Electronic Supplementary Material (ESI) for RSC Advances.

Multi-functional DNA-based synthesis of SWNTs@(TiO_2/Ag/Au) nanocomposites for enhanced light-harvesting and charge collection in DSSCs

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Supplementary information

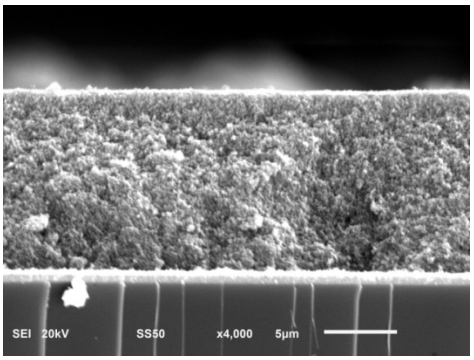


Figure S1 Cross section of the photoanode film

Dye loading tests

The dye loading of the photoanode was determined by eluting the N719 dye from the TiO_2 electrode into 3ml of 0.1 M KOH and using a UV-vis calibration curve to determine the concentration of dye in solution to total amount of dye per square centimetre.

The resulted dye loading value of the photoanodes are summarized in Table S1. The photoanodes with SWNTs@TiO_2, SWNTs@(TiO_2/Ag) and SWNTs@(TiO_2/Ag/Au) have attached similar amount of dye. The dye loading impact

can be excluded when do the comparison among the three samples.

However, compared with P25 TiO_2 (20 nm) photanode, the dye loading of other five photoanodes are better for the incorporation of the 5 nm TiO_2 (2 wt%). The smaller size makes the material have larger specific surface area. And because of the one-dimension morphology of SWNTs, the dye loading of the last four sample decrease a little, however still larger than P25 TiO_2 photanode.

To exclude the impact of different dye loading, the performance of DSSCs with SWNTs@(TiO_2/Ag/Au) was compared with the P25 TiO_2/ 5 nm TiO_2 sample, which has the largest amount of dye loading. As shown in figure S3 and table S2, DSSCs with SWNTs@(TiO_2/Ag/Au) have a higher PCE (8.3%) than the P25 TiO_2/ 5 nm TiO_2 sample (6.3%), and other photovoltaic parameters are also better than the P25 TiO_2/ 5 nm TiO_2 sample. It is known that the incorporation of 5 nm TiO_2 improve the dye loading of the photoanodes, however, the smaller TiO_2 lead to a longer electron transportation length. On the contrary, the SWNTs@(TiO_2/Ag/Au) nanocomposites improve the electron collection and light-harvesting simultaneously, and that make the performance of DSSCs with SWNTs@(TiO_2/Ag/Au) nanocomposites better.

In summary, the SWNTs@TiO_2, SWNTs@(TiO_2/Ag) and SWNTs@(TiO_2/Ag/Au) nanocomposites may improve the dye loading of DSSCs compared with P25 TiO_2 (20 nm) sample to a certain extent. Moreover, the comparison between DSSCs with P25 TiO_2/ 5 nm TiO_2, SWNTs@TiO_2, SWNTs@(TiO_2/Ag) and SWNTs@(TiO_2/Ag/Au) shows that the

SWNTs@(TiO_2/Ag/Au) nanocomposites improve the electron collection and light-harvesting simultaneously.

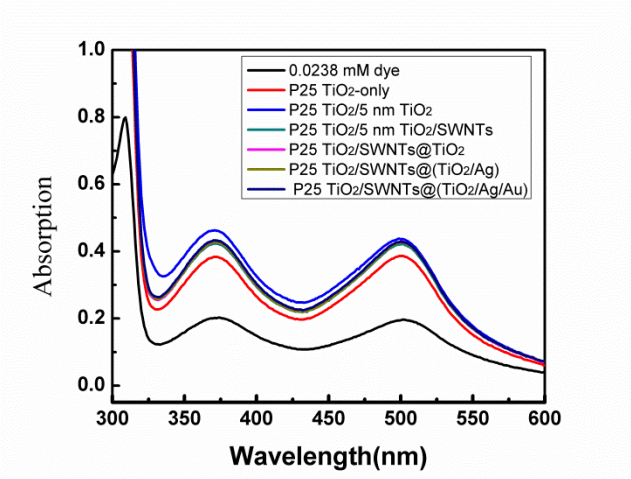
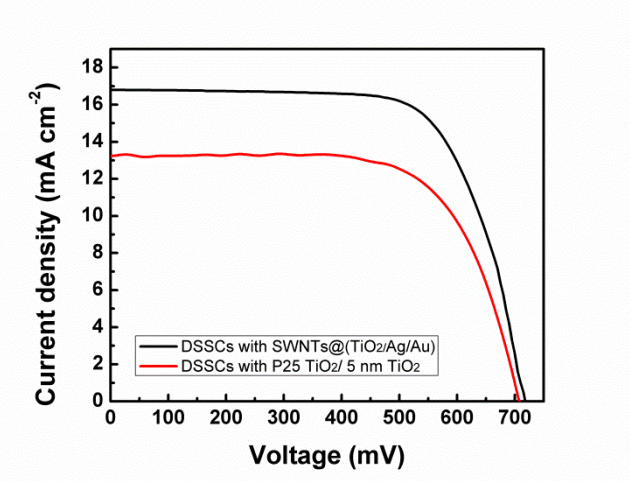


