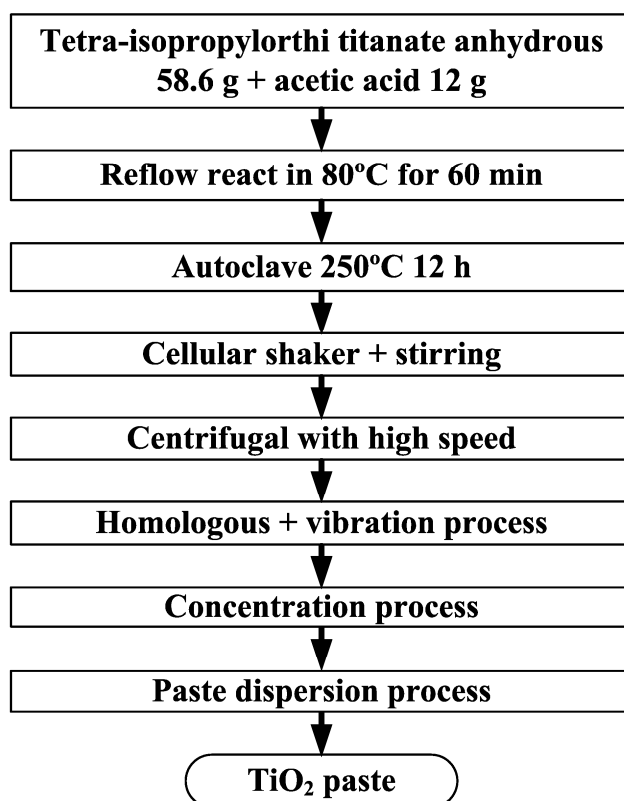


## Experimental

Titanium oxide film was deposited directly on FTO substrate by applying an anodic current density of  $5 \mu\text{A cm}^{-2}$  for 4000 s. The plating solution consisted of a solution of  $0.25 \text{ mol L}^{-1} \text{ TiCl}_3$  (20 wt%  $\text{TiCl}_3$  in 3 wt%  $\text{HCl}$  aqueous solution) at room temperature under a nitrogen atmosphere.<sup>1,2</sup> The plating solution of pH 2.5 was adjusted by  $\text{Na}_2\text{CO}_3$  solution and stirred by a Teflon stir bar on a magnetic hot plate during the entire deposition. The blocking layer formed by  $\text{TiCl}_4$  treatment was carried out to compare the effects of different blocking layers on the photoelectron conversion efficiency of the cells. The detailed procedure of  $\text{TiCl}_4$  treatment was described in a literature.<sup>3</sup> Prior to electrochemical deposition, FTO (Nippon Sheet Glass) was cut into pieces of  $4 \text{ cm} \times 4 \text{ cm}$ , soaked in acetone and ultrasonic vibrated for 20 min to wash away any contaminants off the surface. De-ionized water was then used to rinse the FTO in ultrasonic vibration for another 15 min. A pre-process was applied to ensure the uniformity and adhesion of the deposited titanium oxide: conduct a  $2 \text{ mA cm}^{-2}$  current through each FTO sample in  $\text{NaOH}$  solution ( $1 \text{ mol L}^{-1}$ ) for 30 s for anodic oxidation. The as-deposited films were rinsed several times in de-ionized water and then dried for 1 h in air at  $450^\circ\text{C}$ . All electrochemical experiments were carried out in a three-compartment cell. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum foil with dimension  $4 \text{ cm} \times 4 \text{ cm}$  was the counter electrode.

Surface morphology of the deposited films was examined with a field-emission electron microscope (FE-SEM, Jeol JEOL-6330). Crystal structure of the deposited films was identified by a glance angle X-ray diffractometer (GAXRD, Rigaku D/MAX2500) with a  $\text{Cu K}\alpha$  target (wavelength =  $1.54056 \text{ \AA}$ ) and an incidence angle of  $2^\circ$ . The optical transmittance of the deposited films was carried out with an ultraviolet-visible spectrometer (UV-VIS, PerkinElmer Lambda 35). The photoanode was prepared by screen printing the  $\text{TiO}_2$  paste on the FTO or the  $\text{TiO}_2$ -coated FTO. The  $\text{TiO}_2$  paste used for photoanodes was in-house made by Tripod as shown in Scheme S1. The prepared  $\text{TiO}_2$  film electrode was calcined at  $450^\circ\text{C}$  for 1 h in air. The thickness of resultant  $\text{TiO}_2$  film was approximately  $15 \mu\text{m}$ . The adsorption of dye on the  $\text{TiO}_2$  surface was carried out by soaking the  $\text{TiO}_2$  electrodes in a dry ethanol solution of N719 dye ( $3 \times 10^{-4} \text{ mol L}^{-1}$ ,  $\text{C}_{58}\text{H}_{86}\text{O}_8\text{N}_8\text{S}_2\text{Ru}$ ) at room

temperature for 12 h. In this study, we used a two-step dip coating process to prepare a nanocluster Pt counterelectrode and the detailed procedure was described in a previous publication.<sup>4</sup>

