Electronic Supporting Information (ESI)

Fabrication of Zn$_2$SnO$_4$/SnO$_2$ hollow spheres and their application in dye-sensitized solar cell

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Experimental

Synthesis: The precursor ZnSn(OH)$_6$ solid spheres were prepared through a hydrothermal technique. Typically, 0.284 g of sodium stannate was dissolved in 10 mL of deionized water, to which 10 mL of 2 g/L sodium alginate aqueous solution was added, noted as solution A. 0.438 g of zinc acetate was dissolved in 2 mL of deionized water, to which 5 mL of ammonia aqueous solution was added, noted as solution B. The solution A and the solution B were mixed together in a 50 mL Teflon-lined autoclave, sealed and kept at 160 °C for 6 h. The product was collected by centrifuging, washing with distilled water and ethanol and drying in the air. Then the product was heated in the air to 600 °C with a ramp up rate of 1 °C/min and kept at 600 °C for 2 h to synthesize ZnSnO$_4$/SnO$_2$ hollow spheres.

Characterizations: Scanning electron microscopy (SEM) characterization was performed on Hitachi S-4800 at 15 kV. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 transmission electron microscope operating at 200 kV. Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray powder diffractometer with Cu $K_a$ radiation ($\lambda = 1.5406$ Å). The Brunauer-Emmett-Teller (BET) surface areas of the powders were analyzed by nitrogen adsorption in a Tristar 3000 nitrogen adsorption apparatus. All the
samples were degassed at 80 °C prior to nitrogen adsorption measurements. Diffuse reflectance spectra of the resulting samples films were recorded with a UV-Vis spectrophotometer(UV-2550, Shimadzu) at room temperature.

_Dye-Sensitized Solar Cells preparation and measurements:_ 1 g of the obtained powder was homogeneously mixed with some absolute ethanol in a beaker to form a suspension. Then the suspension was coated onto conducting glass substrates to form thin porous films. The layer of film was sintered at 500 °C in air. After cooled to 80 °C, the film was immersed into N719 ethanol solution for 6 h. The counter electrode was a magnetron sputter platinum mirror. The substrate, film, and counter electrode constituted a sandwich-like open cell. The electrolyte was composed of 1.0 M BMII, 50 mM LiI, 30 mM I₂ and 0.5 M tert-butylpyridine in a mixed solvent of acetonitrile and valeronitrile (v/v, 85:15). Current density-voltage (J-V) curves of the DSSC under AM1.5 (100 mW/cm²) was performed with an active illumination area of 0.132 cm². Electrochemical impedance spectroscopic (EIS) curves of the DSSCs were also observed with a PAR2273 workstation (Princeton Applied Research, USA). The frequency range was from 50 mHz to 100 kHz.
Figure S1 TGA curve of the precursor ZnSn(OH)$_6$ solid spheres.
**Fig. S2** EDX spectrum of the hollow Zn$_2$SnO$_4$/SnO$_2$ spheres.
Fig. S3 An SEM image of the product by heating ZnSn(OH)$_6$ spheres from room temperature to 600 °C in one hour.
Figure S4  SEM images of a,b) commercial SnO$_2$ and c,d) commercial Zn$_2$SnO$_4$. 