Electronic supplementary information

Template-free TiO₂ hollow submicrospheres embedded with SnO₂ nanobeans as a versatile scattering layer for dye-sensitized solar cells

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Synthesis of SnO₂

 SnO_2 was fabricated by a hydrothermal synthesis. In a typical synthesis, a solution of 0.216 g $K_2SnO_3 \cdot 3H_2O$ and 1.35 g urea was added into a solution of ethanol and water (1:1) contained in a 100 mL Teflon liner sealed with the autoclave and subjected to heat treatment at 180 °C for 18 h in an oven. After washing with ethanol and water, the SnO_2 powder was heated at 500 °C for 3 h air.

Synthesis of TiO₂ hollow submicrospheres

The TiO₂ hollow submicrospheres were fabricated with a facile template-free solvothermal synthesis.¹ In a typical synthesis of TiO₂ hollow submicrospheres, a solution containing tetra-n-butyl titanate (2.33 mmol), ethanedioic acid (0.013 mol), and isopropyl alcohol (66.67 mL) was dropped in a 100 mL Teflon liner sealed with the autoclave and subjected to heat treatment at 180 °C for 6 h in an oven. Subsequently, the TiO₂ hollow submicrospheres after washing with ethanol and water several times were collected and dried for 5 h at 100 °C in a vacuum oven. The powder was heated at 500 °C for 3 h under air atmosphere before preparing the paste for doctor blade coating.

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Synthesis of nanobean SnO₂-embedded TiO₂ hollow submicrospheres

The embedment of SnO₂ nanobeans in TiO₂ hollow submicrosphere was performed with hydrothermal synthesis.^{2, 3} In a typical synthesis, 200 mg of as-prepared TiO₂ hollow submicrospheres in a solution of ethanol and water (1:1) was added into a solution of 0.216 g $K_2SnO_3 \cdot 3H_2O$ and 1.35 g urea in a 100 mL Teflon liner sealed with the autoclave and sunjected to heat treatment at 180 °C for 18 h in an oven. After washing with ethanol and water, the SnO₂-embedded TiO₂ hollow submicrospheres were heated at 500 °C for 3 h in air.

Assembly of DSSCs

The bi-layer film-stack photoanode consisting of a scattering layer and a transparent layer was fabricated on fluorine doped tin oxide (FTO) glass substrate. The paste for the transparent layer was prepared with 1 g of P25 powder, 0.2 mL of acetic acid, 3 g of terpineol, 0.5 g of ethyl cellulose, and 10 mL of ethanol. The other paste for the scattering layer was prepared with 50 mg of the SnO₂ (TiO₂ hollow submicrospheres or nanobean SnO₂-embedded TiO₂ hollow submicrospheres) powder, 150 mg of terpineol, 25 mg of ethyl cellulose, and 0.5 ml of ethanol. A transparent layer of ~ 10 μ m and a scattering layer of ~ 4 μ m were achieved by multiple doctor blade coatings with, respectively, the P25 TiO₂ paste and SnO₂ (the TiO₂ hollow submicrospheres or nanobean SnO₂-embedded TiO₂ hollow submicrospheres or nanobean SnO₂ paste and SnO₂ (the TiO₂ hollow submicrospheres or nanobean SnO₂-embedded TiO₂ hollow submicrospheres) paste, followed by a heat treatment for 15 min at 500 °C. The sample was then immersed in 40 mM of an aqueous TiCl₄ solution at 70 °C for 30 min, followed by heat treatment for 15 min at 520 °C to grow a thin TiO₂ layer on the surface. Cross-sectional images of the three photoanodes composed of the scattering layers (SnO₂, TiO₂ hollow submicrospheres, and nanobean SnO₂-embedded TiO₂ hollow submicrospheres) on the nano-sized TiO₂ transparent layer are shown in Fig. S4-S6.

Subsequently, a 0.5 mM solution of N719 dye (acetonitrile and *tert*-butyl alcohol = 1:1) was prepared for dye adsorption and the photoanodes were immersed for 16 h. The Pt counter electrode was synthesized with a 5 mM H₂PtCl₆ isopropanol solution on a FTO glass substrate at 400 °C for 15 min. Then, the sensitized photoanode and the counter electrode were assembled with the electrolyte to construct the DSSC cell. The ingredient of the as-prepared electrolyte contained 0.6 M of 1-methyl-3-propylimidazolium iodide (PMII), 0.05 M of lithium iodide (LiI), 0.03 M of iodine (I₂), 0.1 M of guanidinium thiocyanate (GuNCS), and 0.5 M of 4-tert-butyl-pyridine (tBP) in a mixture of acetonitrile and valeronitrile (85:15 in volume ratio). The current density-voltage characteristics of DSSCs with a defined area of 0.12 cm² were measured under AM 1.5 G illumination with a solar simulator using 100 mW cm⁻².

