Supplementary Information for

**Room-temperature fabrication of dual-functional hierarchical TiO\textsubscript{2} spheres for dye-sensitized solar cells**

Jia Liang*, Gengmin Zhang, Huarong Xia and Wentao Sun

[*] Mr. Jia Liang
Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China.

Email: jial@pku.edu.cn
Preparation of hierarchical TiO\textsubscript{2} spheres. Hierarchical TiO\textsubscript{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\textsubscript{4})\textsubscript{2}TiF\textsubscript{6}, and 0.13 M boric acid, H\textsubscript{3}BO\textsubscript{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 °C for 30 min with the rate of temperature rising was 2 °C min\textsuperscript{-1}.

Preparation of photoanodes. Three types of TiO\textsubscript{2} paste, including nanocrystalline-TiO\textsubscript{2} (commercial product, diameter≈25 nm, P25) paste, submicrocrystalline-TiO\textsubscript{2} (commercial product, diameter≈200 nm, P200) paste and submicrocrystalline-TiO\textsubscript{2} (hierarchical TiO\textsubscript{2} spheres, diameter≈500 nm, P500) paste were prepared using the method developed by Ito \textit{et al.}\textsuperscript{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\textsubscript{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 °C for 5 min, the film was sintered at 450 °C for 30 min with the rate of temperature rising was 2 °C min\textsuperscript{-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\textsubscript{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°C 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\textsubscript{3}/I\textsubscript{1} 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 and 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\textsubscript{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\textsuperscript{-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](image-url) The diameter distribution of hierarchical TiO\textsubscript{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.

Notes and references