Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information

Design and coupling of multifunctional TiO_2 nanotube photonic crystal to nanocrystalline titania layer as semi-transparent photoanode for dye-sensitized solar cell

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Simulation and theoretical calculations:

For the theoretical calculations, the light harvesting efficiency (LHE) is defined as the fraction of light intensity absorbed by the dye at a certain wavelength in the DSSC[1, 2]:

$$\mathrm{LHE}=A=I_A/I_0 \tag{1}$$

where A is absorptance, I_A is the absorbed intensity and I_0 is the incident one. IPCE is defined as the number of generated electrons divided by the number of incident photons, which is proportional to LHE or absorptance, and given by the following equation[3]:

$$\mathrm{IPCE}=(\mathrm{LHE})\varphi\eta=A\varphi\eta \tag{2}$$

where φ is the quantum yield of charge injection, and η is the charge-collection efficiency by the photoanode. The generated J_{sc} can be calculated by the expression[2]:

$$J_{sc}=\int q\mathrm{IPCE}(\lambda)F(\lambda)\mathrm{d}\lambda=\int q\mathrm{LHE}(\lambda)\varphi(\lambda)\eta(\lambda)F(\lambda)\mathrm{d}\lambda \tag{3}$$

where q is the electron charge, and $F(\lambda)$ is the incident photon flux, which is calculated from the standard AM1.5 solar spectral irradiance[4]. Since, in our study, $\varphi(\lambda)$ and $\eta(\lambda)$ are weakly dependent of the wavelength λ, equation (3) can be simplified to the following form:

$$J_{sc}=\int q\mathrm{LHE}(\lambda)F(\lambda)\mathrm{d}\lambda=\int qA(\lambda)F(\lambda)\mathrm{d}\lambda \tag{4}$$

By comparing the absorptance of the TiO_2 NT PC based DSSC ($\mathrm{LHE_{pc}}$) to that of the standard DSSC ($\mathrm{LHE_{standard}}$), the enhancement of the photocurrent efficiency $\Delta J_{sc}/J_{sc}$ can be estimated according to the following expression[2]:

$$\frac{\Delta J_{SC}}{J_{SC}}=\frac{\int LHE_{\mathrm{pc}}(\lambda)F(\lambda)d\lambda-\int LHE_{\mathrm{standard}}(\lambda)F(\lambda)d\lambda}{\int LHE_{\mathrm{standard}}(\lambda)F(\lambda)d\lambda} \tag{5}$$

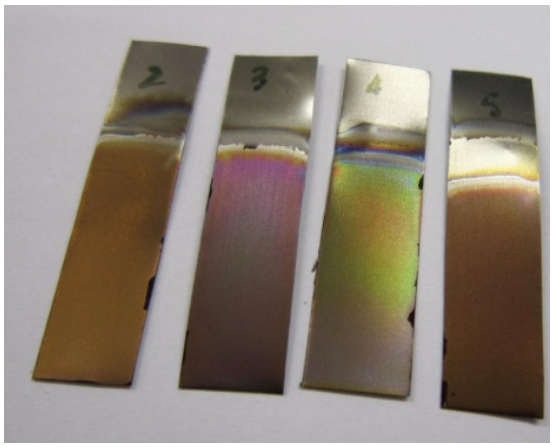

Fig. S1 Photographs of the TiO_2 NT PC samples with different HC pulse durations of 20, 30, 40 and 50s, from left to right, respectively.

