Electronics Supporting Information

Surface Modification of TiO_2 Nanotube Arrays with Y_2O_3 Barrier Layer: Controlling Charge Recombination Dynamics in Dye-sensitized Solar Cells

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1. Surface morphologies of TiO_2 nanotube arrays

Figure S1 shows the dependence of the average diameter and length of TNT on the anodization period. Top and side view SEM images of the TNT anodized at 50 V for 30, 60, 90, 120, 150, 180, 240, and 300 min are shown in **Figure S2** and **Figure S3**, respectively. The average diameter of TNT remains constant for all of the anodization periods as estimated to be about 84 nm. However, the length of TNT increases with increasing anodization period; the lengths were found to be 4.71, 6.73, 8.35, 11.61, 13.26, 16.03, 21.22 and 23.75 μm for the TNT anodized for 30, 60, 90, 120, 150, 180, 240 and 300 min, respectively. A linear relationship is found between the length and the anodization period.

2. Photovoltaic performance and electrochemical impedance spectroscopy analysis of dye-sensitized solar cells with TiO_2 nanotube arrays

Photocurrent density–voltage (*J*–V) curves of the DSSCs with TNT obtained at the anodization voltage of 50 V and anodization periods of 30, 60, 90, 120, 150, 180, 240, and 300 min are shown in **Figure S4**, and the corresponding photovoltaic parameters are summarized in **Table S1**. The open–circuit voltage (V_{OC}) decreases steadily with increasing anodization period; this phenomenon may be attributed to the longer TNT obtained with longer periods of anodization. Longer TNT causes longer diffusion paths for electrons transferring from the point of photo–generation to the point of electron–collection. Longer diffusion path is tantamount to an increase of charge recombination, and thereby to a decrease of V_{OC}. On the other hand, the short–circuit current density (J_{SC}) increases regularly with increasing anodization period up to 240 min, due to the larger surface area available with increasing tube lengths. Larger surface area provides more sites for dye adsorption, so more electrons could be excited, leading to a higher J_{SC}. However, the J_{SC} decreases when the anodization period reaches 300 min. This is probably due to the serious charge recombination caused by the extremely long TNT in this case, *i.e.*, the enhancement in J_{SC} due to higher dye adsorption is smaller than the loss in J_{SC} resulting from the charge recombination reactions. As a result, the highest η of 5.35% was obtained for the DSSC with TNT anodized at 50 V for 240 min, with 0.64 V, 15.31 mA cm^{-2}, and 0.55 as the V_{OC}, J_{SC} and fill factor (*FF*), respectively. In addition, EIS technique was used to study the charge transfer resistances of the cells. **Figure S5** shows the EIS spectra of the DSSCs with TNT obtained by anodization at 50 V for 30, 60, 90, 120, 150, 180, 240, and 300 min, and the equivalent circuit is shown in the inset of this figure. The ohmic serial resistance (R_s) in the equivalent circuit corresponds to the overall series resistance.

In general, the impedance spectra of a DSSC show three semicircles in the frequency

range of 10 mHz to 65 kHz. The first, second and third semicircles correspond to the charge–transfer resistances at the counter electrode (R_{ct1}), at the TNTs/dye/electrolyte interface (R_{ct2}) and to the Warburg diffusion process of I^-/I_3^- in the electrolyte (R_{diff}), respectively. However, in our work the conventional diffusion resistance (R_{diff}) for the redox couple is virtually overlapped by R_{ct2} due to low viscosities of the solvents used in our electrolyte (viscosities of ACN and MPN are 0.37 cp and 1.60 cp, respectively). The corresponding values of R_{ct2} are shown in **Table 1**. The value of R_{ct2} decreases for the DSSC with TNT on its photoanode obtained by longer anodization period up to 240 min. The larger R_{ct2} value for the DSSC with smaller length of TNT prepared through shorter anodization period are supposed to have smaller surface area for dye adsorption, probably leading to fewer injected electrons, and thereby to a smaller electron density and ultimately to a weak driving force for electron transport. This weak driving force causes a high resistance in the photoanode containing the TNT obtained at shorter anodization period. With the same analogy a strong driving force causes a low resistance in the case of the TNT obtained at longer anodization period. However, when the anodization period for obtaining TNT reaches 300 min, the resistance increases relative to that of the TNT obtained for 240 min anodization. This is likely due to the serious recombination caused by the longer TNT obtained at the anodization period of 300 min.

