China). The electrolyte was attracted into the inter-electrode space by capillary forces, and the cell was tested immediately.

Characterization: The morphology observation was performed by a JSM-5610LV scanning electron microscopy (SEM, JEOL, Japan) at an accelerating voltage of 20 kV and an S-4800 field emission SEM (FESEM, Hitachi, Japan) at an accelerating rate of 10 kV, which was linked with an Oxford Instruments X-ray analysis system, at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) analyses were carried out by a JEM-2100F electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu K α irradiation at a scan rate (2θ) of 0.05° s⁻¹ to determine the phase structure of the obtained samples. The accelerating voltage and applied current were 40 kV and 80 mA, respectively.

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Nitrogen adsorption–desorption isotherms were obtained on an ASAP2020 (Micromeritics Instruments, USA) nitrogen adsorption apparatus. All the samples were degassed at 100 °C prior to Brunauer-Emmett-Teller (BET) measurements. The BET specific surface area (S_{BET}) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05-0.25. The desorption isotherm was used to determine the pore-size distribution by the Barret-Joyner-Halender (BJH) method. The nitrogen-adsorption volume at the relative pressure (P/P_0) range of 0.994 was used to determine the pore volume and the average pore size. The photocurrent-voltage measurements were performed using a CHI660C electrochemical analyzer (CH Instruments, Shanghai, China). A solar simulator (Newport 91160) was served as a light source and its light intensity was adjusted to AM 1.5G one sun light intensity via a standard Si solar cell. The active area of DSSC was 4×4 mm². The measurements were repeated three times for each assembled dye-sensitized solar cells to minimize the experimental error, and the experimental error was found to be within ±3%. The electrochemical impedance spectroscopy (EIS) measurements were performed by a computer-controlled electrochemical work station with impedance analyzer (CHI660C Instruments, Shanghai Chenhua Instrument Corp., Shanghai, China) in a two-electrode configuration. The photoanode was used as a working electrode and the Pt electrode as a counter electrode. The measurements were carried out by applying bias of the open circuit voltage (V_{oc}) and recorded over a frequency range of 0.005 to 10⁵ Hz with ac amplitude of 10 mV.

References

[S1] S. Priya, J. Robichaud, M. C. Methot, S. Balaji, J. Ehrman, B. L. Su and Y. Djaoued, *J. Mater. Sci.*, 2009, **44**, 6470.

[S2] M. Wei, H. Zhou, Y. Konishi, M. Ichihara, H. Sugiha and H. Arakawa, *Inorg. Chem.*, 2006, **45**, 5684.

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Table S1. Comparison of physical properties of the calcined HTT and P25 NP.

Samples	Phase	S_{BET} (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)	Crystallite size (nm)
Calcined HTT	A	93.5	9.7	0.226	14.6
P25 NP	A&R	45.0	8.2	0.092	26.7 (A)

A: Anatase, R: rutile

Table S2. Comparison of the I - V characteristics of DSSCs made from HTT, NP and NP/HTT composite films.

Samples	Thickness (μm)	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
HTT	30	9.2	700	0.668	4.3 ± 0.13
NP	30	11.6	736	0.609	5.2 ± 0.16
NP/HTT	30	14.1	730	0.602	6.2 ± 0.19

