Electronic Supplementary Information

The experimental details of the fabrication of TiO₂ NP/ZnO NW photoanode are described below. Firstly, TiO₂ NP film was synthesized directly onto the FTO substrate via screen printing technic. Before TiO₂ printing, the FTO substrates are initially cleaned by sonication in acetone, 2-propanol, and methanol, subsequently rinsed with deionized water, and finally dried in a nitrogen stream. After each printing, the coated substrate was dried at 120°C for 5 min and annealed at 500°C for 30 min to remove organic compounds in the paste and obtain porous TiO₂ network. Then a ZnO seed layer was deposited on the TiO₂ film through a sputtering process. C-axis oriented ZnO seed layer with thickness of 150 nm was prepared on the TiO₂ film by radio frequency (RF) magnetron sputtering technique. When the TiO_2 film substrate was loaded into the chamber the deposition chamber was evacuated down to $\sim 4 \times 10^{-4}$ Pa, high purity argon gas was introduced at a flow rate of 20 SCCM (SCCM denotes standard cubic centimeters per minute at STP) and the working pressure in the chamber was fixed at 0.5 Pa. The substrate temperature was 200°C, and the RF power of 90 W was used to sputter ZnO target (99.99%) for 15 min and the ZnO seed layer was obtained. Finally, ZnO NW arrays were grown on the seeded TiO₂ film by a hydrothermal method. In a typical process, the precursor was prepared by firstly dissolving 50 mM zinc nitrate hexahydrate in deionized water, and followed by adding ammonium hydroxide into the above solution dropwise to kept the precursor solution with pH value of 10.00. The seeded TiO₂ film was put into the solution and was heated at 105° for 6h. Finally the as-prepared film was rinsed with water and dried in air.

The fabrication and assemble of the DSSC was using a classical method. The size of the photoanode used cm^2 . 0.258 The was photoanodes nanostructures were first immersed in 0.3 mМ cisbis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N719, Solaronix SA, Switzerland) absolute ethanol solution at room temperature for 24 h to absorb enough dye molecules, and then the sensitized film were washed with ethanol, blown dry, and sandwiched together and bonded to thermally Pt counter electrodes separated by $\sim 25 \,\mu m$ polypropylene spacer, finally the internal space of each cell was filled with liquid electrolyte by vacuum backfilling. The electrolyte compositions were as follows: 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M LiI, 0.1 M guanidinium thiocyanate, 0.03 M I₂, and 0.5 M tert-butylpyridine in a mixture of acetonitrile and valeronitrile (85/15, v/v).

The morphologies of the photoanode nanostructures were investigated using a field emission scanning electron microscopy (FESEM, JEOL JSM 6700F). The crystal structure of the products was characterized using a Rigaku-Dmax2500 x-ray diffractometer with high intensity Cu K₀ ($\lambda = 1.5418$ Å) incident radiation. The microstructure of ZnO NW arrays and TiO₂ NPs were examined using a high-resolution transmission electron

microscopy (HRTEM, JEOL, JEM-3010). The amount of absorbed dye was determined by a spectroscopic method by measuring the concentration of the dye desorbed from the photoanode surface in a mixed solution of 0.1 M NaOH and ethanol (1:1 volume fraction). A 450 W Xe lamp source (Oriel, U.S.A.) was used to give an irradiance of 100 mW cm⁻² (at air mass (AM) 1.5G) at the surface of the solar cell. The current-voltage characteristics of the cells were measured by applying external potential bias to the cell and measuring the generated photocurrent with a Keithly model 2400 digital source meter (Keithly, U.S.A.). The photovoltage transient experiments were performed by employing a white light-emitting diode array powered by varied driving voltages to supply different steady-state light intensities. By adjusting output light intensities of the white light-emitting diodes to generate different V_{oc} , we measured the pseudo-first-order recombination rate (*k*r) from the transient photovoltage decay by a fast and small light perturbation. Photovoltaic performance was measured by using a metal mask with an aperture area of 0.158 cm².

The cross sectional SEM images of ZnO NW and TiO₂ NP are shown in Fig. S1 (a) and (b), it is clear that the ZnO NWs with diameter in the range of 80-120 nm and length of about 5 μ m vertically grown on the seeded FTO substrate, and porous TiO₂ NP film with a thickness of ~12.5 μ m directly formed on the FTO substrate.



Fig. S1 Cross sectional SEM images of ZnO NW array grown on seeded FTO substrate (a) and TiO₂ NP film (b) grown directly on FTO substrate.