Table S1 Photovoltaic parameters and the charge transfer resistances (R_{ct2}) of the DSSCs with TNT anodized at 50 V for 30, 60, 90, 120, 150, 180, 240, and 300 min, measured at 100 mW cm^{-2}.

Anodization period/min	V_{OC}/V	J_{SC}/mA cm^{-2}	FF	η (%)	R_{ct2}/Ω
30	0.76	3.66	0.63	1.74	62.04
60	0.74	6.10	0.63	2.82	53.65
90	0.72	7.00	0.58	2.94	47.89
120	0.69	10.00	0.59	4.04	41.18
150	0.68	11.31	0.60	4.65	28.33
180	0.68	12.56	0.59	5.05	26.71
240	0.64	15.31	0.55	5.35	21.41
300	0.62	13.13	0.55	4.53	32.91

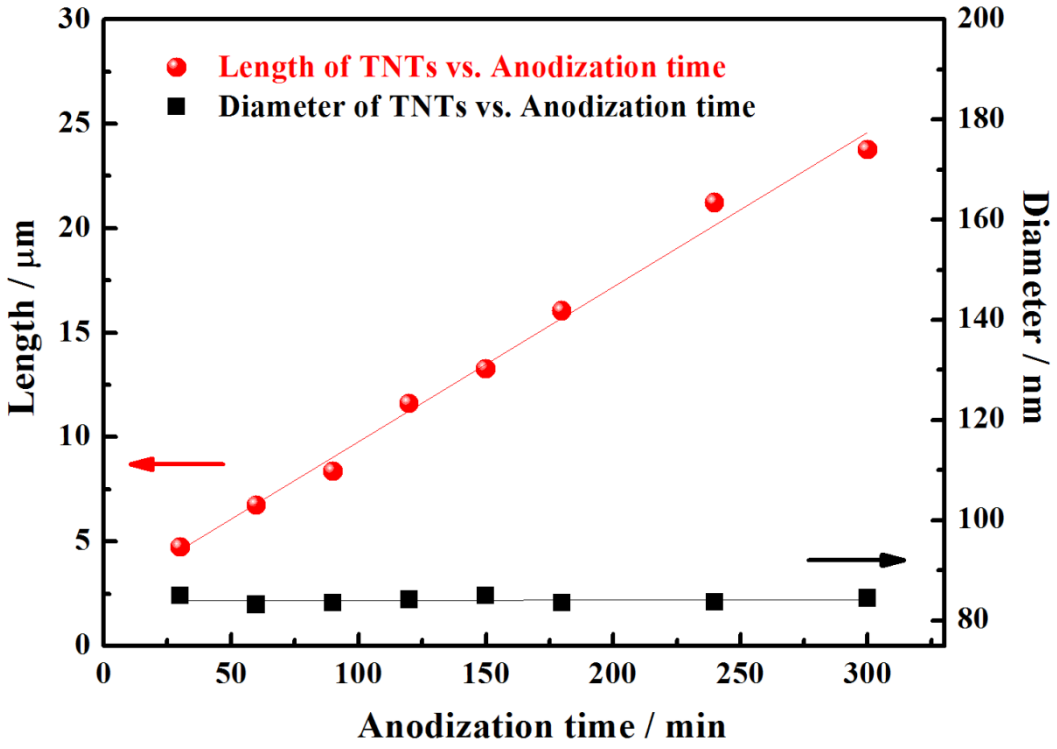

Figure S1 Dependence of the diameter and length of the TNT on the anodization period.

