ELECTRONIC SUPPLEMENTARY INFORMATION

A facile Synthesis of Anatase TiO$_2$ Nanosheets-based Hierarchical Spheres with over 90 % {001} Facets for Dye-Sensitized solar cells

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Experimental Section

Materials Synthesis: The anatase TiO$_2$ nanosheets-based hierarchical spheres (ATNHSs) were prepared by solvothermal method. In a typical experiment, titanium tetrafluoride (Sigma Chemical) was added to diethylene glycol (Sigma Chemical) to give concentrations of 0.01-0.03 M, and then magnetically stirred for 3 h at room temperature. 5 mL of acetic acid (Beijing Chemical Co.) was added to 40 mL of the above TiF$_4$ solution under vigorous stirring for 1 h. The mixed solution was transferred to a Teflon-lined stainless steel autoclave of 50 mL capacity and heated for 8 h at 180°C with the heating rate of 50°C/h. After reaction, the ATNHSs were obtained by centrifugation, followed by rinsing with ethanol and deionized water for several times. Finally, the product was heated in air at 600°C for 2 h to remove the surface fluorine of the product.

The ATNHSs film preparation: For preparation of the ATNHSs paste, hydroxypropyl cellulose (Aldrich) was added to diethylene glycol with a concentration of about 10 wt%. The mixed solution was added into the dried product and was stirred for 2 day to yield the slurry. The resulting slurry was spread onto FTO glass substrates (TEC-8, LOF) by doctor blading using Scotch tape as frame and spacer, dried at 200°C for 10 min and subsequently heated in air for 40 min at 470°C.

Fabrication of DSSCs: After sintering at 470°C for 40 min, the ATNHSs films were cooled to 80°C, and immersed in dry ethanol containing 0.3 mM of cis-di(thiocyanate)bis(2,2′-bipyridyl-4,4′-dicarboxylate)-ruthenium(II) bis-tetrabutylammonium(also called N719, Solaronix SA, Switzerland) over night for dye-adsorption. To assemble
the solar cells, a Pt-coated conducting glass was placed on the dye-sensitized ATNHSs film separated by a 50 μm thin membrane spacer. The assembled cell was then clipped together as an open cell. An electrolyte, which was made with 0.1 M LiI (Aldrich), 0.1 M I₂ (Aldrich), 0.6 M dimethylpropylimidazolium iodide (DMPImI, Aldrich) and 0.5 M tert-butylpyridine (Aldrich) in dry acetonitrile (Aldrich) was injected into the open cell from the edges by capillarity.

**Characterization:** The ATNHSs were characterized with use of scanning electron microscope (SEM, Zeiss Supra-55), high-resolution TEM (HRTEM, Phillips, Tecnai F30 operated at 300 kV), X-ray powder diffraction (XRD, Rigaku D/max-2500 diffractometer with CuKα radiation, λ=0.1542, 40 kV, 100 mA), BET (Micrometrics ASAP 2020). Photocurrent-voltage measurements were performed using simulated AM 1.5 sunlight with an output power of 100 mW cm⁻². Incident monochromatic photo-to-electron conversion efficiency (IPCE) was recorded on a Keithley 2000 sourcemeter under the irradiation of a 150 W tungsten lamp with a 1/4 m monochromator (Spectral Product DK240). The diffuse-reflectance spectra were measured by using U-4100 spectrophotometer.
Fig. S1 SEM image of the hierarchically structured TiO$_2$ nanosheets prepared by using triethylene glycol as a solvent at a TiF$_4$ concentration of 0.02 M.
**Fig. S2** Diffuse-reflectance spectra of the two films of anatase TiO$_2$ nanosheets-based hierarchical spheres and P25 TiO$_2$ with the similar thickness of about 14 μm.