Supplementary Information for

Room-temperature fabrication of dual-functional hierarchical TiO_2 spheres for dye-sensitized solar cells

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Preparation of hierarchical TiO_2 spheres. Hierarchical TiO_2 spheres were prepared by a facile and low-cost method. Typically, a 40 mL mixture aqueous solution, containing 0.05 M ammonium hexafluorotitanate, $(NH_4)_2TiF_6$, and 0.13 M boric acid, H_3BO_3, was transferred into a 100 mL beaker and stand for 2 days. Following, the precipitate was collected by centrifugation after being washed with deionized water several times. Then, the powder was dried naturally at room temperature. Finally, the product was sintered at 450 ℃ for 30 min with the rate of temperature rising was 2 ℃ min^{-1}.

Preparation of photoanodes. Three types of TiO_2 paste, including nanocrystalline-TiO_2 (commercial product, diameter≈25 nm, P25) paste, submicrocrystalline-TiO_2 (commercial product, diameter≈200 nm, P200) paste and submicrocrystalline-TiO_2 (hierarchical TiO_2 spheres, diameter≈500 nm, P500) paste were prepared using the method developed by Ito *et al.*[1] In short, 0.1 mL of acetic acid, 0.5 mL of deionized water, 17 mL of ethanol, 2 g of terpinol and 0.3 g of ethyl cellulose were added into 0.6 g of TiO_2 powder (P25, P200 and P500) in order, and then grinded in a mortar for 5 min, respectively. Ethanol and water were removed by a rotary evaporator. The obtained paste was spread on a clean FTO glass by using the screen printing method. After drying at 120 ℃ for 5 min, the film was sintered at 450 ℃ for 30 min with the rate of temperature rising was 2 ℃ min^{-1}. The samples were left to cool naturally after annealing. The thicknesses of the films were detected by the Stylus Profiler.

Fabrication of DSSCs. The as-prepared TiO_2 photoanodes were immersed in a 0.3 mM cis-diisothiocyanato-bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719, Dalian HeptaChromaSolarTech, China) solution for 24 hr when they cooled from the sintering temperature to about 80 ℃ to avoid contact with water. Then, the dye-sensitized working electrodes were sandwiched together with Pt-coated FTO glass as counter electrodes using a hot-melt Surlyn spacer, with a spacer thickness of approximately 25 μm. A I^-/I_3^- based liquid electrolyte was injected into the holes in the reverse of the counter electrode, and then the holes were sealed using the same hot-melt Surlyn spacer.

Characterizations an photoelectrochemical measurement. The morphology and microstructure of the samples were examined by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The crystallinities of the samples were investigated using X-ray diffraction (XRD). For ensuring the components, the samples were subjected to X-ray photoelectron spectroscopy (XPS). Transmittance spectra of the resulting dye-sensitized TiO_2 films were collected on a UV-vis spectrophotometer (UV 5000 spectrometer, Cary). To estimate the amount of the dye, the sensitized electrodes were dipped into the NaOH solutions (0.2M), which was in a mixed solvent (water:ethanol=1:1). The concentration of desorbed N719 was measured by absorbance using a UV-vis spectrophotometer. The photovoltaic performance of the DSSCs was measured under AM 1.5 simulated sunlight, produced by a 300-W Oriel Solar Simulator (Model, 91160) with the illumination intensity being 100 mW cm^{-2}. An electrochemical analyzer was used to record the information of photocurrent and photovoltage. The incident photon to current conversion efficiency (IPCE) spectra was measured as a function of wavelength on the basis of a monochromator.

