Supporting Information

# T-ZnOw/ZnONP Double-layer Composite Photoanode with One-Dimensional Low Resistance Photoelectron Channels for High Efficiency DSSCs

*Yashuai Pang*[†], *Yang Zhang*[†], *Haiwu Zheng*[†], *Qiongzhe Yu*[†], *Xu Chen*[†], *Jihuai Wu*[‡], *and Qiwei Jiang*[†,*]

[†]Department of Physics, School of Physics and Electronic, Henan University, Kaifeng 475004, P. R. China.

[‡]Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou 362021, P. R. China.

AUTHOR INFORMATION

**Corresponding Author**: * Prof. Qiwei Jiang, Department of Physics,School of Physics and Electronic, Henan University.

E-mail: jqw@henu.edu.cn

## Experimental Details

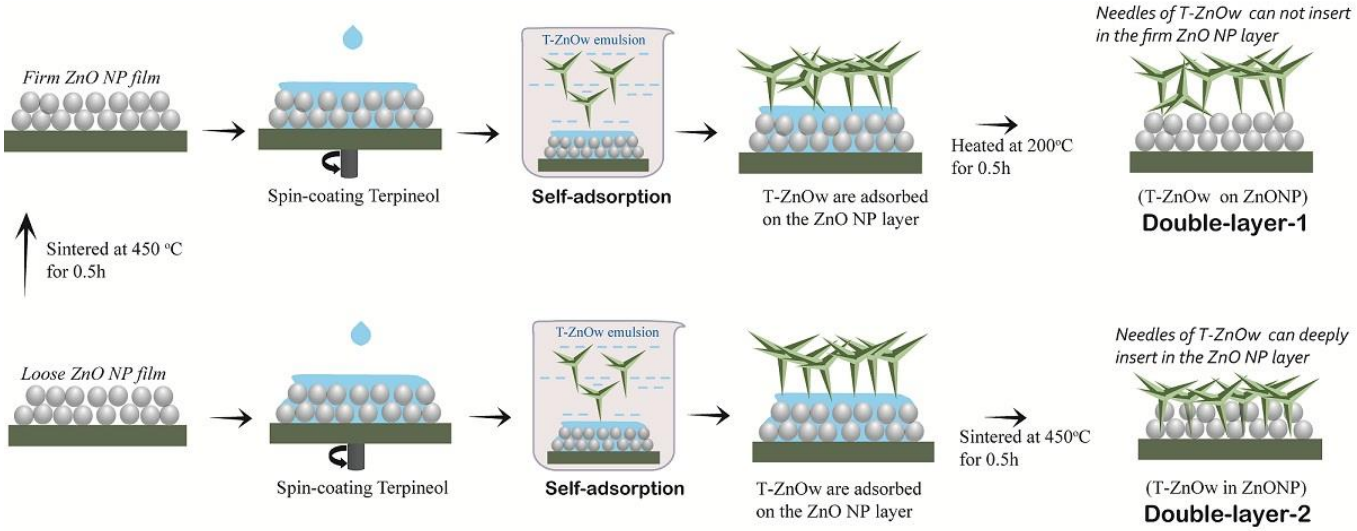


**Figure S1** Schematic diagram of preparation process of T-ZnOw/ZnONP double layer structure photoanode: Double-layer-1 type (T-ZnOw on ZnONP), Double-layer-2 type (T-ZnOw in ZnONP).

