

Electronic Supplementary Information

Hierarchical TiO₂ flowers built by TiO₂ nanotubes for efficient Pt-free based flexible dye-sensitized solar cells†

Bing-Xin Lei, Qiu-Ping Luo, Xiao-Yun Yu, Wu-Qiang Wu, Cheng-Yong Su and Dai-Bin Kuang*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China. Fax: +86-20-8411-3015; Tel: +86-20-8411-3015; E-mail: kuangdb@mail.sysu.edu.cn;

Experimental section

Assembly and measurements of DSSCs: The as-prepared TiO₂ nanoparticles/Ti and TiO₂ flowers/Ti were used as photoelectrode for DSSCs. Prior to dye sensitization, the as-prepared TiO₂ nanoparticles/Ti and TiO₂ flowers/Ti electrodes immersed into a 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and washed with water and ethanol, then sintered at 520 °C for 30 min. After cooling down to 80 °C, the TiO₂ nanoparticles/Ti and TiO₂ flowers/Ti electrodes were putted into 0.5 mM N719 dye (Ru[LL'-(NCS)₂], L= 2,2'-bipyridyl-4,4'-dicarboxylic acid, L=2, 2'-bipyridyl-4, 4'-ditetrabutylammonium carboxylate, Solaronix Co.) in tert-butanol/acetonitrile (1:1 v/v), and kept for 20 h at room temperature. The Pt/FTO-glass, and PEDOT/ITO-PET were used as CEs. The electrolyte consisted of 1-propyl-3-methyl-imidazolium iodide (PMII, 0.6 M), LiI (0.05 M), I₂ (0.03 M), Guanidine thiocyanate (GuNCS, 0.1 M, Aldrich), and 4-tert-butylpyridine (t-BP, 0.5 M, Aldrich) in acetonitrile and valeronitrile (85:15 v/v). The active area of the dye-coated TiO₂ film was 0.160 cm².

The phase purity of the products was characterized by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ =1.5418 Å). The Field emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscope (TEM) and high-resolution transmission electron microscope

Supplementary Material (ESI) for Energy & Environmental Science
This journal is © Royal Society of Chemistry 2012

(HRTEM) were performed on a JEOL-2010 HR transmission electron microscope to characterize the morphology, size and the intrinsic structure. The adsorbed dye amounts were obtained by measuring the detached dye solution from the hierarchical TiO₂ nanorod arrays films with the UV-Vis absorption spectroscopy (UV, Shimadzu UV-3150).

The current-voltage characteristics were performed using a Keithley 2400 source meter under simulated AM 1.5 G illumination (100 mW cm^{-2}) provided by a solar light simulator (Oriel, Model: 91192). The incident light intensity was calibrated with a NREL-calibrated Si solar cell.

Intensity-modulated photovoltage spectroscopy (IMVS) and intensity-modulated photocurrent spectroscopy (IMPS) measurements were carried out on a electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under a modulated green light emitting diodes (457 nm) driven by a source supply (Zahner, PP211), which can provide both dc and ac components of the illumination. The modulated light intensity was 10 % or less than the base light intensity. The frequency range was set from 100 KHz to 0.1 Hz.

The electrochemical impedance spectroscopy (EIS) measurements were performed with a Zennium electrochemical workstation (ZAHNER) with the frequency range from 10 mHz to 1000 kHz. The magnitude of the alternative signal was 10 mV. The impedance measurements were carried out under forward bias of -0.75 V in the dark.

Supplementary Material (ESI) for Energy & Environmental Science
This journal is © Royal Society of Chemistry 2012

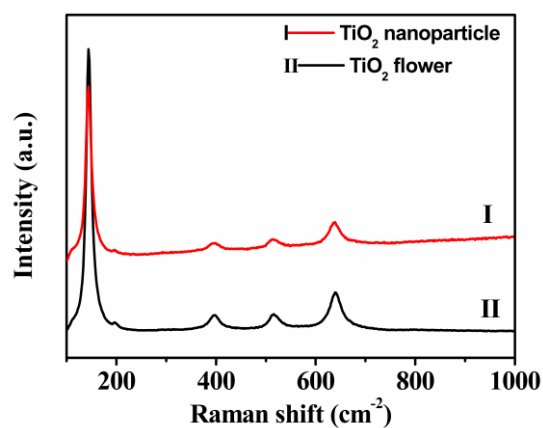


Fig. S1 Raman spectrum of the as-prepared TiO₂ nanoparticle (I) and TiO₂ flower (II).