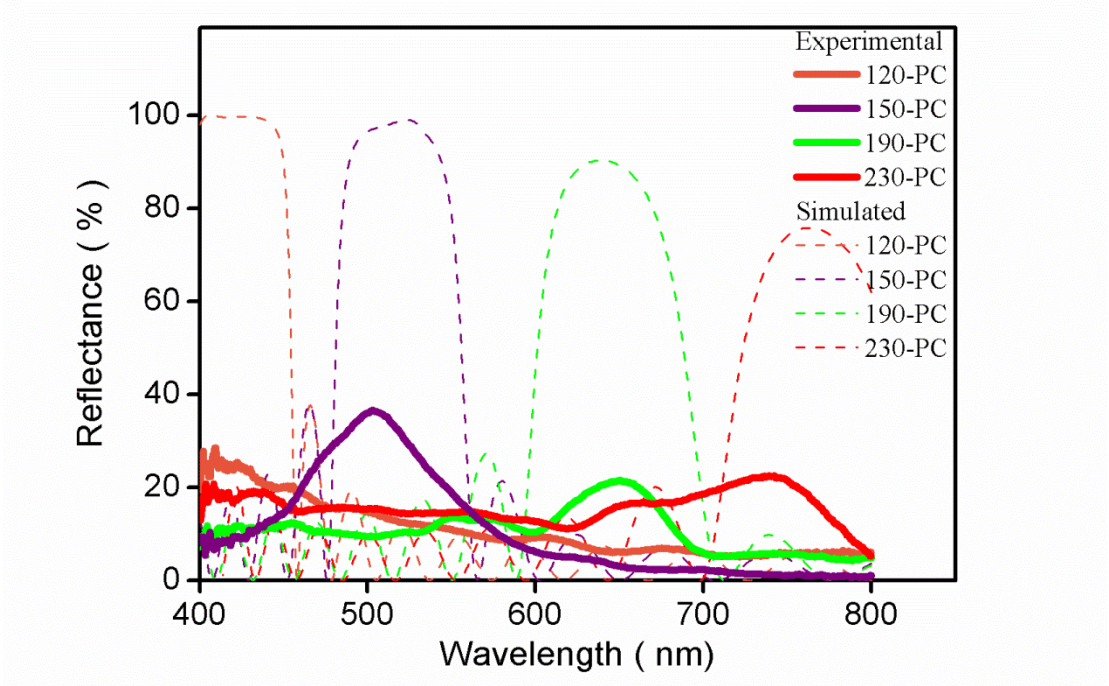

Fig. S2 Experimental and simulated reflectance spectra under near normal incidence on the photoanodes with lattice constants of 120, 150, 190 and 230 nm (120-PC/TiO_2 NP, 150-PC/TiO_2 NP, 190-PC/TiO_2 NP, and 230-PC/TiO_2 NP, respectively) in ethanol. The background reflectance from the FTO-coated glass substrate covered with TiO_2 NP was subtracted.

As seen from Fig. S3, the thickness of the TiO_2 NP absorbing layer and TiO_2 NT PC is about 10 and 2.3 μm, respectively, for the TiO_2 NT PC/TiO_2 NP photoanode (Fig. S3a and d). The thickness of TiO_2 NT/TiO_2 NP photoanode (Fig. S3b and e) is the same as that of the TiO_2 NT PC/TiO_2 NP one, while that of the TiO_2 NP layer is about 12 μm in the reference cell (Fig. S3c and f).