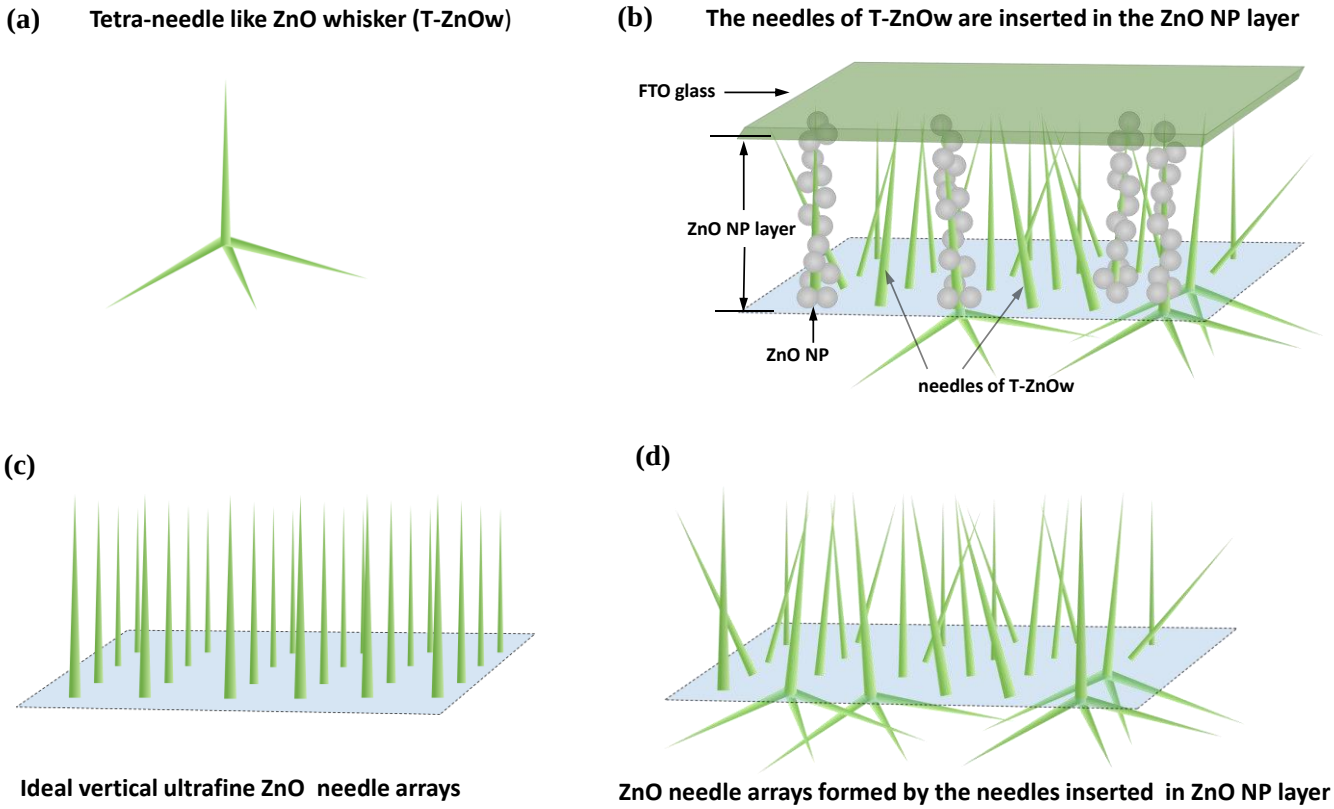


**Figure S2** Structure diagram of ZnO needle array formed by T-ZnOw. a) Tera-needle like ZnO whisker (T-ZnOw); b) The needles of T-ZnOw are inserted in the ZnO NP layer (Double-layer-2 type photoanode); c) Ideal vertical ultrafine ZnO needle arrays; d) ZnO needle arrays formed by the needles inserted in the ZnO NP layer (Double-layer-2 type photoanode).

**Figure S2** shows the structural schematic diagram of the ZnO needle arrays formed by the T-ZnOw. We found that when the T-ZnOw was absorbed on the loose ZnO NP layer, the formed sample was sintered at 450℃ for 0.5h, quite a few T-ZnOw needles could be inserted in the ZnO NP layer, and the inserted part could form a 1-D ZnO ultrafine needle arrays (as shown in **Figure S2b**). It should be noted that many inserted needles are obviously inclined, although it is not an ideal vertical array (as shown in **Figure S2c**), it is obviously a needle array structure composed of ultra-fine needles (as shown in **Figure S2d**).

