Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Nanoparticle self-assembled hollow TiO_2 spheres to well matching visible scattering for high performance dye-sensitized solar cells

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Experimental Section

Preparation of matching visible light hollow TiO_2*:* The submicrometer-sized hollow TiO_2 was prepared by one-pot hydrothermal method. In a classic synthesis, 0.1g commercial anatase (SEM image as shown in Fig. S6) was added into 5 mL oil of vitriol under magnetic stirring for 5 h. Subsequently 30 mL deionized water was carefully dropped with continuous stirring. MgO powder was gradually added to adjust pH to 3. And then the mixture was transferred into 50 mL capacity Teflon-lined stainless steel autoclave, sealed and heated at 180 ^{o}C for 48 h. The precipitated powders were filtered, washed thoroughly with absolute ethanol, dried at 100 ^{o}C and collected.

Fabrication of DSCs: Both pastes of TiO_2 P25 (purchased from Degussa) and hollow TiO_2 spheres were conducted according to the previous literature. The P25 films were uniformly spread on the surface of the pre-cleaned FTO glass by the doctor-blade technique, subsequently sintered at 450 ^{o}C in air for 30 min. To obtain the bilayer structure, the hollow TiO_2 spheres layer was deposited on top of the annealed P25 film and heated over the same heating procedure as previously. Subsequently, the prepared bilayer photoelectrode and P25 photoelectrode were soaked in an acetonitrile solution containing 0.5 mM N719 dye at room temperature for 24 h, and then washed with ethanol and dried in dry air. Finally, the DSCs were assembled from TiO_2 photoelectrode to Pt counter electrode with a spacer of 30 μm thickness with 5 μL of the I^-/I_3^- electrolyte solution for further characterization.

Characterization of hollow TiO_2 *and devices:* The morphology of the hollow TiO_2 product was tested by field-emission scanning electron microscope (FE-SEM, JSM-6700F and HITACHI-4800S) and transmission electron microscope (TEM, Tecnai G^2 20 instrument). The UV-visible light diffused reflectance spectra was measured by UV-2450 spectrophotometer. The XRD pattern was conducted using Rigaku D/max 2400 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ=1.5406 Å). A scan rate of 0.02 $^{o}\cdot s^{-1}$ was applied to record the pattern in the 2θ range from 10 ^{o} to 70 ^{o}. The characteristics of current density (J) versus voltage (V) were measured by Keithley 2420 in dark and under illumination of an Oriel solar simulator with 100 mW·cm^{-2} AM1.5G spectrum as well. The intensity of the solar simulator was calibrated by standard Si photovoltaic cell. The area of all tested devices was 16 mm^2. All measurements were carried out in air at room temperature without encapsulation.

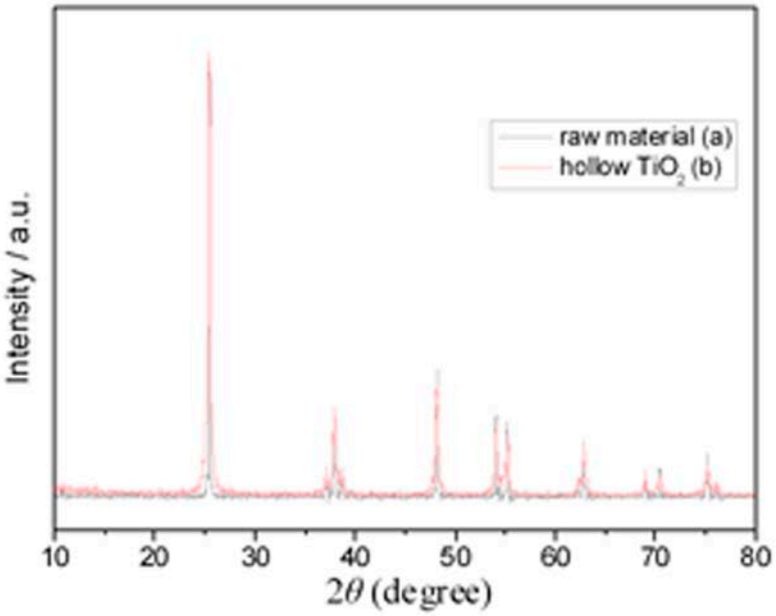

Figure S1. XRD patterns of raw material TiO_2 (a) and hollow TiO_2 (b).

