

## TiO<sub>2</sub> Nanoparticle and ZnO Nanowire Composite for Solar Cell Application

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Dye-sensitized solar cells (DSSC) are one of the most promising photovoltaic devices for solar energy conversion [1]. In an effort to develop a materials system that can efficiently convert light-electricity into power [2], we demonstrate the fabrication of a DSSC by using a nanostructure made of TiO<sub>2</sub> nanoparticles (NP) and ZnO nanowire (NW) arrays, as illustrated in Figure 1a and 1b.

Figure 1c shows a scanning electron microscopy (SEM) image of the brush-like electrode substrate fabricated by growing a ZnO NW array on fluorine-doped SnO<sub>2</sub> (FTO) transparent conducting glass via thermal vaporization of Zn powder. An aqueous solution consisting of 2 g/L TiO<sub>2</sub> NPs (diameter, around 25 nm) and 1 M Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> were then coated on the brush-like electrode. After applying one coat of the solution and then allowing the sample to dry at 90 °C for 2 h, a layer of TiO<sub>2</sub> NPs were formed on the ZnO NW array (inset of Figure 1d). After repeating this process five times, the interspaces of the ZnO NW array were filled with TiO<sub>2</sub> NPs as shown in Figure 1d. The photoanode was soaked in 0.5 mM N 719 dye (from Dyesol) in ethanol for 72 h. The photoanode was then washed once with ethanol and used for photovoltaic measurements. The redox electrolyte was composed of 0.1 M 1-Aminopyridinium iodide, 0.1 M KI and 0.05 M I<sub>2</sub> in acetonitrile. The counter electrode was Pt-coated FTO. Cell measurement was performed using a Keithley 2400 source meter under simulated AM 1.5 G sunlight with an intensity of 100 mW/cm<sup>2</sup>. As illustrated in Figure 2a and 2b, the current density-bias (*J-V*) plot of the as-fabricated cell was formed by the overlap of two curves. The first curve resulted from the dye sensitized ZnO NWs showing low open-circuit voltage (*V*<sub>oc</sub>) caused by the direct contact to the electrolyte; the second was attributed to the dye sensitized TiO<sub>2</sub> NPs demonstrating low short-cut photocurrent (*J*<sub>sc</sub>) because of the slow electron transport in TiO<sub>2</sub> NP layer. This was due to the fact that as-deposited TiO<sub>2</sub> NPs were stacked loosely on the ZnO NW array. An annealing process at 400 °C for 1 h was conducted to improve the compactness of the TiO<sub>2</sub> NP and ZnO NW composite. This effort resulted in the increase of the light to electricity conversion efficiency ( $\eta_{\text{PCE}}$ ) from 0.68 % to 2.67 % and the enhancement of the fill factor (*FF*) from 0.21 to 0.29. The high *J*<sub>sc</sub> demonstrates the ZnO NW array is an effective antireflection coating material with good transparency, which has been proved by Lee, et al [3]. In addition, the ZnO NWs serve as fast electron paths. This because the band gaps and band edge energies of ZnO and anatase TiO<sub>2</sub> are similar, TiO<sub>2</sub> NP and ZnO NW can therefore form a heterojunction free of band discontinuities and with a built-in potential, neglecting any difference in densities of states [4]. Through this investigation it is expected that the integration of a ZnO NW array on the DSSC leads to the enhancement of  $\eta_{\text{PCE}}$  by improving light harvesting as well as charge separation.

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### References

- [1] O'Regan, B.; Grätzel, M. *Nature* 1991, 353, 737-740.
- [2] Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. *Nature Mater.* 2005, 4, 455-459.
- [3] Lee, Y.; Ruby, D.; Peters, D.; McKenzie, B.; Hsu, J. P. *Nano Lett.* 2008, 8, 1501-1505.

[4] Law, M.; Greene, L. E.; Radenovic, A.; Kuykendall, T.; Liphardt, J.; Yang, P. *J. Phys. Chem. B* **2006**, *110*, 22652-22663.