Compared with the traditional 1-D ZnO arrays prepared by the hydrothermal method,[1, 2] the arrays structure (formed by inserting T-ZnOw needles into ZnO NP film) characteristics are obviously different. The ultrafine ZnO needle arrays formed by self-adsorbing to the terpineol layer and self-inserting into ZnO NP layer is a special array structure with scattering layer. The density of fine needles in this array can be

controlled by the concentration of T-ZnOw or the size of the T-ZnOw needle. It is important that the self-adsorption and self-insertion preparation method of the T-ZnOw scattering layer invented herein also offer a novel and easy to implement strategy to form the 1-D ultrafine needle arrays structure. And the easy to implement self-assembly preparation method is favorable for reducing cost and large-scale production.

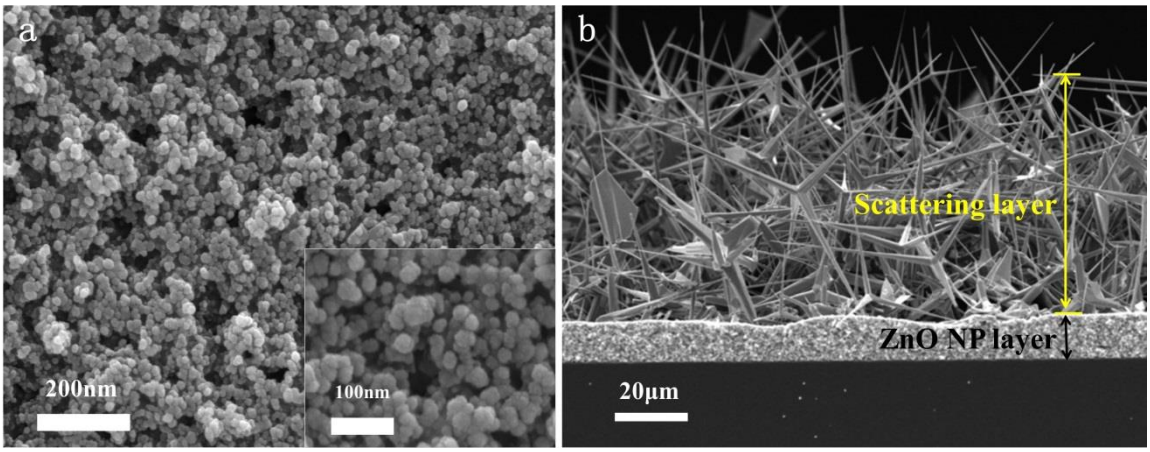


**Figure S3** SEM images of a) the ZnO NP, b) Cross-section view of the Double-layer-1 photoanode (T-ZnOw on ZnONP).

**Figure S3b** shows that most of the needles of T-ZnOw are not inserted into the relatively firm ZnO NP layer.

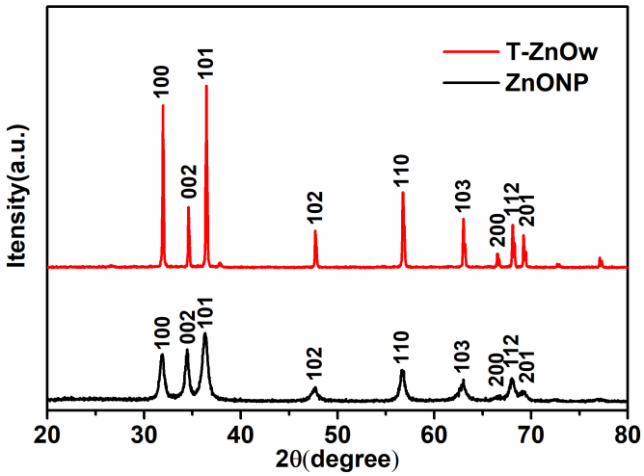


**Figure. S4** XRD patterns of ZnONP and T-ZnOw

**Figure S4** shows the XRD patterns of T-ZnOw and the ZnONP film. All of the peaks could be indexed to the hexagonal ZnO wurtzite structure (JCPDS No. 36-1451) and there is no other diffraction peaks could be found, this indicates the high purity of the product. As observed from XRD patterns, the peaks for the ZnONP are relatively wider compared with the T-ZnOw which the peaks are narrow and sharp.