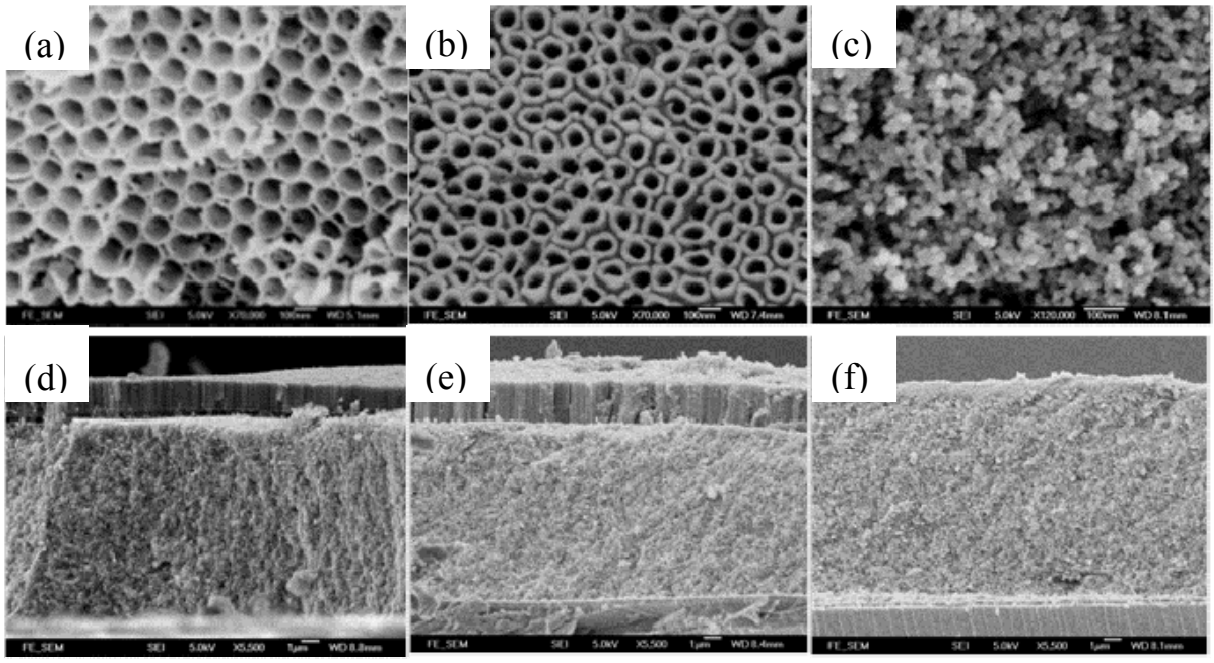

Fig. S3 (a) FESEM top view and (d) cross-section images of the TiO_2 NT PC/TiO_2 NP photoanode; (b) FESEM top view and (e) cross-section images of the TiO_2 NT /TiO_2 NP photoanode; (c) FESEM top view and (f) cross-section image of the TiO_2 NP photoanode.

Figure S4 shows the Bode phase plot of the electrochemical impedance spectroscopy (EIS) of different photoanodes. The electron lifetime (τ_r) was calculated from the plot shown in Fig. S4 by $\tau_r=1/(2\pi f_{peak})$, where f_{peak} is the frequency where the characteristic peak locates in the mid-frequency (1-100 Hz) range. It can be found that the electron lifetimes for all the photoanodes with TiO_2 nanotubes (no matter with or without the PC structure) are quite similar, ranging from 12.7~13.7 ms. This is slightly higher than that of the photoanode without nanotubes (TiO_2 NP), which is around 10.7 ms. Such an increase in the life time may contribute to the slight increase in V_{oc} from 0.68 eV (for photoanodes without nanotubes) to 0.69~0.70 eV (for photoanodes with nanotubes), but is insufficient to contribute significantly to the power conversion efficiency enhancement observed in our samples. For comparison, a 10-fold change in recombination rate generally results in a change of 0.05 eV in V_{oc} and a 2-fold change only shifts the V_{oc} by 0.02-0.03 eV.[5,6] The insignificant increase of electron lifetime in photoanodes (with TiO_2 nanotubes) can be attributed to the limited thickness of the nanotube layer used (as compared to the thickness of the nanoparticle layer).

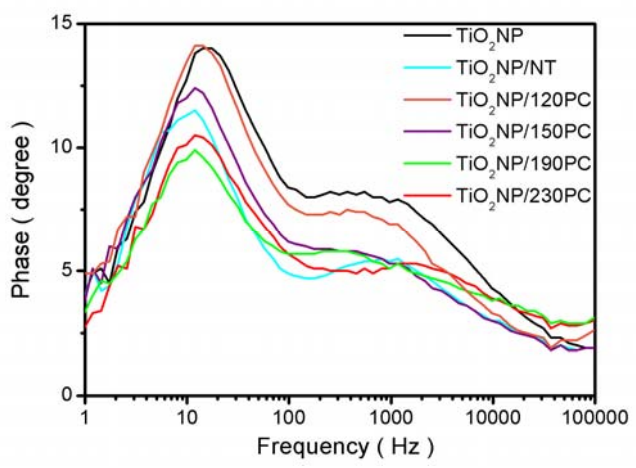

Fig. S4 Bode phase plots of different photoanodes measured with an alternating-current amplitude of 10 mV under the AM1.5 illumination.