Figure S2 UV-vis spectra of dye solution eluted from the TiO_2 electrode.

Table S1 Dye loading value of each photoanodes

sample	Dye loading (10^{-7} mol cm^{-2})
P25 TiO_2-only	1.62
P25 TiO_2/ 5 nm TiO_2	1.86
P25 TiO_2/ 5 nm TiO_2/ SWNTs	1.77
P25 TiO_2/ SWNTs@TiO_2	1.80
P25 TiO_2/ SWNTs@(TiO_2/Ag)	1.80
P25 TiO_2/ SWNTs@(TiO_2/Ag/Au)	1.81



FigureS3 J-V curves of DSSC with SWNTs@(TiO_2/Ag/Au) and P25 TiO_2/ 5 nm TiO_2.

Table R2 Photovoltaic parameters of DSSC with P25 TiO_2/ 5 nm TiO_2 and SWNTs@(TiO_2/Ag/Au)

Sample DSSCs	Jsc ($mA\ cm^{-2}$)	Voc (mV)	FF (%)	PCE (%)	η_{COL} (%)
SWNTs@(TiO_2/Ag/Au)	16.8	722	69.7	8.3	99.7
P25 TiO_2/ 5 nm TiO_2	13.2	708	68.2	6.3	93

Calculation of electron diffusion length from electrochemical impedance spectra

The electron diffusion length (L_n) can be calculated as

$$L_n=L(R_{REC}/R_T)^{1/2}.$$

Where L is the film thickness, R_{REC} is electron recombination resistance, and R_T is electron transport resistance. R_{REC} and R_T were obtained by fitting the measured electronchemical impedance spectra to the equivalent circuit (shown in Figure S1) with Z-view software. More detailed information about fitting electrochemical impedance spectra to the transmission line model and extracting electron diffusion length from fitted electrochemical impedance spectra can be found in reference[1-5].

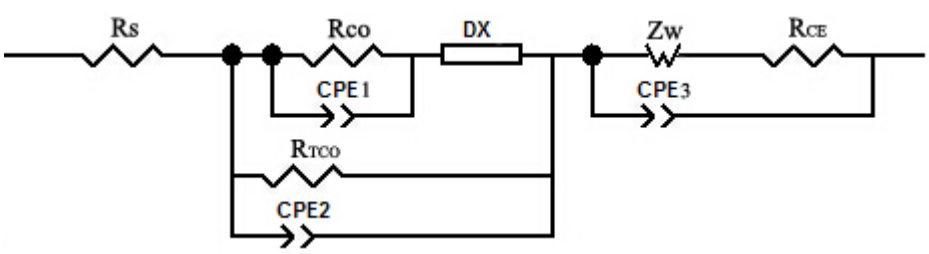


Figure S1 equivalent circuit used to fit the impedance measurements on the DSSCs. Rs is the series resistance. R_{CO} and CPE1 are the contact resistance and capacitance at the interface between the FTO and the TiO_2 photoanode film. RTCO and CPE2 are the charge transfer resistance and the interface capacitance at the uncovered layer of FTO to the electrolyte. DX is transmission line impedance of the TiO_2 photoanode film. The element DX consist of r_T (resistivity of electron transport in the photoanode film), r_{REC} (charge recombination resistance at the TiO_2/dye/electrolyte interface), and c_μ (chemical capacitance of the photoanode film). Zw is the mass transport impedance at the counter electrode. R_{CE} and CPE3 charge transfer resistance and double layer capacitance at the counter electrode/electrolyte interface.