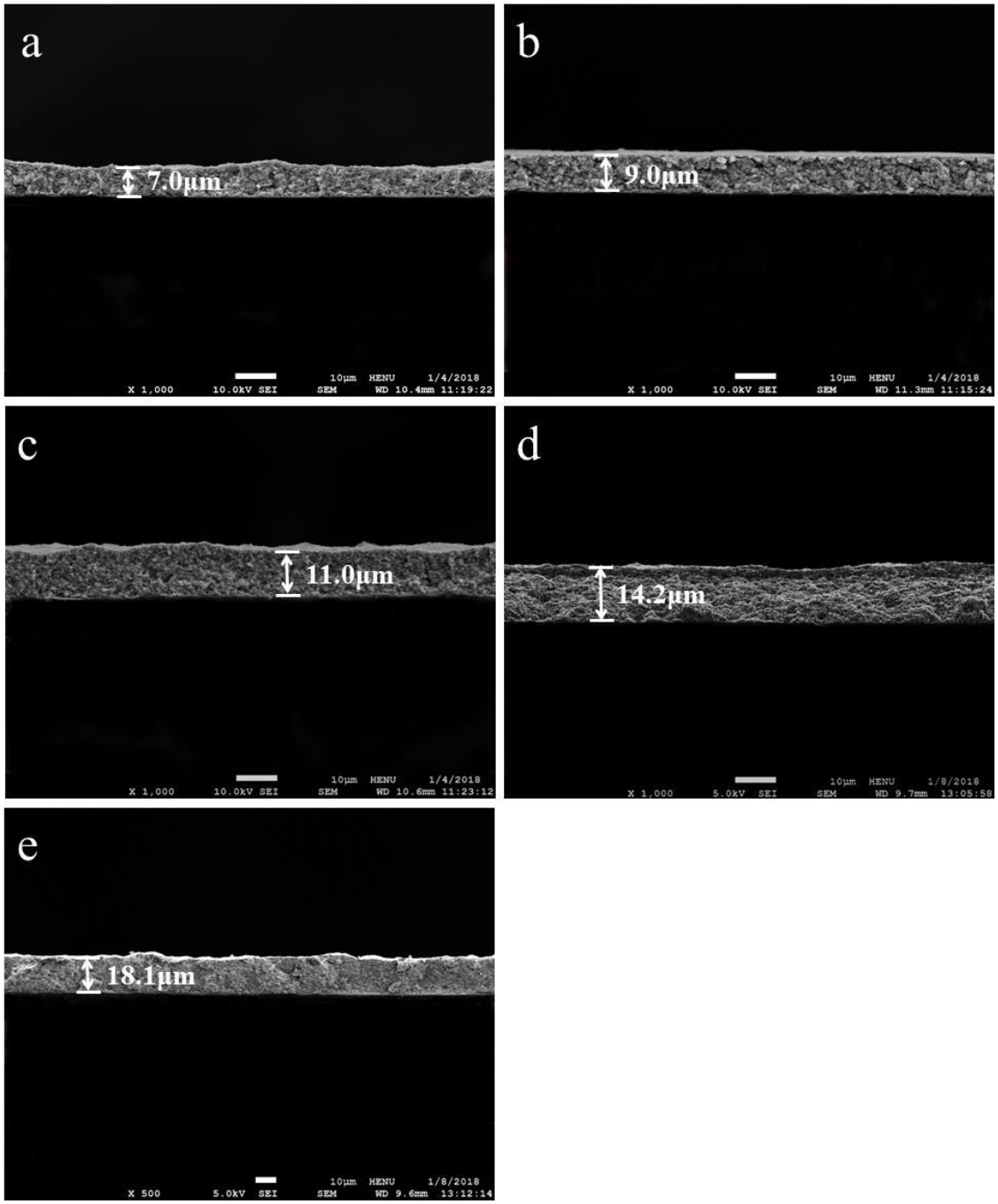


**Figure S5** SEM of the single layer ZnONP film with different thickness of a) 7.0 µm, b) 9.0 µm, c) 11.0 µm, d) 14.2 µm, and e) 18.1 µm respectively.