It can be seen from Fig. S5 that, within the photonic bandgap range, the PC acts as a Bragg mirror to reflect photons back, which causes strong photon resonance modes in the absorbing layer. For the frequency at the red edge of the bandgap, the field maxima are located at the parts of higher refractive index (dye-sensitized TiO_2), which may also result in a higher red light absorption near the low-frequency edge of the bandgap. Meanwhile, at the high-frequency edge, the field maxima are shifted to the parts of lower refractive index (electrolyte).

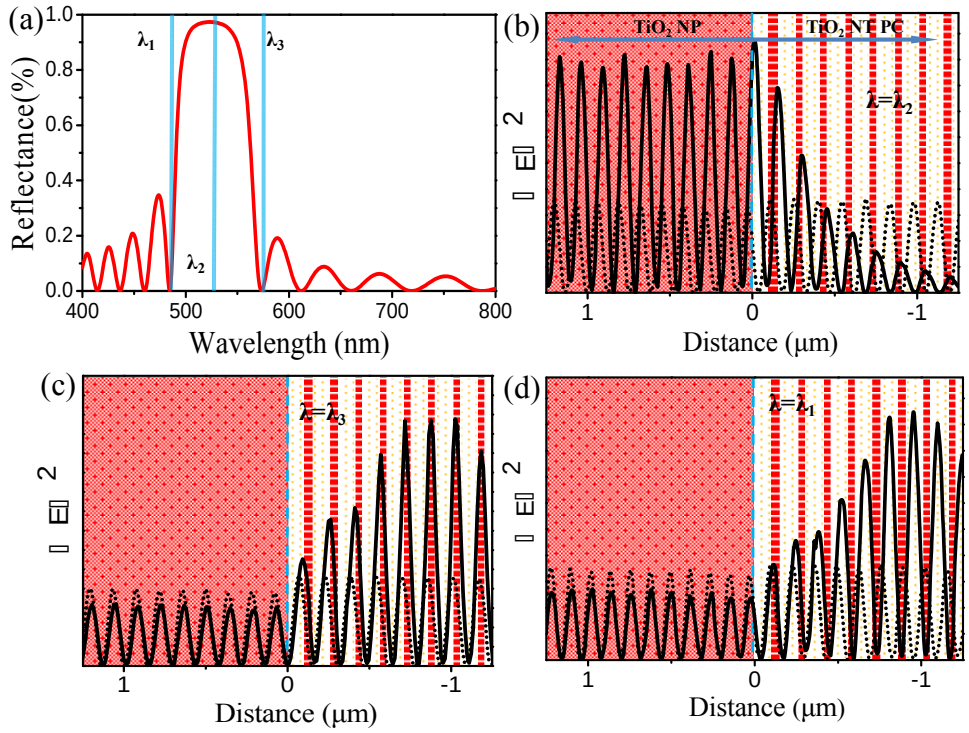

Fig. S5 (a) Simulated reflectance spectrum of NT PC (with lattice constants of 150nm) in electrolyte. (b-d) Distribution of the amplitude square of the electric field in different parts of the photoanode at three selected wavelengths shown in (a): (b) λ_2, within the bandgap, (c) λ_3, at the red edge and (d) λ_1, at the blue edge of the bandgap. For comparison, the distribution of the amplitude square of the electric field in a standard DSSC is also plotted (dotted line).

References:

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4. Standard spectrum taken from http://www.nrel.gov/r-redc/

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