## Supporting Information

## Changes of dye adsorption state induced by ferroelectric polarization to improve photoelectric performance

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## **Supplemental figures**



Figure S1 XPS spectra of BaTiO<sub>3</sub> powder (up), XPS spectra of B/T(4) powder (down)

XPS was used to confirm the presence and chemical states of Ba, O and Ti in our samples. As shown in Figure S1, the Ba<sub>3d</sub> photoelectron peak from BaTiO<sub>3</sub> and B/T(4)was almost unchanged. The signal-to-noise ratio of B/T(4) spectrum decreased, indicating that BaTiO<sub>3</sub> was covered by TiO<sub>2</sub>. Compared to BaTiO<sub>3</sub>, the Ti<sub>2p</sub> photoelectron peak from B/T(4) revealed positive shift about 0.5eV. This can be attributed to the formation of TiO<sub>2</sub>. The O<sub>1s</sub> spectrum for B/T(4) can be deconvoluted to three peaks. The large peak at 529.75 eV from B/T(4) was assigned to lattice oxygen in BaTiO<sub>3</sub> and TiO<sub>2</sub>, whereas the photoelectron peaks located at 531.84eV and 533.02 eV could be attributed to hydroxyl O atoms and C-O groups, respectively. TiO<sub>2</sub> induced increasement of hydroxyl O atoms peak intensity and the appearance of the peak of C-O groups.These observations confirmed the coating of TiO<sub>2</sub> on BaTiO<sub>3</sub> by TiCl<sub>4</sub> treatment.<sup>1-4</sup>



Figure S2. Current density-voltage characteristics of the DSSCs employing the  $B/T((0)\sim(5))$  photoanodes.

Table S1. Photovoltaic properties of DSSCs employing the $B/T((0)\sim(5))$ photoanodes.							
Samples	$J_{ m sc}$	$V_{ m oc}$	FF	PCE	Dye loading		
	(mA cm <sup>-2</sup> )	(mV)		(%)	(×10 <sup>-8</sup> mol cm <sup>-2</sup> )		
B/T(0)	0.07	760	0.45	0.03	0.49		
B/T(1)	3.89	740	0.83	2.39	0.66		
B/T(2)	7.70	740	0.71	4.08	0.75		
B/T(3)	9.04	740	0.71	4.76	0.87		

B/T(4)	12.59	745	0.66	6.22	1.24
B/T(5)	4.25	720	0.67	2.07	2.26

The photoelectric performance of the film affected by cycles of TiCl<sub>4</sub> treatment is presented in Figure S2. The corresponding photovoltaic parameters are listed in Table S1. The PCE of the DSSC with B/T(0) photoanode (pure BaTiO<sub>3</sub>) was close to zero and increased to 2.39% after 1 cycle of TiCl<sub>4</sub> treatment. The cell with B/T(4) photoanode obtains the maximum  $J_{sc}$  and PCE of 12.59 mA cm<sup>-2</sup> and 6.22% respectively. With the increase cycles of TiCl<sub>4</sub> treatment, the  $J_{sc}$  changed most obviously among all the photovoltaic parameters of the cell. One of the reason about the  $J_{sc}$  enhancement was associated with the increment of TiO<sub>2</sub> particles amount as shown in TEM (Fig. 2b~f), which could absorb more dye. In addition, more and more TiO<sub>2</sub> particles made cohesiveness between particles better and formed conductive network promoting electrons transportation. On the other side, much more TiO<sub>2</sub> particles made the pores in the nanocrystalline film smaller and even blocked the channels, thus inhibiting the penetration of electrolyte. That was the reason for the reduction of the  $J_{sc}$  after the 5 cycles of the TiCl<sub>4</sub> treatment.



Figure S3. The cross-section SEM images of BaTiO<sub>3</sub> with one layer (a), two layers (b), three

layers (c) and the current density-voltage characteristics of the DSSCs employing the B/T(4) photoanodes of different BaTiO<sub>3</sub> layer number.

Table S2. Photovoltaic properties of DSSCs employing the B/T(4) photoanodes of different BaTiO<sub>3</sub> layer number

Layer number	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	V <sub>oc</sub> (mV)	FF	PCE (%)	Thickness of BaTiO <sub>3</sub> thin films (μm)
One layer	12.59	745	0.66	6.22	4
Two layers	10.87	775	0.72	6.06	4.2
Three layers	10.14	775	0.75	5.91	4.2

Figure S3 a~c shows the thickness of BaTiO<sub>3</sub> film of different layer number. We can observe that the thickness of BaTiO<sub>3</sub> film remains almost constant from one layer to three layers. The paste may be not easy to adhesive on the top of BaTiO<sub>3</sub> film. So, the successive paste did not increase film thickness very much. We also investigated the effect of the thickness of BaTiO<sub>3</sub> film of B/T(4) on the cell performances. The current density-voltage (J-V) curves are shown in Figure S2 and the photoelectric conversion parameters are listed in Table S2. As the number of BaTiO<sub>3</sub> layers increased, the  $J_{sc}$  and PCE of the cell decreased, and the  $V_{oc}$  and FF of the cell increased. As the BaTiO<sub>3</sub> film thickness increases not much with the film layers, dye adsorption amount is also only increase slightly. And multi-layer coating of BaTiO<sub>3</sub> may destroy the pore structure of the first layer. These reasons lead to the  $J_{sc}$  decline. The PCE of the cell with one BaTiO<sub>3</sub> layers, two BaTiO<sub>3</sub> layers and three BaTiO<sub>3</sub> layers were 6.22%, 6.06% and 5.91% respectively. Considering the best photoelectric performance, we choose BaTiO<sub>3</sub> film with one layer to prepare B/T(4) photoanode.

## References

- 1. Miot, C.; E. Husson, C.; Proust, R. E.; and Coutures, J. P.; *Journal of the European Ceramic Society* **1998**, 18, 339-343
- 2. Duan Y.D.; Fu, N.Q.; Liu, Q.P.; Fang, Y.Y.; Zhou, X.W.; Zhang, J.B.; and Lin, Y.,
- J. Phys. Chem. C 2012, 116, 8888-8893
- 3. Xu, H.; Zhang, L. J. Phys. Chem. C 2010, 114 (26), 11534–11541.
- 4. Bullock, E. L.; Patthey, L.; Steinemann, S. G., Surf. Sci. 1996, 352-354 (0), 504-510.