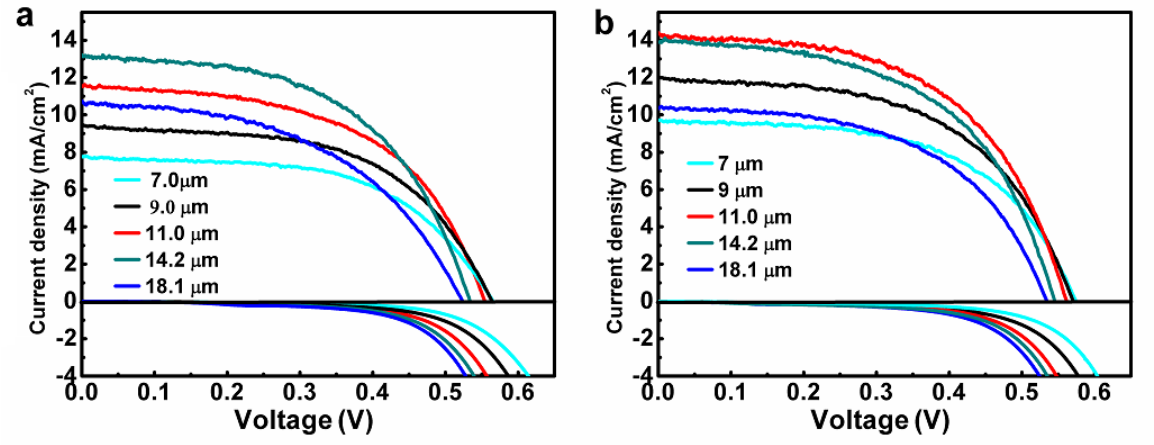


**Figure S6** a) J-V curves and the corresponding dark current curves of the single layer ZnONP photoanode with different thickness; b) J-V curves and the corresponding dark current curves of the Double-layer-1 type (T-ZnOw on ZnONP) photoanode based on different thickness of ZnONP layer.

**Table S1a.** Photovoltaic parameters of the single layer ZnONP photoanode with different thickness (all the parameters are summarized from **Figure S6a**).

| Sample | Thickness (μm) | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | η (%) |
|---|---|---|---|---|---|
| Single layer ZnONP | 7.0 | 7.8 | 0.566 | 0.566 | 2.28 |
| Single layer ZnONP | 9.0 | 9.4 | 0.565 | 0.555 | 2.96 |
| Single layer ZnONP | 11.0 | 11.5 | 0.556 | 0.541 | 3.45 |
| Single layer ZnONP | 14.2 | 13.2 | 0.535 | 0.536 | 3.77 |
| Single layer ZnONP | 18.1 | 10.8 | 0.523 | 0.486 | 2.73 |

**Table S1b.** The photovoltaic parameters of the Double-layer-1 type (T-ZnOw on ZnONP) photoanode based on different thickness of ZnONP layer (all the parameters are summarized from **Figure S6b**).

| Sample | ZnONP Thickness (μm) | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | η (%) |
|---|---|---|---|---|---|
| Double-layer-1 type (T-ZnOw on ZnONP) | 7.0 | 9.7 | 0.576 | 0.562 | 3.14 |
| Double-layer-1 type (T-ZnOw on ZnONP) | 9.0 | 12.0 | 0.572 | 0.547 | 3.72 |
| Double-layer-1 type (T-ZnOw on ZnONP) | 11.0 | 14.4 | 0.562 | 0.539 | 4.36 |
| Double-layer-1 type (T-ZnOw on ZnONP) | 14.2 | 13.9 | 0.547 | 0.539 | 4.10 |
| Double-layer-1 type (T-ZnOw on ZnONP) | 18.1 | 10.3 | 0.537 | 0.537 | 2.96 |