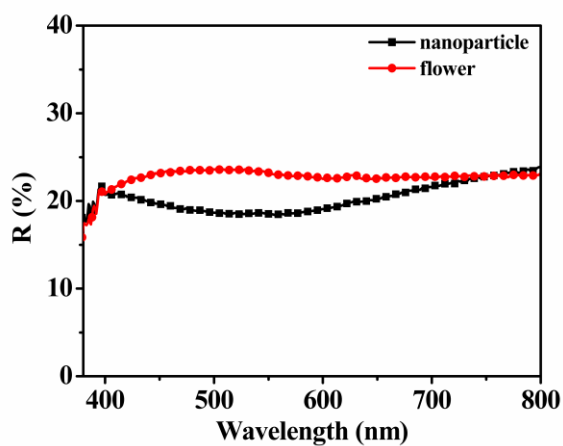


Fig. S2 The comparison of UV-vis diffused reflectance spectra of TiO₂ nanoparticle and flower films.

Supplementary Material (ESI) for Energy & Environmental Science
This journal is © Royal Society of Chemistry 2012

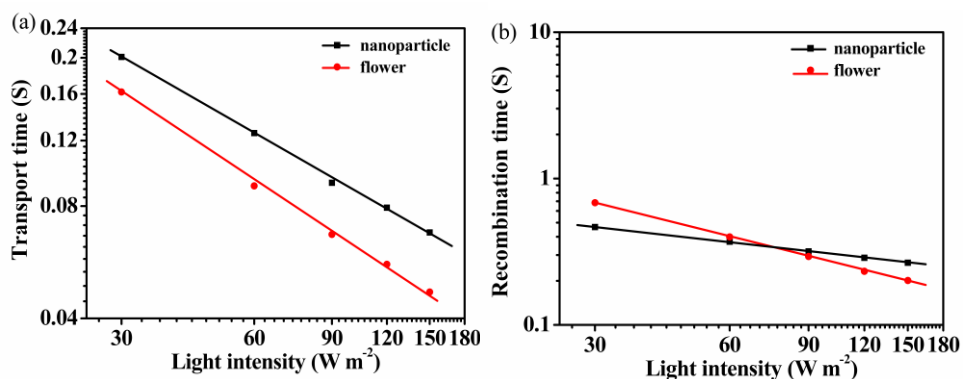


Fig. S3 (a) Electron transfer time (τ_c), and (b) Recombination time (τ_r) constants calculated from IMPS and IMVS measurements for TiO₂ nanoparticles and flowers DSSCs.

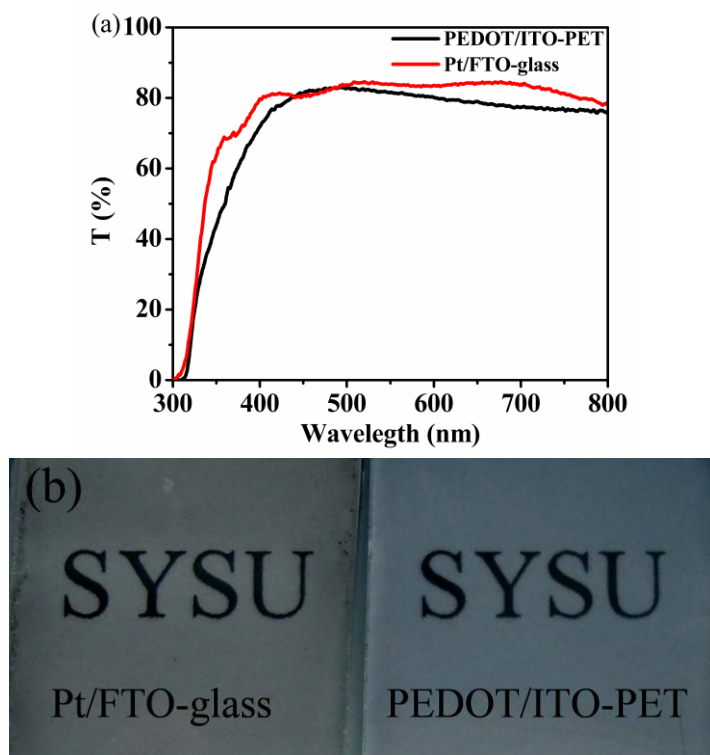


Fig. S4 UV-vis curves (a), and photographs (b) of the films for different substrates.