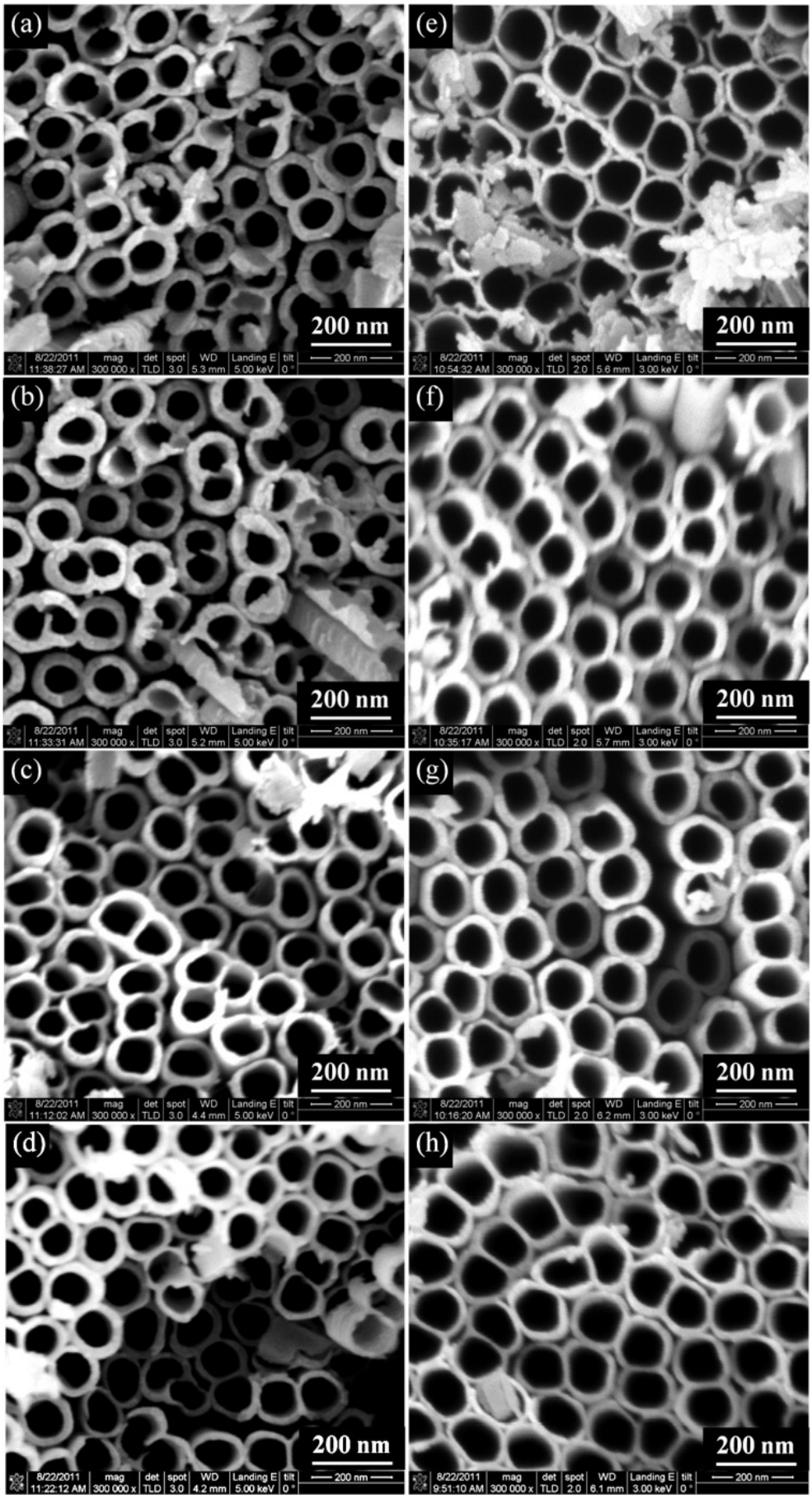

Figure S2 SEM images of the top views of TNTs anodized at 50 V for (a) 30, (b) 60, (c) 90, (d) 120, (e) 150, (f) 180, (g) 240 and (h) 300 min.

