

## Supplementary Information to

### **Polarization-Enhanced Photoelectrochemical Properties of BaTiO<sub>3</sub>/BaTiO<sub>3-x</sub>/CdS Heterostructure Nanocubes**

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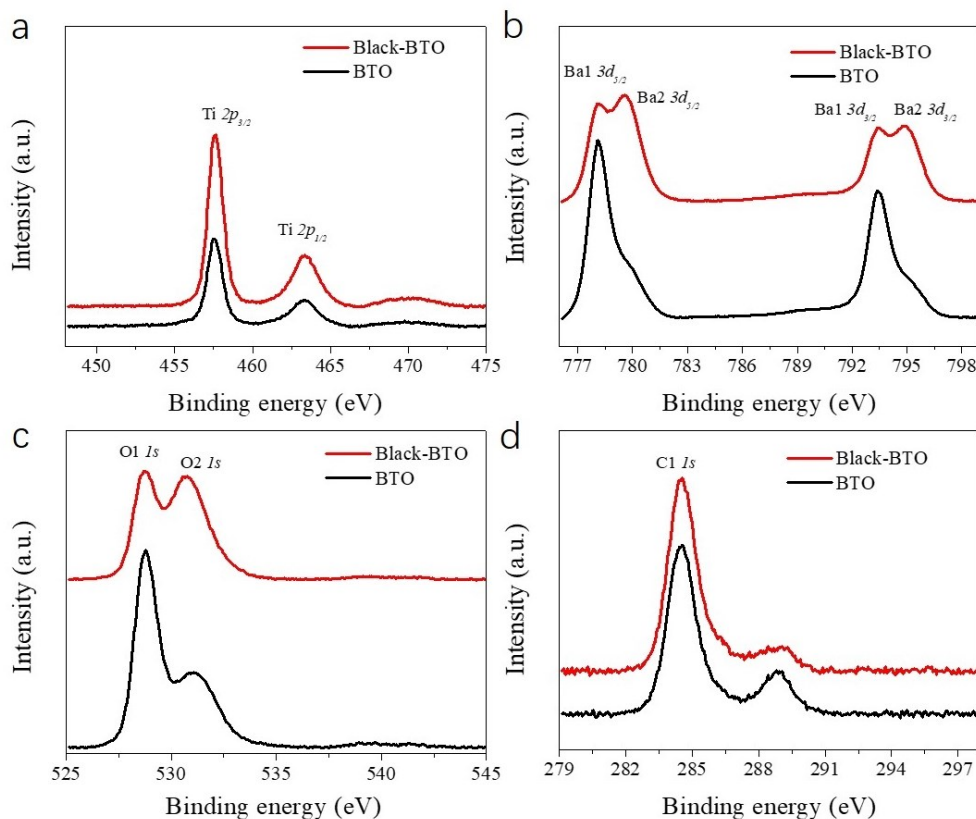
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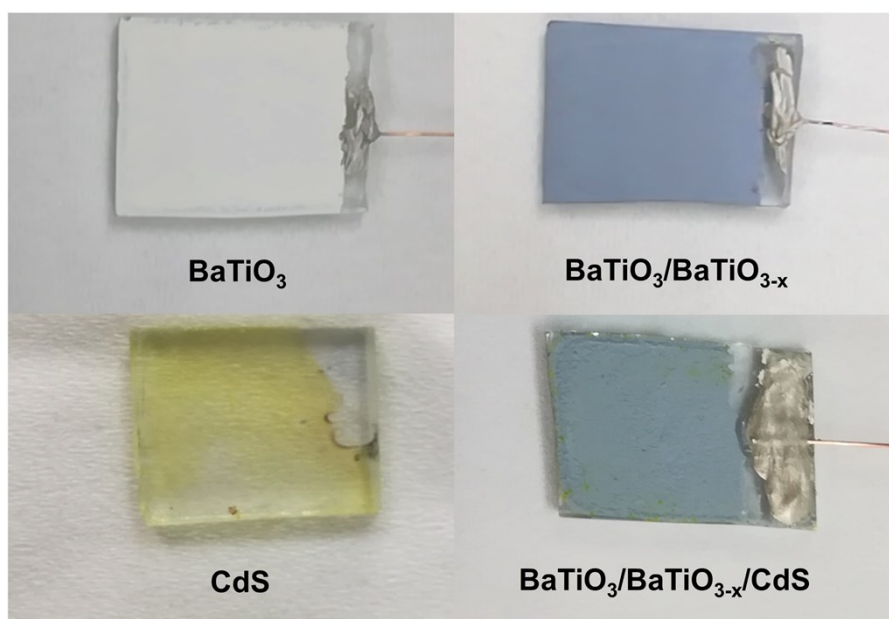
For pristine BaTiO<sub>3</sub>, the Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks center at binding energies of 458.2 eV and 463.9 eV, indicating a typical value of Ti<sup>4+</sup> in pristine BaTiO<sub>3</sub>.<sup>[1]</sup> For black-BTO, the Ti 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks shift notably to lower energy at 457.9 eV and 463.7 eV, which are intermediate value between those of Ti<sup>4+</sup> and Ti<sup>3+</sup> (457.6 eV for Ti 2p<sub>3/2</sub> and 463.5 eV for Ti 2p<sub>1/2</sub>).<sup>[2]</sup> Therefore, the shift of Ti 2p peaks should be related to the existence of Ti<sup>3+</sup> states in black-BTO surface induced by Al-reduction. Two chemical states for Ba and O at Al-reduced BaTiO<sub>3</sub> surface can be detected significantly in the XPS spectra of Ba 3d. For pristine BaTiO<sub>3</sub>, the Ba1 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks center at binding energies of 778.2 eV and 793.5 eV, which are consistent with the reported Ba<sup>2+</sup> in BaTiO<sub>3</sub>.<sup>[1]</sup> After Al reduction, two additional peaks defined as Ba2 3d<sub>5/2</sub> ~ 779.6 eV and 3d<sub>3/2</sub> ~ 794.9 eV appeared at the side of both Ba1 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks, which can be properly related to the change of the coordination environment of Ba induced by the oxygen vacancy. For both samples, the XPS peak of O 1s also exhibits two components: O1 1s at 528.8 eV corresponds to a perovskite environment of BaTiO<sub>3</sub> and O2 1s at 531.1 eV can be assigned to the adsorbed oxygen on the surface of the samples as reported previously. The contribution from surface adsorbed oxygen species (O2) to the O 1s spectra for black-BTO sample is significantly larger than that for the pristine BaTiO<sub>3</sub>, suggesting that the oxygen vacancy caused by Al-reduction treatments enhanced surface adsorption of oxygen species.