**Explanation of Figure S6**

In order to evaluate the influence of film thickness change on the performance of photoanode, we systematically researched the J-V characteristics curves of single layer ZnONP photoanode with different thicknesses. As shown in **Figure S6a**, when the thickness increases from 7.0 to 14.2 μm, the Jsc increased from 7.8 to 13.2 mA $cm^{-2}$. This improvement could be explained that when the ZnO film thickness is increased, more dye molecules could be adsorbed and the higher light harvesting could be got. However, when an excessively thick ZnONP film (18.1μm) is used, the JSC decreased from 13.2 to 10.8 mA cm-2. This could be explained that too much thickness can lead to a large dark current (the large dark current is not benefit for the photovoltaic efficiency of the DSSC). This is because as the thickness of ZnO film increases, a large number of surface state traps and surface defects in the nanometer ZnO film will increase correspondingly. These increased traps and defects will constrain the movement of electron in the film, and increase the probability of electron recombination, leading to the increase of dark current.[3] Moreover, unlike the increasing $J_{sc}$ trend, the Voc gradually decreases along with the increasing film thickness (all the photovoltaic parameters of **Figure S6a** are summarized in **Table S1a**).

Based on the above results, it could be concluded that if the thickness of the film is too thin, the films usually show poor light harvesting efficiency and exhibit high transparency to visible light. Increasing the thickness of ZnONP thin film can accordingly enhance the light harvesting and improve the photovoltaic performance of the DSSC correspondingly. However, the surface traps and surface defects also increase along with the increase of the ZnONP film thickness. The increased traps and defects could greatly retard photoelectron transport and increase the probability of electron recombination if it increases to more than the appropriate level, and this will lead to an increase in dark current and a decrease in the whole photovoltaic efficiency.

In order to achieve the goal of increasing the light absorption efficiency of ZnONP photoanode without increasing the dark current by a large margin simultaneously, here we add a scattering layer on the single-layer ZnONP film through an easy to be realized self-adsorption method in the T-ZnOw water solution to form the T-ZnOw/ZnONP double layer photoanode (Double-layer-1 type, T-ZnOw on ZnONP). The

photoelectric properties of Double-layer-1 type electrodes with the same thickness of scattering layer and different thicknesses of ZnONP substrates were systematically studied. As shown in **Figure S6b** and **Table S1b**, when a scattering layer is added on the ZnONP substrate layer with a thickness of 7.0 μm, 9.0 μm, 11.0 μm respectively, the enhancement of Jsc for all the double layer ZnO photoanodes (Double-layer-1 type, T-ZnOw on ZnONP) could be observed compared to the single layered ZnONP photoanodes. This is because the scattering layer could improve the absorption efficiency of light. In addition, for the Double-layer-1 type photoanode (the photovoltaic efficiency of the photoanode with the ZnONP layer thickness of 11.0 μm is higher than that of the 14.2 μm. However, for the single-layer ZnONP photoanode, the photovoltaic efficiency of the photoanode with the ZnONP layer thickness of 11.0 μm is comparatively lower than that of the 14.2 μm This difference before and after the T-ZnOw scattering layer is added could be attributed to the excellent T-ZnOw light scattering ability and the less electron recombination in a thinner ZnONP substrate layer for the T-ZnOw/ZnONP double layer photoanode.

**Electrochemical Impedance Spectroscopy (EIS) Analysis.** As shown in **Figure 4c**, there are three semicircles in the Nyquist diagram as the frequency increase, The first semicircle in the high frequency region represents the impedance corresponding to charge transfer at the counter Pt electrode ($R_1$), while the middle semicircle the intermediate frequency response is associated with the electron transport resistance at the ZnO/dye/electrolyte interface ($R_k$). The $R_w$ represents the transmission resistance of the effective photoelectrons within the ZnO photoanode. The low-frequency region is corresponding to the Warburg diffusion process of $I/I_3^-$ in the electrolyte ($Z_N$) [4]. Figure 5d shows the Bode phase plots of the EIS from the three different DSSC. The lifetime of photoelectrons ($\tau_e$) can be calculated according to the following equations [5]:

$$\tau_e = R_k \times C_\mu = \frac{1}{\omega_k} \qquad R_k = \frac{\omega_d}{\omega_k} R_w$$

The $R_k$ represents the photoelectron recombination resistance between the interface of the ZnO photoanode and electrolyte. The $\omega_k$ represents the rate constant and the $\omega_d$ represents the characteristic frequency of diffusion. Besides, $C_\mu$ is the chemical capacitance of ZnO electrode. All the fit EIS parameters are summarized in **Table S2**.

