Hierarchical TiO$_2$ flowers built by TiO$_2$ nanotubes for efficient Pt-free based flexible dye-sensitized solar cells†

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**Experimental section**

**Assembly and measurements of DSSCs:** The as-prepared TiO$_2$ nanoparticles/Ti and TiO$_2$ flowers/Ti were used as photoelectrode for DSSCs. Prior to dye sensitization, the as-prepared TiO$_2$ nanoparticles/Ti and TiO$_2$ flowers/Ti electrodes immersed into a 40 mM TiCl$_4$ 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 TiO$_2$ nanoparticles/Ti and TiO$_2$ 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’-ditetradecylammonium 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), I$_2$ (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 TiO$_2$ film was 0.160 cm$^2$.

The phase purity of the products was characterized by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using Cu Kα 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...
(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.
Fig. S1 Raman spectrum of the as-prepared TiO$_2$ nanoparticle (I) and TiO$_2$ flower (II).

Fig. S2 The comparison of UV-vis diffused reflectance spectra of TiO$_2$ nanoparticle and flower films.
**Fig. S3** (a) Electron transfer time (τₜₑ), and (b) Recombination time (τᵣₑ) 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.