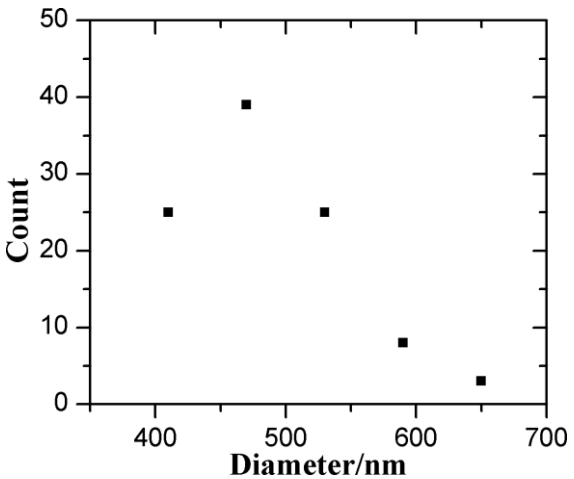

Figure S1 The diameter distribution of hierarchical TiO_2 spheres (P500) with a total of 100 samples.

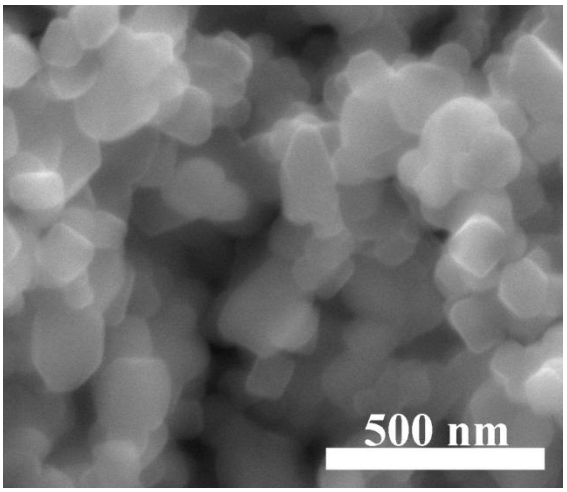

Figure S2 Typical SEM image of the commercial submicrocrystalline-TiO_2 particles (P200).

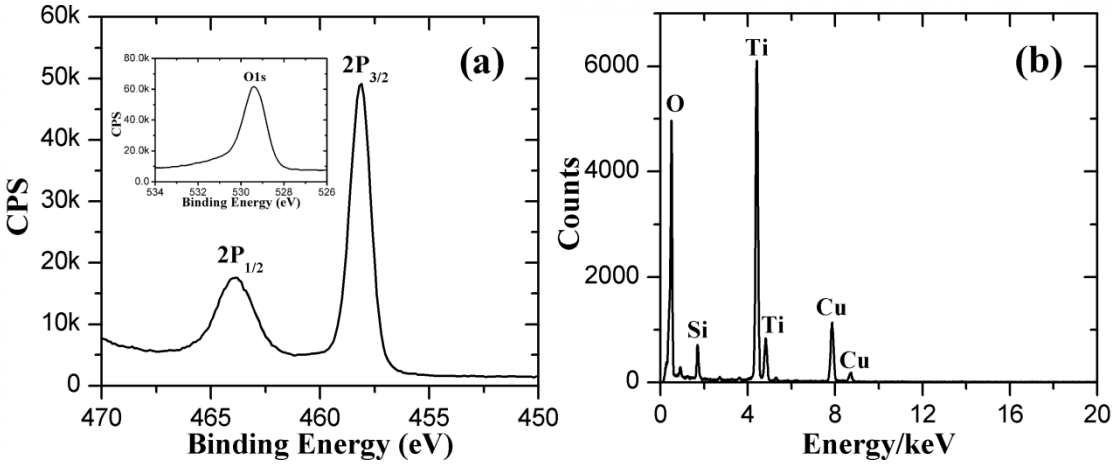

Figure S3 XPS full spectra of Ti (a) and O (inset in (a)) of the hierarchical TiO_2 spheres (P500); (b) Energy dispersive spectrum (EDS) of P500.