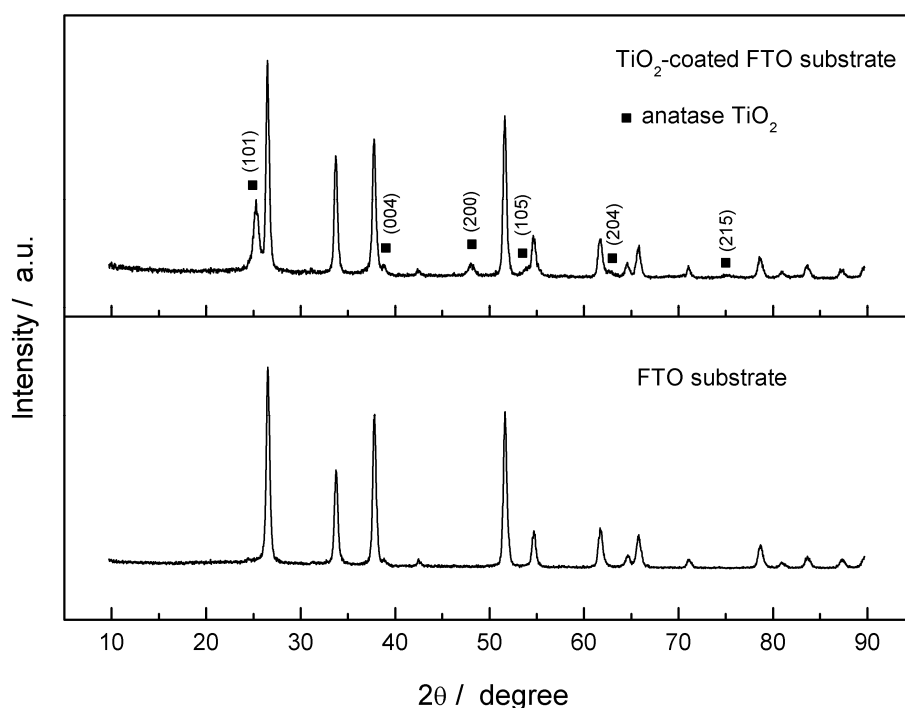


**Scheme S1** Flow diagram of TiO<sub>2</sub> paste used in screen-printing process.

A dye-coated photoanode was assembled with a counterelectrode by using a sealing plastic (25  $\mu\text{m}$ , SX-1170-25, Solaronix) to form a sandwich-type DSSC. An electrolyte containing 0.6 mol L<sup>-1</sup> DMPII (1-propyl-2,3-dimethylimidazolium iodide), 0.1 mol L<sup>-1</sup> LiI (lithium iodide), 0.05 mol L<sup>-1</sup> iodine, and 0.5 mol L<sup>-1</sup> TBP (4-tert-butylpyridine) in AN (acetonitrile) was then infiltrated into voids between the two electrodes of the cell. The photovoltaic properties of the fabricated DSSCs were carried out by scanning DSSCs from the open-circuit voltage ( $V_{oc}$ ) of the cell to the short-circuit condition ( $V_{sc}$ ) at 5 mV s<sup>-1</sup> with a source meter (Keithley 2400) under one-sun illumination by a solar simulator (AM1.5, 100 mW cm<sup>-2</sup>). Electrochemical impedance measurement was carried out under one-sun illumination using an AUTOLAB P10 potentiostat with ac amplitude of 5 mV at a frequency range of 50 kHz down to 0.1 Hz.

## X-ray diffraction

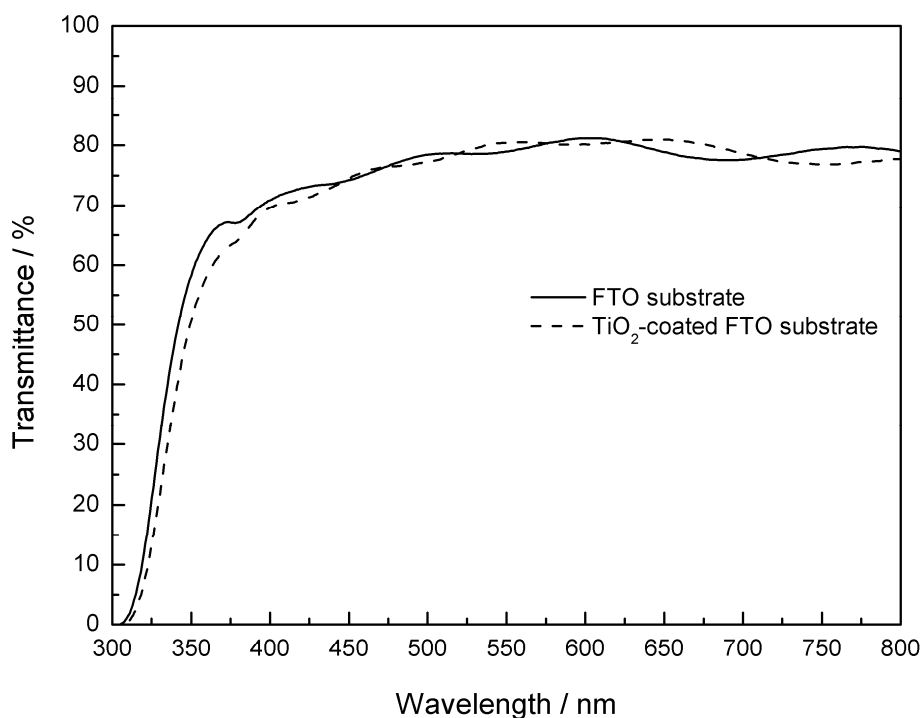
Figure S1 shows XRD patterns of the bare FTO and TiO<sub>2</sub>-coated FTO substrates after annealing at 450°C for 1 h. Clearly, in addition to the characteristic peaks of the FTO substrate, the diffraction peaks of the deposited film could be identified as anatase TiO<sub>2</sub> (JCPDS 89-4921). In addition to crystal structure, the optical transmittance of the TiO<sub>2</sub>-coated FTO should be assured when used as the TCO (transparent conductive oxide) layer of DSSCs.