Calculation of electron collection efficiency from electron diffusion length

The electron collection efficiency is [1,2]:

$$\eta_{col} = \frac{L_n\alpha\left[-L_n\alpha\cosh\left(\frac{L}{L_n}\right)+\sinh\left(\frac{L}{L_n}\right)+L_n\alpha e^{-\alpha L}\right]}{\left(1-e^{-\alpha L}\right)\left[1-L_n^2\alpha^2\right]cosh(\frac{L}{L_n})}$$

Where L is the thickness of the TiO_2 film, L_n is the electron diffusion length, and α is the extinction coefficient of the dye sensitized TiO_2 film. For calculation, we assume αL=1, indicating 90% incident light is absorbed.

At bias value of 550mV, for DSSCs with SWNT@(TiO_2/Ag/Au) nanocomposites, L_n/L=10.4, η_{col}=99.7%; for TiO_2-only DSSCs, L_n/L=3.9, η_{col}=94%; for SWNT@TiO_2 nanocomposites, L_n/L=12.1, η_{col}=99.8%.

CNT/TiO_2& SWNTs@(TiO_2/Ag/Au)

As shown in the figures below, the DSSCs with SWNTs@(TiO_2/Ag/Au) composites have a PCE of 8.3%, while the PCE of the DSSCs with SWNTs are 6.6%. The Jsc, Voc, andη_{COL} of DSSCs with SWNTs@(TiO_2/Ag/Au) composites are better too. Thus, DSSCs with SWNTs@(TiO_2/Ag/Au) composites have has better performance than DSSCs with SWNTs.

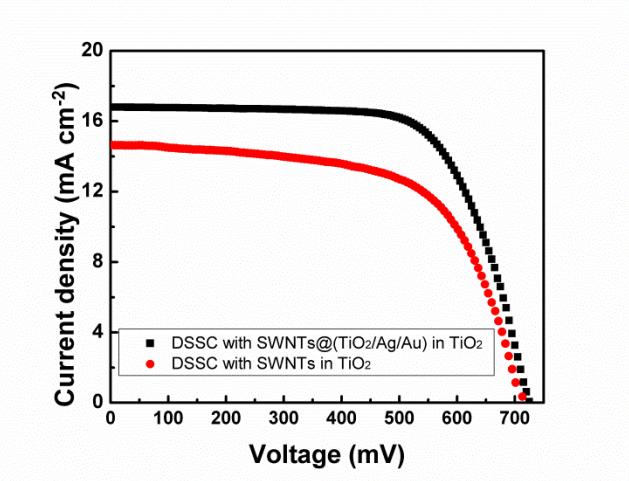


Figure R4 J-V curves of DSSC with SWNTs@(TiO_2/Ag/Au) and SWNTs.

Table R3 Photovoltaic parameters of DSSC with SWNTs and SWNTs@(TiO_2/Ag/Au)

Sample DSSCs	Jsc (mA cm^{-2})	Voc (mV)	FF (%)	PCE (%)	η_{COL} (%)
SWNTs@(TiO_2/Ag/Au)	16.8	722	69.7	8.3	99.7
SWNTs	14.6	716	62.2	6.6	98.1

Reference

[1] Xiangnan Dang, Hyunjung Yi, Moon-Ho Ham, Jifa Qi, Dong Soo Yun, Rebecca Ladewski, Michael S. Strano, Paula T. Hammond, Angela M. Belcher. Virus-templated self-assembled single-walled carbon nanotubes for highly efficient electron collection in photovoltaic devices. Nature Nanotechnology 2011; 6, 377-384.

[2] Janne Halme, Paula Vahermaa, Kati Miettunen, Peter Lund. Device Physics of Dye Solar Cells. Adv Mater 2010; 22, 210-234.

[3] Mingkui Wang, Peter Chen, Robin Humphry-Baker, Shaik M. Zakeeruddin, Michael Gratzel. The Influence of Charge Transport and Recombination on the Performance of Dye-Sensitized Solar Cells. ChemPhysChem 2009; 10, 290-299.

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[5] Juan Bisquert, Francisco Fabregat-Santiago, Iva´n Mora-Sero´, Germa` Garcia-Belmonte, Sixto Gime´nez. Electron Lifetime in Dye-Sensitized Solar Cells: Theory and Interpretation of Measurements. J Phys Chem C 2009;113, 17278-17290.