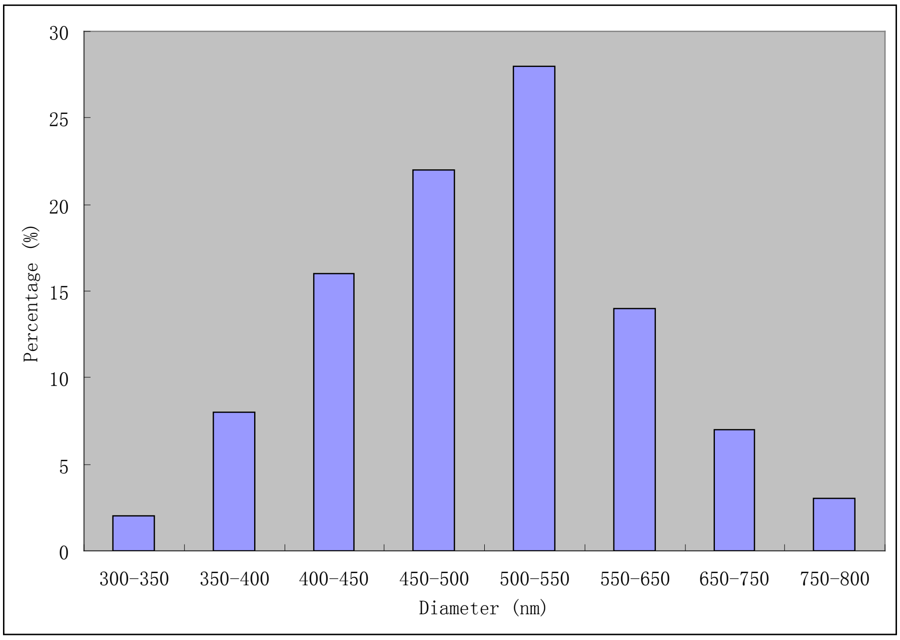

Figure S2. Diameter distribution histogram of the hollow TiO_2.

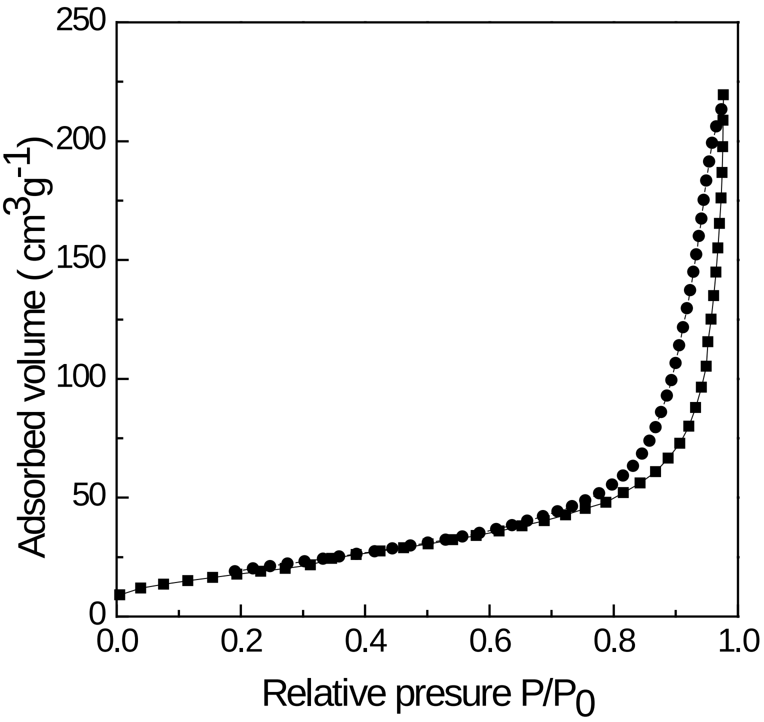

Figure S3. Nitrogen sorption isotherm of the hollow TiO_2.