## References

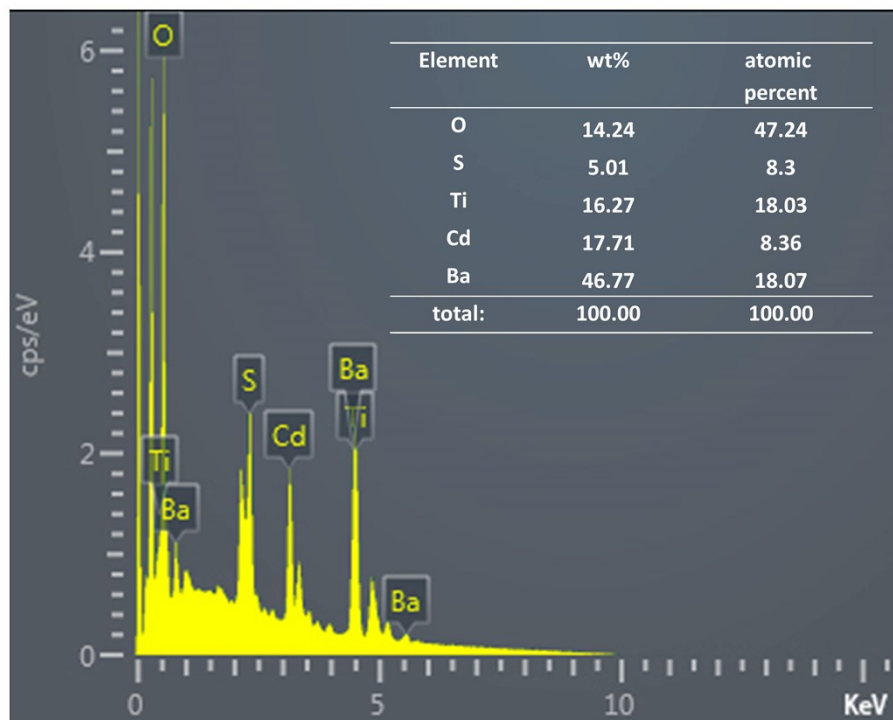
- [1] M. C. B. Lo'pez, G. Fournalis, B. Rand and F. L. Riley, *J. Am. Chem. Soc.*, 1999, **82**, 1777.  
 [2] S. Kumar, V. S. Raju and T. Kutty, *Appl. Surf. Sci.*, 2003, **206**, 250.



