Supporting Information

Morphology-controllable 1D/3D Nanostructured TiO₂ Bilayer Photoanodes for Dye-sensitized Solar Cells

Ziqi Sun⁴, Jung Ho Kim⁴,* Yue Zhao⁴, Darren Attard⁵ and Shi Xue Dou⁴

¹ Institute for Superconducting and Electronic Materials, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, NSW 2500, Australia
² AIIM Electron Microscopy Centre, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, NSW 2500, Australia
* jhk@uow.edu.au

Experimental Procedures

Materials The chemical reagents used for the “one-step” synthesis of bifunctional photoanodes are commercially available reagents. Titanium isopropoxide (TTIP, 98%), hydrochloric acid (HCl, 37%), ethylene glycol (EG, 99.5%), and urea (98%) were purchased from Sigma-Aldrich, and cetyltrimethyl ammonium bromide (CTAB, C₁₉H₄₂BrN, 98.5%) was purchased from Ajax. P25 TiO₂ nanoparticles were purchased from Sigma-Aldrich (25 nm particle size, 99.7%). All the chemicals were used as received without further purification.

Synthesis of 1D nanowire/3D dendritic microsphere bilayer structures In a typical synthesis, aqueous TTIP solution was obtained by mixing 0.57 g TTIP, 13.80 g concentrated HCl, 27.3 ml distilled water, and 0.15 g CTAB with strong stirring. Then the aqueous TTIP solution was mixed with EG in a preset volume ratio of 1:1, 1:4, and 1:6, respectively, to form the reaction solution for the hydrothermal synthesis of the bilayer photoanodes. During the synthesis, an F-doped SnO₂ (FTO) glass substrate was
put on the bottom of a Teflon lined autoclave with the conducting layer facing up. After synthesis, the loaded FTO substrates were taken out and heat treated at 400-500 °C for 30 min.

Characterizations The phase compositions of the bifunctional photonoades were examined with a powder X-ray diffractometer (XRD, MMA, GBC Scientific Equipment LLC, USA) with Cu Kα radiation. The morphology of the samples was observed with a scanning electron microscope (SEM, JSM-7500FA, JEOL, Japan). The details of the nanostructures were examined with a high resolution transmission electron microscope operated at 200 kV (HRTEM, JEM-2011F, JEOL, Japan). Ultraviolet-visible (UV-Vis) absorption spectra were collected with a UV-Visible light absorption spectroscope in the wavelength range of 200-800 nm (Perkin-Elmer 1600, USA).

Assembly and testing of dye-sensitized solar cells Dye absorption was carried out by immersing the FTO substrates loaded with the bilayer nanostructures into ethanol-based commercial N719 (Sigma-Aldrich) dye solution at 25 °C for 24 h. The solar cells were prepared by assembling a Pt counter-electrode and a dye-adsorbed photoanode, and then sealing the assembly by using a Surlyn thermoplastic frame (Dupont, 25 μm thick). The assembled cell was filled with a commercial electrolyte purchased from Solaronix (Iodolyte AN-50), and then the cell was sealed again. The active area of the solar cell for testing was 0.0237 cm². Photocurrent density-voltage (J-V) characteristics were measured by exposing the cell to air mass (AM) 1.5 simulated sunlight from a solar simulator (PEL-L12, Peccell Technologies, Japan)
combined with a Keithley 2400 source meter. Incident photon-to-current quantum conversion efficiency (IPCE) was measured as an action spectrum, for which an optical fiber (3 µm diameter) was used for monochromatic irradiation (PEC-S20DC, Peccell Technologies, Japan). Monochromatic photocurrent was monitored by the continuous irradiation (dc measurement) method.

**TiCl$_4$ post-treatment** The post-treatment with TiCl$_4$ was applied to the sintered 1D/3D TiO$_2$ bilayer nanostructured photoanode, by immersing the photoanodes into 0.1 M TiCl$_4$ solution at 70 °C for 30 min. After dyeing, the electrodes were again sintered at 400 °C for 30 min again.
Figure S1: XRD patterns of the photoanodes with single-layer 1D nanowire arrays and with bilayer structure synthesized from the solution TTIP\textsubscript{aq}:EG = 1:1.
**Figure S2**: UV-Vis spectra of photoanodes with single-layer 1D nanowire arrays and with bilayer structure synthesized from the solution TTIP$_{aq}$:EG = 1:1.
**Figure S3:** SEM images of NW-F bilayer photoanodes after TiCl₄ treatment: (a) low magnification cross-sectional view of the bilayer nanostructure, (b) 3D dendritic TiO₂ microsphere, and (c) the 1D nanowire TiO₂ arrays; (d) typical J-V curves of the DSCs with the TiCl₄ treated photoanodes; the inset is the corresponding IPCE action spectrum.