HRTEM and SAED images of the NW, shown in Fig. S2(a) and (b), confirms that the NWs are single crystalline with a [0001] growth direction; HRTEM image of the TiO_2 NPs, shown in Fig. S2(c), indicates that the NPs are with a diameter of about 10 nm, and the (101) interplane distance of 0.35 nm indicates that the NPs are tetragonal anatase phase.



Fig. S2 HRTEM (a) and SAED (b) images of ZnO NW; HRTEM (c) image of TiO₂ NP.

Fig. S3 shows and compares the XRD patterns of TiO_2 NP film (a) and TiO_2 NP/ZnO NW (b) composite photoanodes. In the XRD pattern of the NP film, only diffraction peaks from anatase TiO_2 were observed. In the composite film, in addition to diffraction peaks from TiO_2 NPs, well defined (100), (002) and (101) diffraction peaks resulted from ZnO NWs can also be observed. The strongest (002) diffraction peak is mainly attributed to the wurtzite structure of well aligned ZnO NWs, indicating the high c-axis oriented.



Fig. S3 XRD patterns of TiO₂ NP (a) and TiO₂ NP/ZnO NW (b) composite photoanodes.

Table S1 shows the cell performance parameters of TiO_2 NP and TiO_2 NP/ZnO NW DSSCs with photoanode film thickness of 7.5 μ m, 10 μ m and 12.5 μ m, and their *J-V* curves are compared in Fig. S4a and Fig. S4b, respectively. It is clear that all of the cell performance are improved with the increase of film thickness.

Table S1 Characteristic	s of DSSCs u	using different	phtotoanodes.
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Samples	Thickness of photoanodes (µm)	J_{sc}	V_{oc}	FF	η
		$(mA \cdot cm^{-2})$	(mV)		(%)
TiO ₂ NP-1	~7.5 (NP)	6.58	643	0.52	2.17
TiO ₂ NP-2	~10 (NP)	8.28	652	0.55	2.97
TiO ₂ NP-3	~12.5 (NP)	9.37	676	0.56	3.56
TiO ₂ NP/ZnO NW-1	~5+2.5 (NW+NP)	8.10	659	0.53	2.83
TiO ₂ NP/ZnO NW-2	~5+5 (NW+NP)	10.66	678	0.52	3.76
TiO ₂ NP/ZnO NW-3	~5+7.5 (NW+NP)	11.77	698	0.55	4.52



Fig. S4 Comparison of the *J-V* curves of TiO₂ NP (a) and TiO₂ NP/ZnO NW (b) DSSCs with film thickness of 7.5 μm, 10 μm and 12.5 μm.

Fig. S5 (a) and (b) compares the *J-V* curves of DSSCs with TiO₂ NP and TiO₂ NP/ZnO NW film thickness of 7.5 μ m and 10 μ m (with NW film thickness of 5 μ m), respectively. It is clear that, no matter of the photoanode film thickness, the cell performance of TiO₂ NP/ZnO NW DSSC are always better than these of ZnO NW and TiO₂ NP DSSCs.



Fig. S5 The J-V curves of ZnO NW (5 μm), TiO₂ NP and TiO₂ NP/ZnO NW cells with photoanode film thickness of 7.5 μm (a) and 10 μm (b), measured under AM 1.5G at 100 mW cm⁻² illumination.

Fig. S6a compares the reflectance spectra of dye-free TiO₂ NP/ZnO NW and TiO₂ films with the same thickness of 12.5 μ m. The reflectance intensity of TiO₂ NP/ZnO NW film is much stronger than that of TiO₂ NP film, indicating the composite film has improved light scattering ability in the visible and near-infrared region. Fig. S6b compares the absorption spectra of dye-sensitized TiO₂ NP/ZnO NW and TiO₂ films with the same thickness of 12.5 μ m. Although the amount of absorbed dyes in TiO₂ NP/ZnO NW photoanode is lower, the TiO₂ NP/ZnO NW photoanode also has better absorption ability in the visible region than that of TiO₂ NP film. Accordingly, we speculate that the ZnO NWs on the top of NPs may serve as scattering layer, and the enhanced J_{sc} is mainly ascribed to the light scattering effect of the ZnO NWs.



Fig. S6 The reflectance (a) and absorption (b) spectra of dye-free and dye-sensitized TiO₂ NP/ZnO NW and TiO₂ photoanodes with the same thickness of 12.5 μm, respectively.