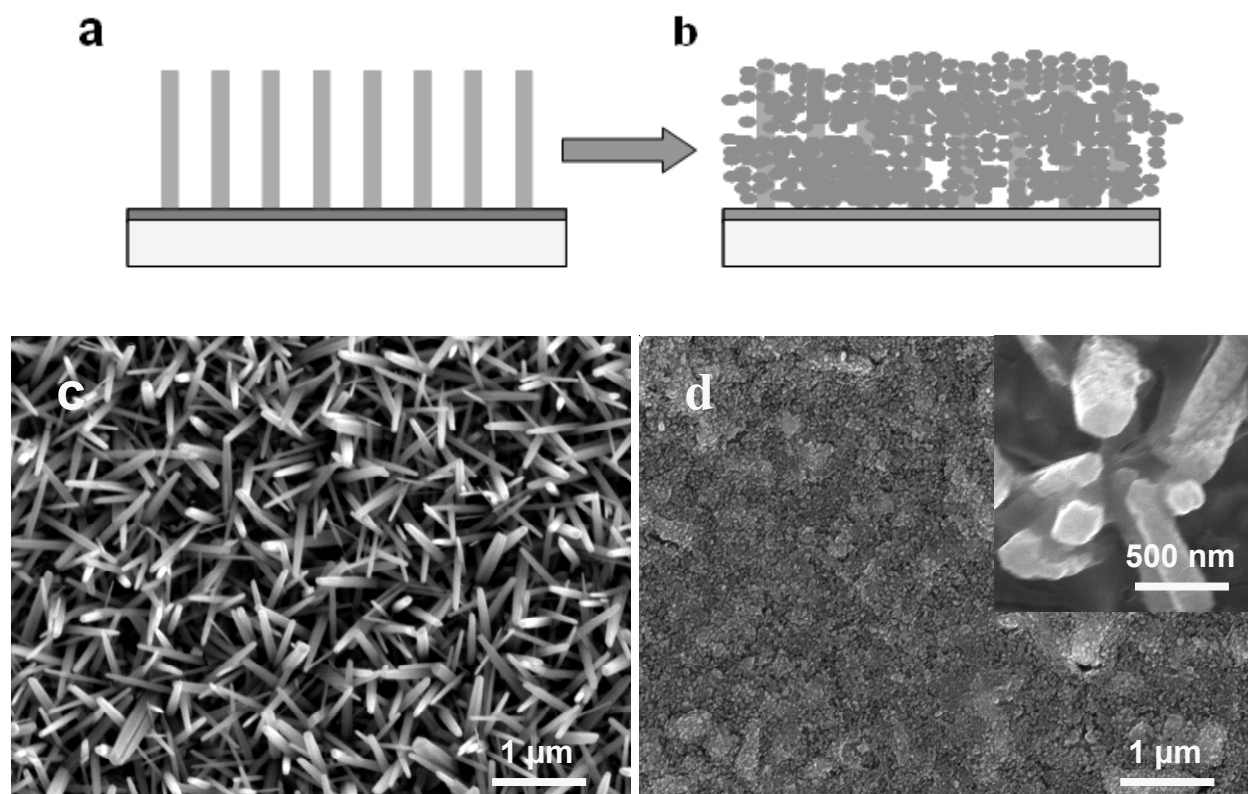


Figure 1 Schematic diagrams of the fabrication process demonstrating the deposition of  $\text{TiO}_2$  NPs on a ZnO NW array. (a) ZnO NW array and (b)  $\text{TiO}_2$  NP-coated ZnO NW array. (c) and (d) are SEM images of the samples as illustrated in (a) and (b) correspondingly.

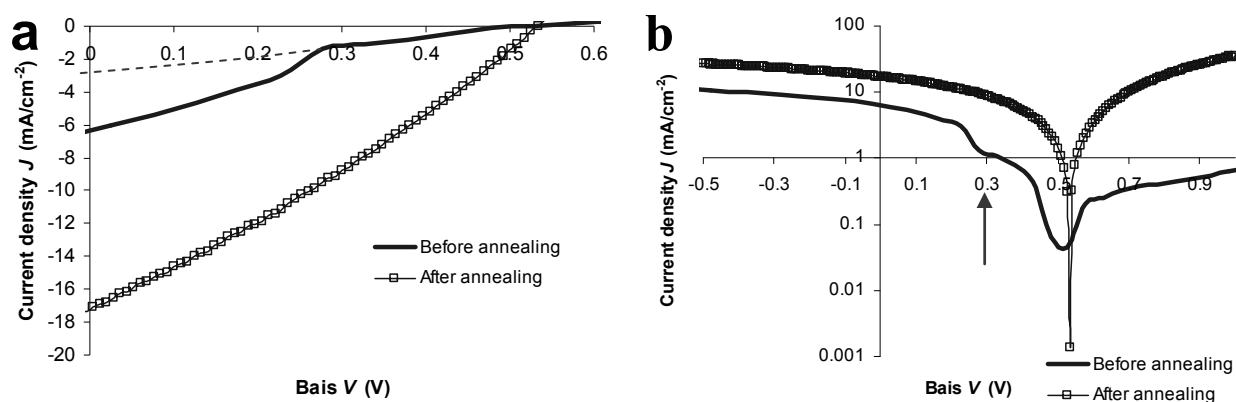


Figure 2 (a)  $J$ - $V$  plots and (b) semilogarithmic plots of as-fabricated  $\text{TiO}_2$  NP/ZnO NW array-based DSSCs. Before annealing,  $V_{oc}$  0.53 V,  $J_{sc}$  6.06  $\text{mA}/\text{cm}^2$ ,  $FF$  0.21,  $\eta_{PCE}$  0.68 %; after annealing,  $V_{oc}$  0.53 V,  $J_{sc}$  17.06  $\text{mA}/\text{cm}^2$ ,  $FF$  0.29,  $\eta_{PCE}$  2.67 %.