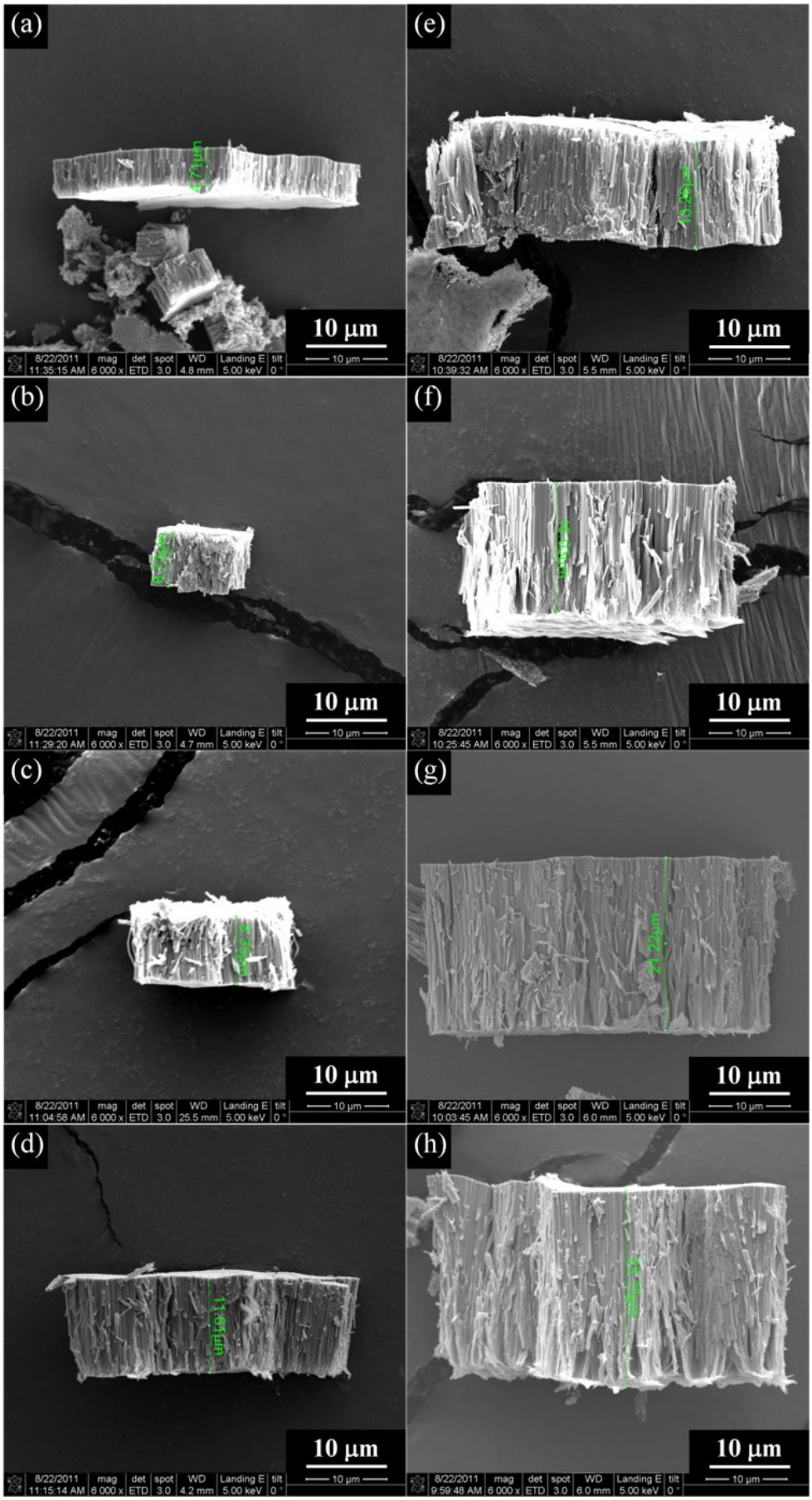

Figure S3 SEM images of the side views of TNTs anodized at 50 V for (a) 30, (b) 60, (c) 90, (d) 120, (e) 150, (f) 180, (g) 240 and (h) 300 min.