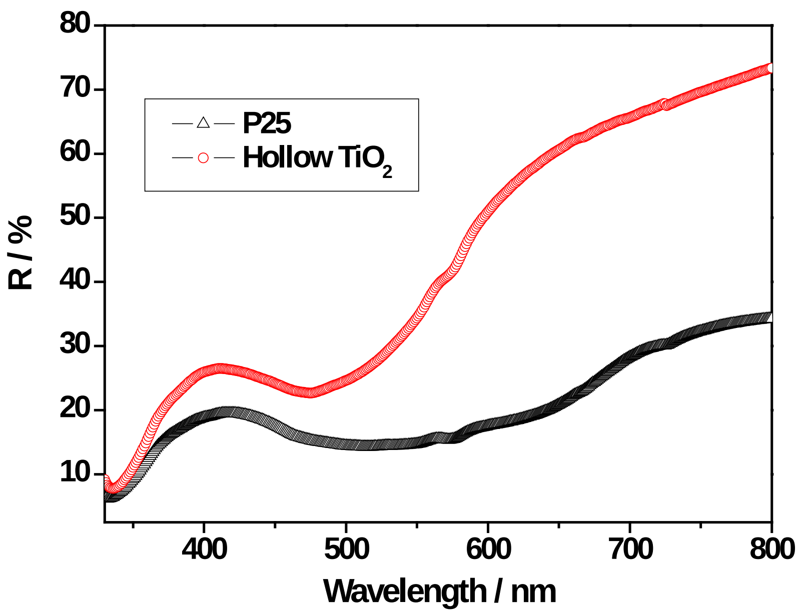

Figure S4. Diffused reflectance spectra of the P25 and bilayer structured films with absorbed N719 dye.

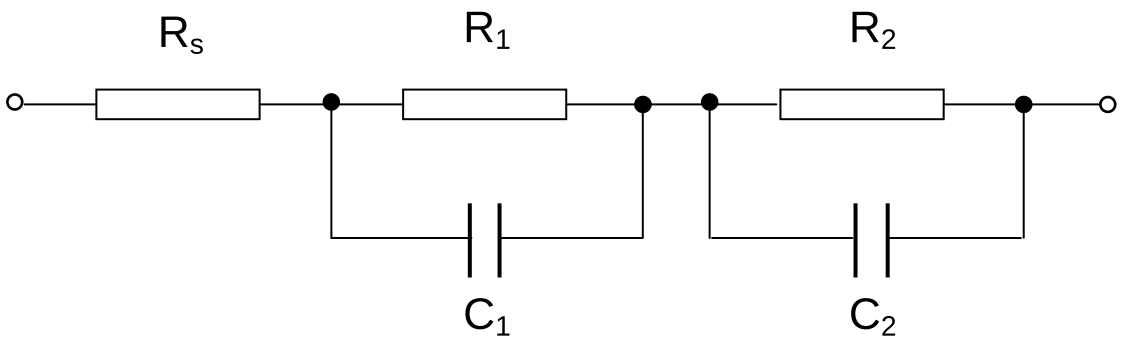

Figure S5. Equivalent circuit of DSC.

The equivalent circuit assisted to further interpret the complex interface reaction in the DSC device, where the R_s, R_1 and R_2 represent the ohmic serial resistances for electrolyte/conductive glass, the platinum electrode, and TiO_2/dye/electrolyte interface, respectively, and C_1 and C_2 are the respective constant phase elements. Compared with P25 photocathode, the hollow TiO_2/P25 double layer photocathodes have smaller R_2, thus clearly indicating an enhancement of the charge transfer in hollow TiO_2/P25 photocathodes. The capacitance C_2 at the hollow TiO_2/dye/electrolyte interface also increases in comparison with bare P25 one. The higher capacitance corresponds to the presence of more charges being separated effectively at the interface, thus indicating the reduction of charge recombination events in hollow TiO_2/dye/electrolyte.

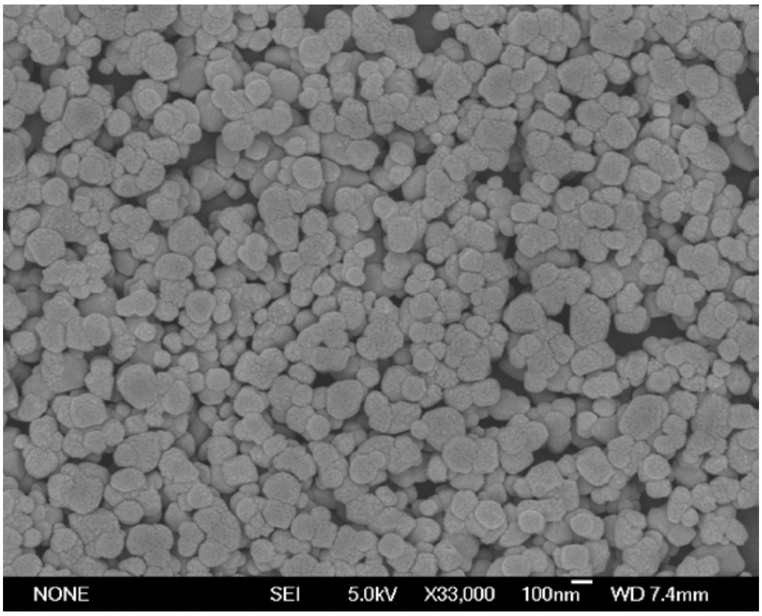

Figure S6. SEM image of raw material anatase.