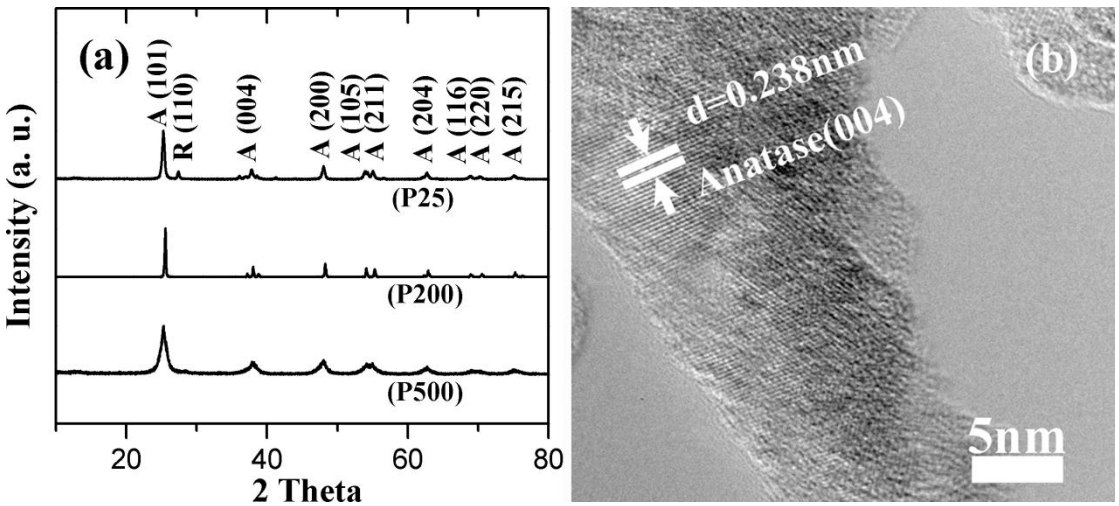

Figure S4 (a) XRD patterns of P25, P200 and P500, respectively; (b) HRTEM image of P500.

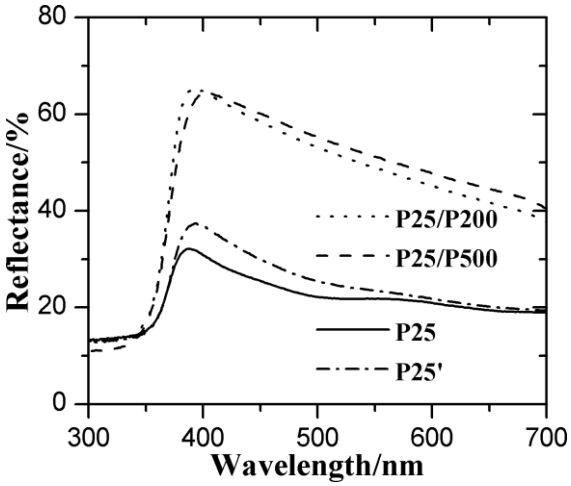

Figure S5 UV-Vis diffuse reflectance spectra of four different undyed electrodes..

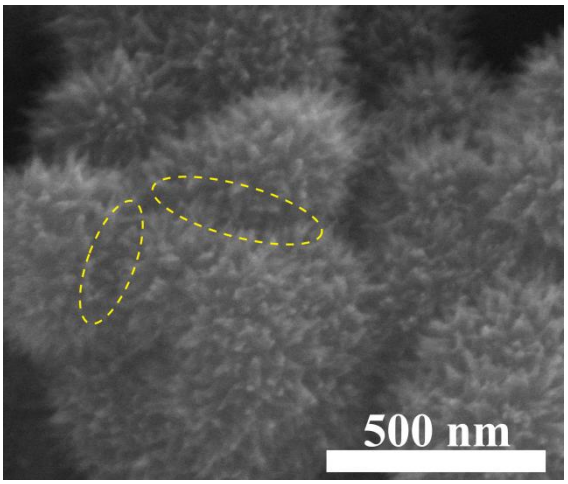

Figure S6 Junction SEM image between two hierarchical TiO_2 spheres.

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Notes and references

1 S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, M. Gratzel, *Prog. Photovolt: Res. Appl.*, 2007, **15**, 603.