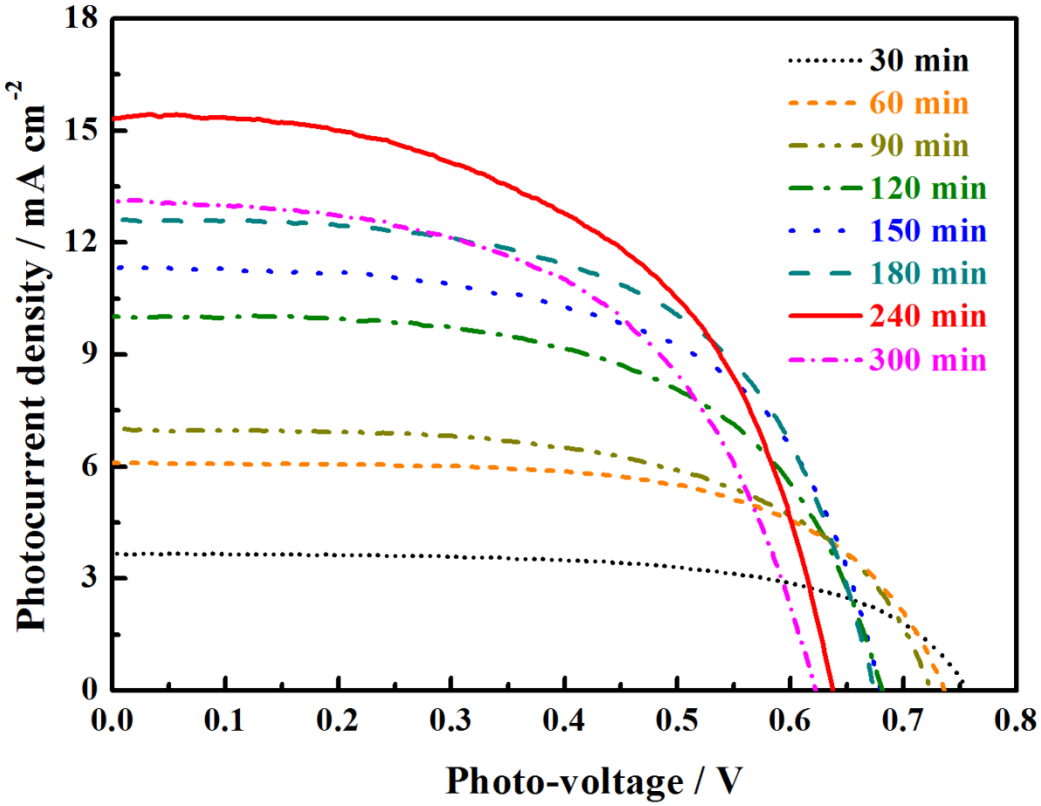

Figure S4 Photocurrent density–voltage curves of the DSSCs with TNT anodized at 50 V for 30, 60, 90, 120, 150, 180, 240, and 300 min, measured at 100 mW cm^{-2}.

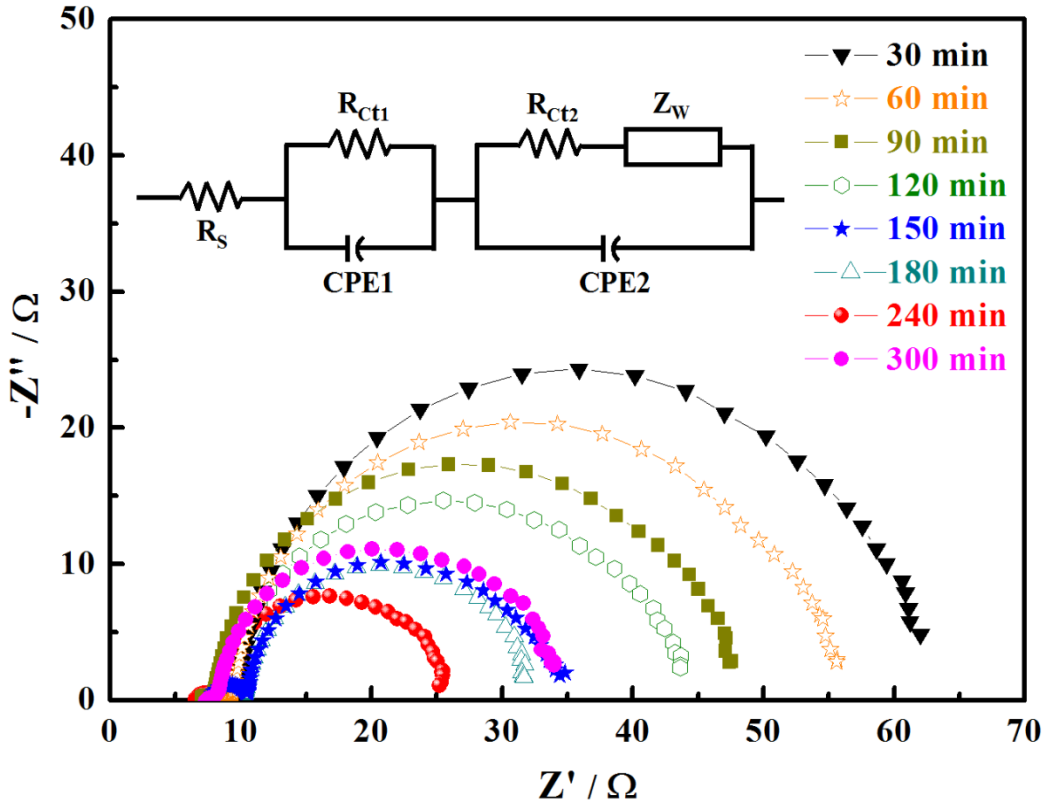

Figure S5 EIS spectra of the DSSCs with TNT anodized at 50 V for 30, 60, 90, 120, 150, 180, 240, and 300 min, measured at 100 mW cm^{-2} under open–circuit voltage.