Characterization of Materials

The crystallization structure of the scattering materials were characterized by a Rigaku X-ray diffractometer (XRD) and JEOL 2010F transmission electron microscope (TEM). The morphologies and the elemental mapping of the materials were collected with a Hitachi S5500 scanning electron microscope (SEM)/scanning transmission electron microscope (STEM) equipped with energy dispersive spectroscopy (EDS). The surface area and pore-size distributions were measured by the Brunauer-Emmett-Teller (BET) method with an automated gas sorption analyzer (AutoSorb iQ2, Quantachrome Instruments). Diffuse reflectance spectra were recorded with a Varian Cary 500 UV-VIS NIR instrument equipped with an integrating sphere of a Labsphere DRA-CA-5500. The amount of dye adsorption was acquired with a Cary 500 UV-VIS NIR spectrometer. The electrochemical properties were analyzed by

electrochemical impedance spectroscopy (EIS) data collected with a program-controlled instrument of Solartron SI 1287 and SI 1260.



Fig. S1. High and low magnification SEM images of SnO₂.



Fig. S2. High and low magnification SEM images of TiO_2 hollow submicrospheres.



Fig. S3. High and low magnification SEM images of nanobean SnO₂-embedded TiO₂ hollow submicrospheres.



Fig. S4. Cross-sectional SEM image of the bilayer photoanode of SnO_2 on the nano-sized TiO_2

transparent layer.



Fig. S5. Cross-sectional SEM image of the bilayer photoanode of TiO_2 hollow submicrospheres on the nano-sized TiO_2 transparent layer.



Fig. S6. Cross-sectional SEM image of the bilayer photoanode of nanobean SnO₂-embedded

TiO₂ hollow submicrospheres on the nano-sized TiO₂ transparent layer.



Fig. S7. Raman spectra of SnO₂, TiO₂ hollow microspheres, and nanobean SnO₂-embedded TiO₂ hollow submicrospheres. In Fig. S6(a) of the SnO₂, in addition to the observation of the typical peaks at 469, 629, and 769 cm⁻¹,⁴ the additional peaks at 574 and 682 cm⁻¹ due to the size effect indicates the formation of nano-sized SnO₂.⁵ In Fig. S6(b) of the TiO₂ hollow submicrospheres, all the peaks of 144, 195, 395, 514, and 636 cm⁻¹ can correspond to the anatase TiO₂ phase.⁶ In Fig. S6(c), the similarity of the Raman spectra can be observed in the nanobean SnO₂-embedded TiO₂ hollow submicrospheres, except that the intensity of the peaks at 514 and 636 cm⁻¹ is slightly stronger than those of TiO₂ hollow submicrospheres due to the overlap of the SnO₂ peaks in those regions.



Fig. S8. Equivalent circuit model for DSSCs. R_s represents the series resistance. R_{cr} (chargerecombination resistance) reflects the charge recombination associated with the charge-transfer resistance at the interface of metal oxides/dye/electrolyte and the electron transport in the photoanodes of the metal oxides. CPE represents the chemical capacitance. Z_d represents the impedance of the diffusion of redox species in the electrolyte. R_{ct} (charge-transfer resistance) represents the charge transfer between the electrolyte and the counter electrode. EIS data were collected at each of their own open-circuit voltage (*i.e.*, -720 mV for SnO₂, -743 mV for TiO₂ HS, and -754 mV for SnO₂-embedded TiO₂ HS) with an AC amplitude of 10 mV in the frequency range from 0.1 Hz to 1 MHz in the dark. The Nyquist plots were modelled according to the equivalent-circuit diagram and all the EIS parameters were directly extracted by Z-view software.



Fig. S9. Bode plots of TiO₂ hollow microspheres and nanobean SnO₂-embedded TiO₂ hollow submicrospheres. Electron lifetime τ_n can be estimated with $\tau_n = 1/(2\pi f_c)$, where f_c represents the peak frequency.⁷ The data show that the peak frequency of SnO₂-embedded TiO₂ HS (4.47 Hz) is lower than that of TiO₂ HS (6.30 Hz), indicating that SnO₂-embedded TiO₂ HS has longer electron lifetime than TiO₂ HS due to the fast electron transport in TiO₂ HS after the embedding of SnO₂.



Fig. S10. Open-circuit voltage decay (OCVD) measurement of TiO_2 hollow microspheres and nanobean SnO_2 -embedded TiO_2 hollow submicrospheres. It can be found that the voltage decay rate of the SnO_2 -embedded TiO_2 HS is lower than that of TiO_2 HS, indicating that the former has a lower recombination rate,⁸ which agrees well with the result of the Bode plot.

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