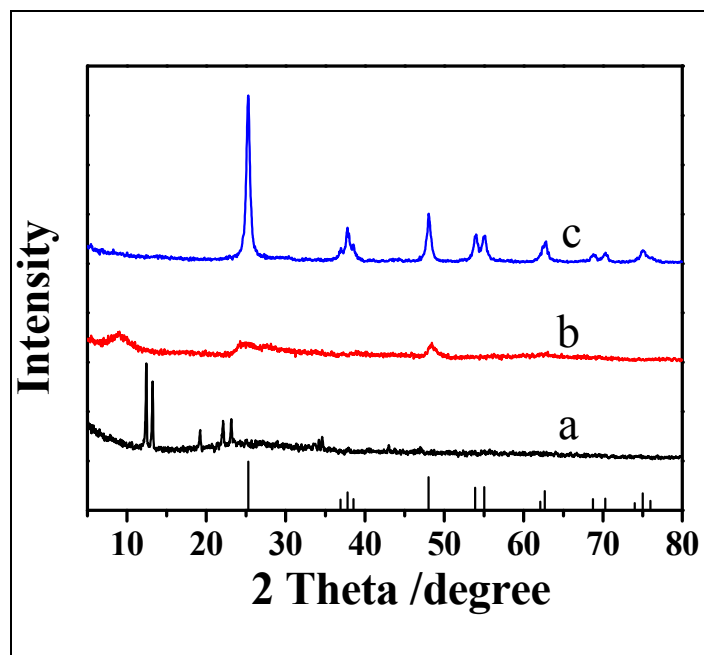


Fig. S1 XRD patterns of (a) titanium glycolate rods, (b) protonated titanate (HTT), and (c) the calcined HTT (anatase TiO_2). Vertical bars below the patterns represent the standard diffraction data from the JCPDS file for anatase (no.21-1272).

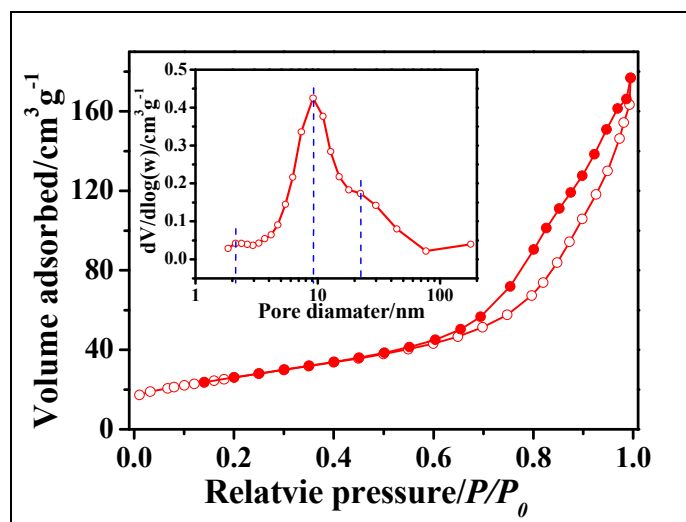


Fig. S2 Nitrogen adsorption-desorption isotherms and pore size distribution curves of tubular anatase TiO_2 sample (the calcined HTT).

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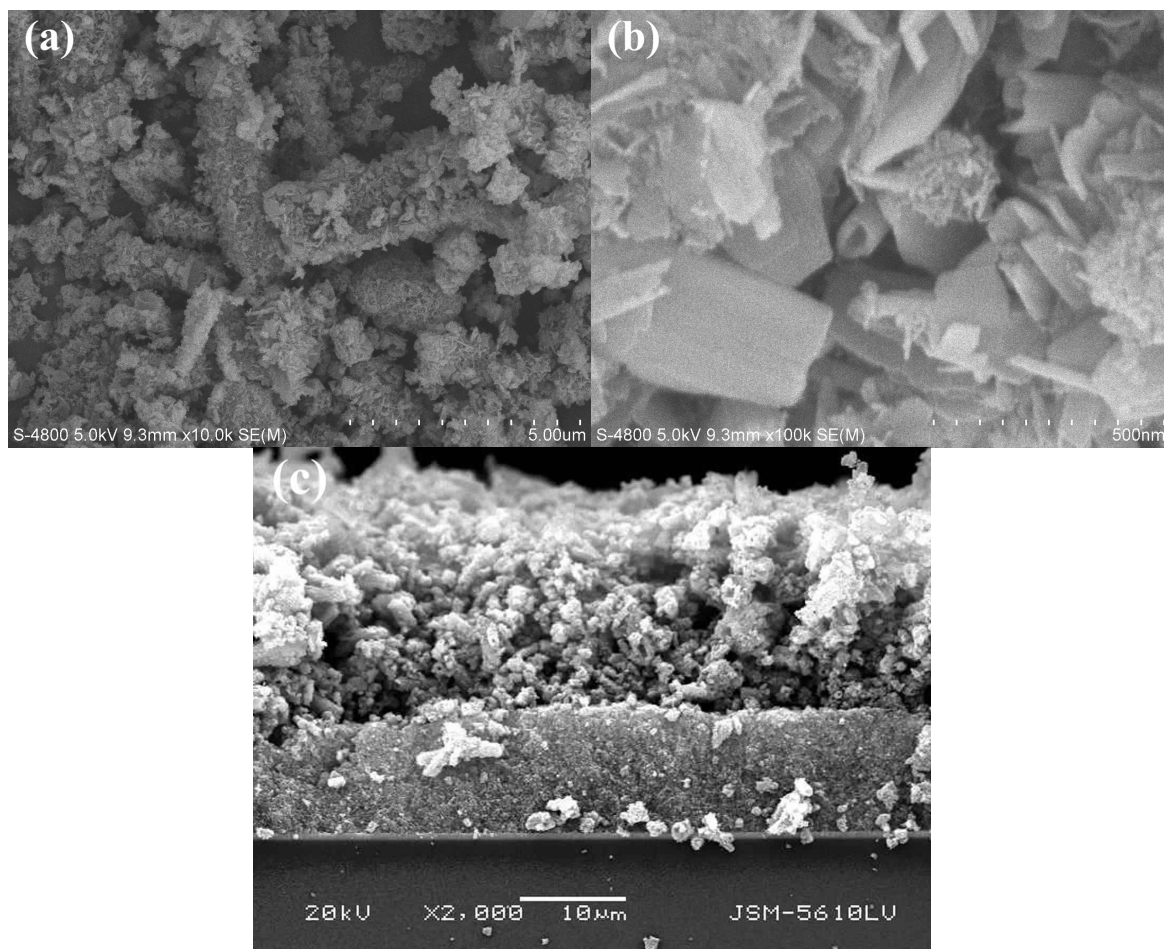


