

Supporting Information

Low temperature growth of hybrid ZnO/TiO₂ nano-sculptured foxtail-structures for dye-sensitized solar cells

Chao. Zhao ^a, David. Child ^a, Yue. Hu ^b, Neil. Robertson ^b, Des. Gibson ^{a, c}, Shun. Cai. Wang ^d and Yong.Qing. Fu ^{a, *}

^a Thin Film Centre, Scottish Universities Physics Alliance (SUPA), University of the West of Scotland, Paisley, PA1 2BE, UK.

^b EaStCHEM School of Chemistry, University of Edinburgh, King's Buildings, Edinburgh, EH9 3JJ

^c Thin Film Solutions Ltd, Block 7, West of Scotland Science Park, Kelvin Campus, Maryhill Rd, Glasgow G20 0SP, UK.

^d School of Engineering and the Environment, University of Southampton, Highfield, Southampton, SO17 1BJ, UK.

* Corresponding author: Dr. Richard Y. Q. Fu, e-mail: richard.fu@uws.ac.uk

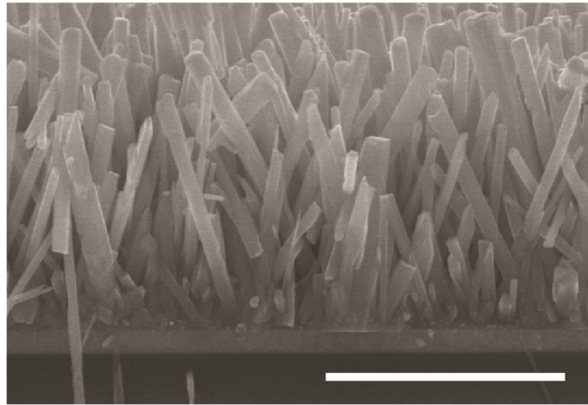


Figure S-1. Cross-sectional SEM image of the bare-ZnO NRs obtained after 4hrs growth (Z0). Scale bar is 3 μ m.

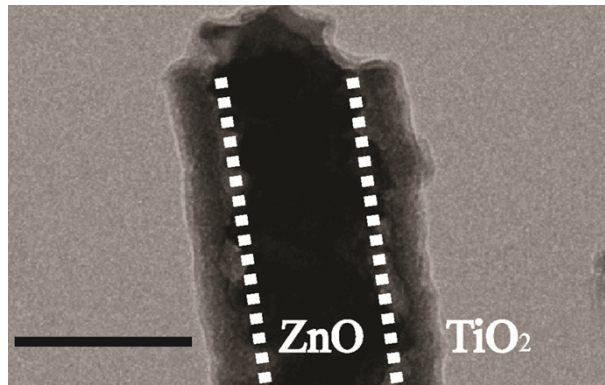


Figure S-2. TEM image of a single ZnO core-TiO₂ shell hybrid structure with the modification time of 120mins (TZ4). Scale bar is 200nm. The thickness of the shell is around 55nm

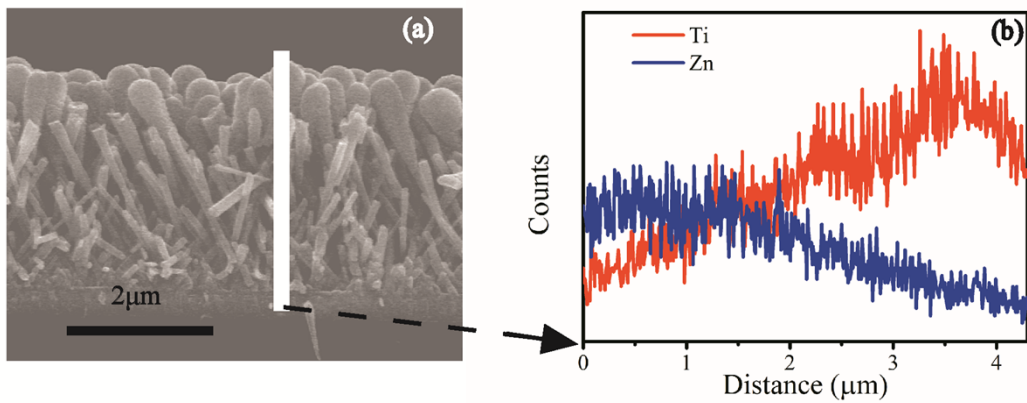


Figure S-3. (a) Cross section of the TZ4 and (b) the corresponding EDS line scan

Impedance spectra

Equivalent circuit used to fit EIS results are followed by previous studies [1,2,3]. The fitting was achieved by zview software (Scribner Associates, Inc.) using non-linear least squares regression. Constant phase elements (CPEs) are used to replace all capacitances to improve quality of fits. However, the EIS results do not show a clear transmission-line feature in this experiment, which is commonly attributed to a good electron transport in the semiconductor oxide (i.e. ZnO) [4,5]. For this reason, it is not possible to extract reliable values from the equivalent circuit-fitting and we limited our study to analyse the recombination behavior of the NRs and hybrid nanostructures.