**Table S2** Parameters of Nyquist plots (Figure 4c) and Bode-phase plots (Figure 4d).

| Sample | Rs(Ω) | $R_1$( Ω) | CPE1 | $R_k$(Ω) | CPE2 | $Z_N$ | $R_w$(Ω) | $\tau_e$ (s) |
|---|---|---|---|---|---|---|---|---|
| ZnONP (single layer) | 20.5 | 5.24 | CPE-T=$2.10\times10^{-5}$ CPE-P=0.917 | 29.1 | CPE-T=$4.22\times10^{-4}$ CPE-P=0.906 | Ws-R=3.99 Ws-T=2.01 Ws-p=0.567 | 17.5 | 0.0120 |
| Double-layer-1 (T-ZnOw on ZnONP) | 17.6 | 5.99 | CPE-T=$3.40\times10^{-5}$ CPE-P=0.809 | 21.6 | CPE-T=$3.20\times10^{-4}$ CPE-P=0.950 | Ws-R=5.90 Ws-T=2.22 Ws-p=0.516 | 19.1 | 0.0069 |
| Double-layer-2 (T-ZnOw in ZnONP) | 16.7 | 6.10 | CPE-T=$4.78\times10^{-5}$ CPE-P=0.811 | 35.4 | CPE-T=$5.80\times10^{-4}$ CPE-P=0.927 | Ws-P= 6.00 Ws-R=2.98 Ws-T=0.448 | 13.1 | 0.0200 |

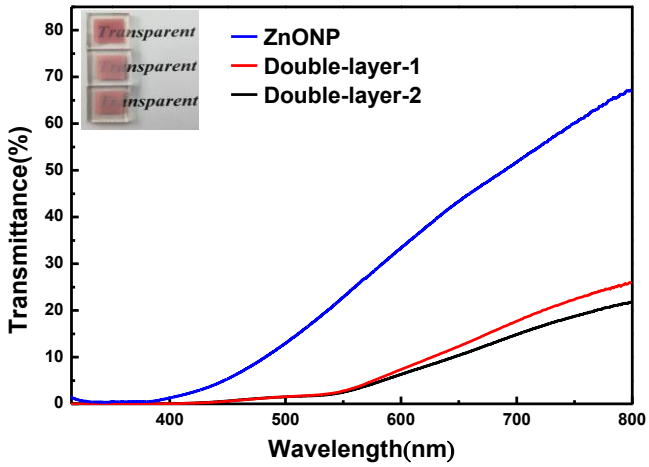


**Figure S7.** Ultraviolet-visible transmittance spectra of the different photoanodes

The data in Figure S7 shows that the T-ZnOw layer can greatly reduce the light transmittance and accordingly improve the light absorption efficiency of the photoanode.

**References**

[1] X. Wu, H. Bai, C. Li, G. Lu, G. Shi, Controlled one-step fabrication of highly oriented ZnO nanoneedle/nanorods arrays at near room temperature, *Chemical Communications*, 15 (2006) 1655-1657.

[2] M. Y. Lu, Y. T. Tseng, C. Y. Chiu, Angle-dependent photodegradation over ZnO nanowire arrays on flexible paper substrates, *Nanoscale Research Letters*, 9 (2014) 667.

[3] S. Ito, P. Liska, P. Comte, R. Charvet, P. Pechy, U. Bach, L. Schmidtmende, S.M. Zakeeruddin, A. Kay, M.K. Nazeeruddin, Control of dark current in photoelectrochemical ($TiO_2/I^-$-$I_3^-$) and dye-sensitized solar cells, *Chemical Communications*, 34 (2005) 4351-4353.

[4] C. Y. Lin, Y. H. Lai, H. W. Chen, J. G. Chen, C. W. Kung, R. Vittal, K. C. Ho, Highly efficient dye-sensitized solar cell with a ZnO nanosheet-based photoanode, *Energy & Environmental Science*, 4 (2011) 3448-3455.

[5] J. Bisquert, Theory of the impedance of charge transfer via surface states in dye-sensitized solar cells, *Journal of Electroanalytical Chemistry*, 646 (2010) 43-51.