Fig. S3 Top (a,b) and cross-sectional SEM image (c) of double-layered NP/HTT composite film electrode consisting of a P25 NP underlayer and a HTT overlayer.

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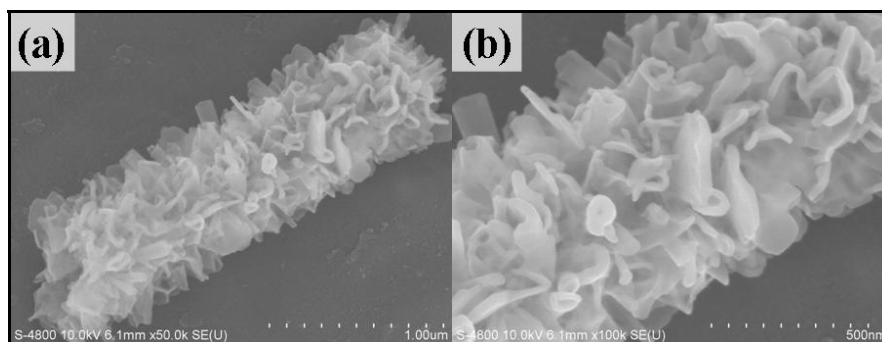


Fig. S4 SEM images (a,b) of the sample prepared at 180 °C for 24 h without H₂O₂.

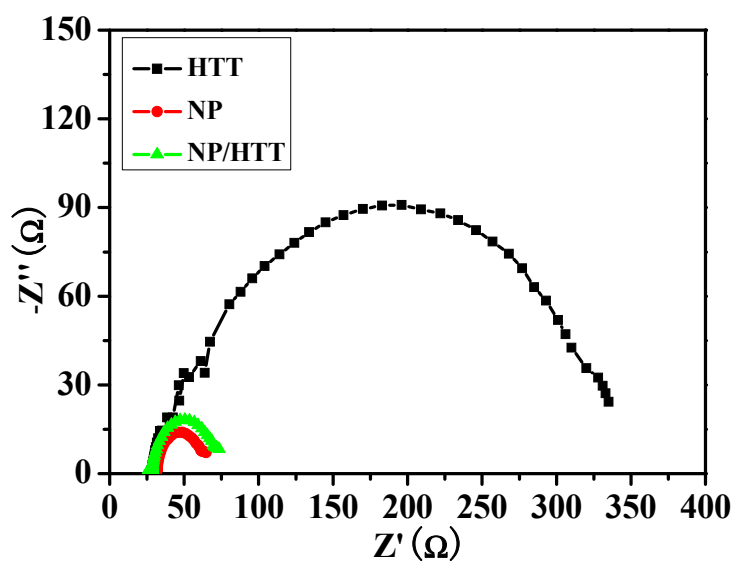


Fig. S5 Nyquist plots of DSSCs based on the HTT, NP and NP/HTT composite film electrodes.