The details of the circuit are:

R_s : series resistance, including the sheet resistance of TCO glass and contact resistance of the cell

R_{co} : resistance at ITO/seed layer/nanostructure contact

C_{CO} : the capacitance at ITO/seed layer/nanostructure contact

R_{ct} & C_{ct} : the charge-transfer resistance and the corresponding double-layer capacitance at exposed ITO/electrolyte interface

r_t : the transport resistance of electrons in ZnO/TiO₂ nanostructure

r_{ct} : charge-transfer resistance of the charge recombination process

C_{μ} : the capacitance of the nanostructure/electrolyte interface

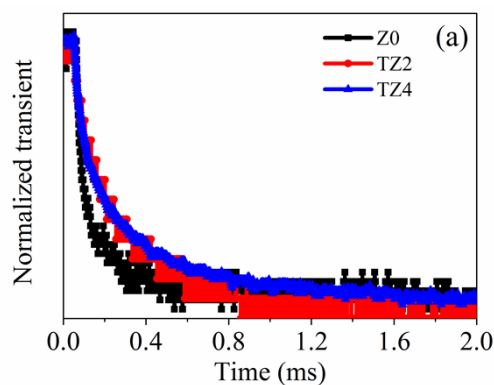
R_{Pt} : charge-transfer resistance at the counter electrode (Pt coated ITO)

C_{Pt} : double-layer capacitance at the counter electrode (Pt coated ITO)

Z_d : Warburg element showing the Nernst diffusion of I₃⁻ in electrolyte

Electron transport

Measurements of electron transport time followed procedures reported in Ref. [6]. A square-wave pulse was applied to a white-light LED, used to illuminate the DSSCs. The modulation amplitude produced a <10% change in DSSC current. The current was determined by ohm law and an average of 5 photocurrent transient signals was recorded for each test.



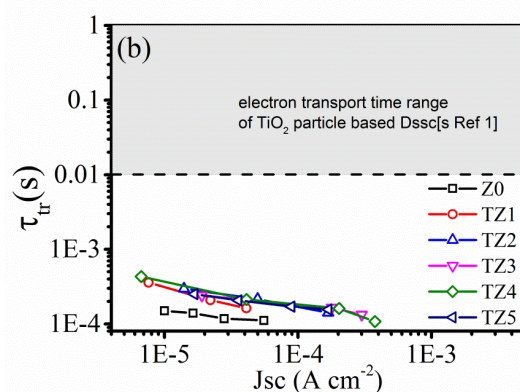


Figure S-4. (a) Representative transient photo current decay at a short circuit work condition of Z0, TZ2 and TZ4 (b) Fitted electron transport time constants (τ_{tr}) versus short circuit current for all the samples.

Fig. S-4(a) shows representative transient photo current decay at a short circuit work condition for Z0, TZ2, and TZ4. Each transient is fitted by the following equation:

$$y = y_0 + Ae^{-t/\tau_{tr}}$$

where τ_{tr} is the characteristic time for electron transport. The values of characteristic time for τ_{tr} under a range of light intensities are plotted against the corresponding short-circuit current density J_{sc} in Fig. S-4(b).

¹ J. Bisquert, *J. Phys. Chem. B*, 2002, **106**, 325-333

² F. Fabregat-Santiago, J. Bisquert, E. Palomares, L. Otero, D. Kuang, S. M. Zakeeruddin and M. Grätzel, *J. Phys. Chem. C*, 2007, **111**, 6550-6560.

³ P. R. F. Barnes, K. Miettunen, X. Li, A. Y. Anderson, T. Bessho, M. Gratzel and B. C. O'Regan, *Adv. Mater.*, 2013, **25**, 1881-1922.

⁴ F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo and A. Hagfeldt, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 117-131.

⁵ E. Guillen, E. Azaceta, L. M. Peter, A. Zukal, R. Tena-Zaera and J. A. Anta, *Energy Environ. Sci.*, 2011, **4**, 3400-3407.

⁶ V. Manthina, J. P. Correa Baena, G. Liu and A. G. Agrios, *J. Phys. Chem. C*, 2012, **116**, 23864-23870.