**Fig. S1** XRD patterns of the bare FTO and TiO<sub>2</sub>-coated FTO substrates.

## Optical transmittance

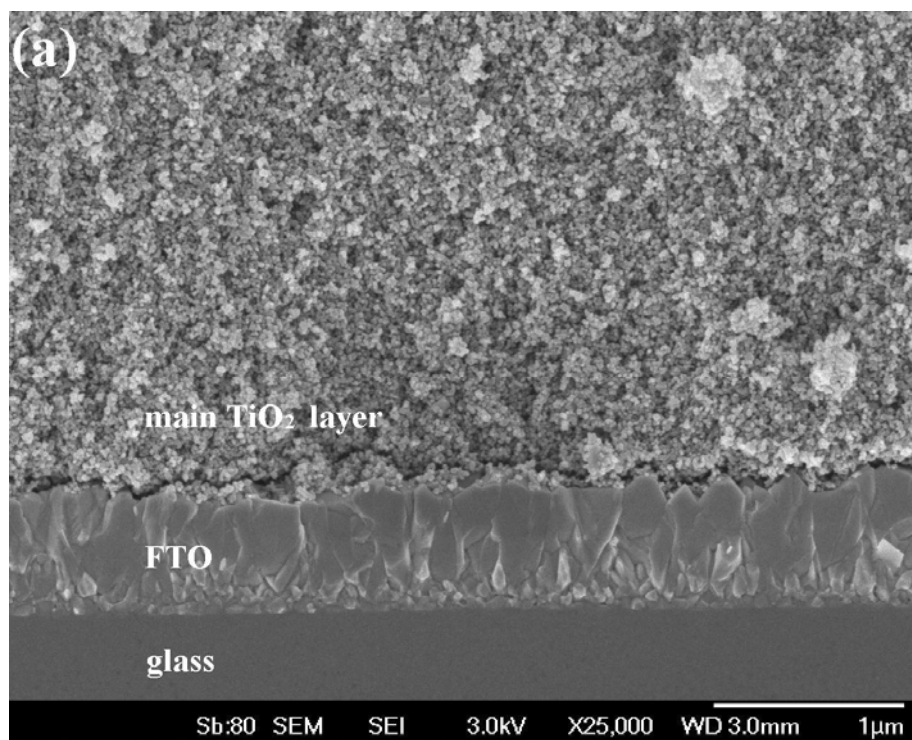
Figure S2 shows the UV-vis spectra of the bare FTO and TiO<sub>2</sub>-coated FTO substrates. The transmittance of the TiO<sub>2</sub>-coated FTO was similar to that of the bare FTO in all wavelength regions, indicating that the deposited porous TiO<sub>2</sub> film did not significantly decrease the substrate transmittance since a very thin layer was obtained. As a result of this, the proposed TiO<sub>2</sub> bifunctional layer did not result in the loss of harvest of light.



**Fig. S2** UV-vis spectra of the bare FTO and TiO<sub>2</sub>-coated FTO substrates.

### **Cross-sectional SEM micrographs of photoanodes**

Figure S3 shows the cross-sectional SEM micrographs of photoanodes employing bare FTO substrate and TiO<sub>2</sub>-coated FTO substrate (bifunctional TiO<sub>2</sub> layer). Clearly, a small gap between the FTO substrate and main TiO<sub>2</sub> layer was found in the photoanode employing bare FTO substrate (Fig. S3a). The interfacial adhesion between the FTO substrate and main TiO<sub>2</sub> layer was significantly improved by employing the TiO<sub>2</sub>-coated FTO substrate (Fig. S3b). The deposited TiO<sub>2</sub> film could employ as a bifunctional layer in DSSC, which acts as a blocking layer to suppress the charge recombination and an anchoring layer to reduce the interfacial contact resistance.



**Fig. S3** Cross-sectional micrographs of photoanodes employing (a) FTO substrate and (b) TiO<sub>2</sub>-coated FTO substrate.

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