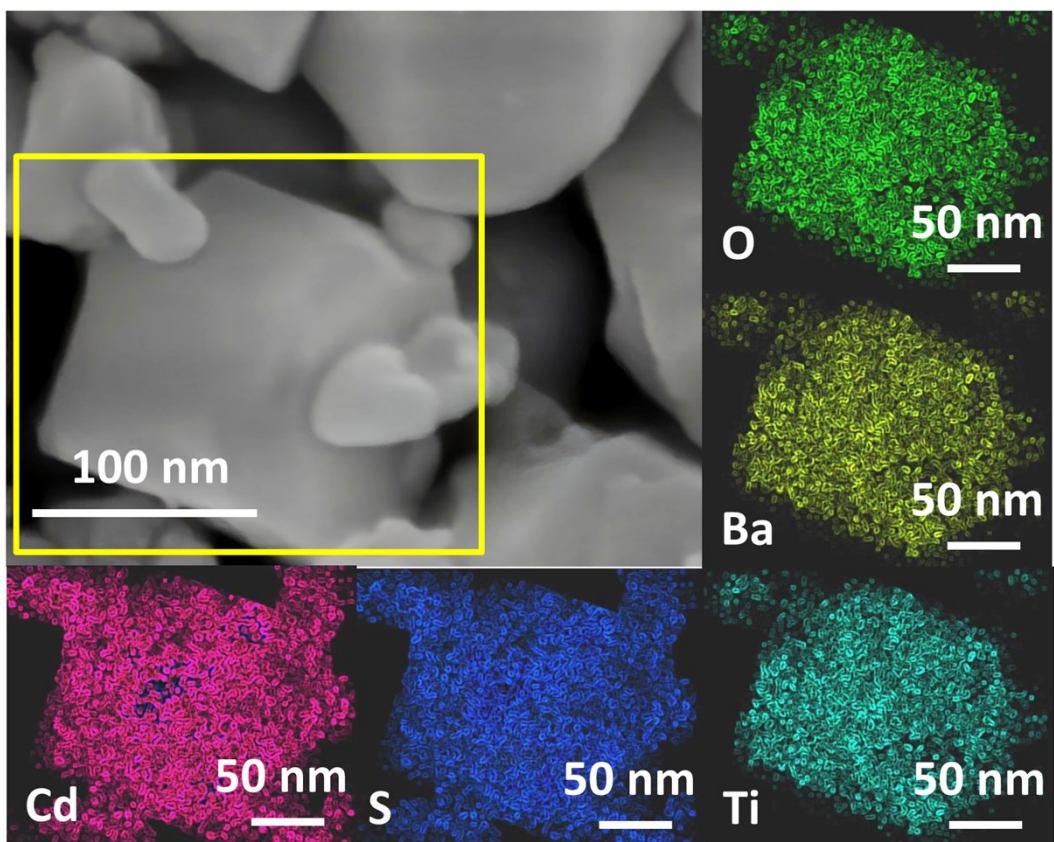
**Fig. S1.** The XPS spectra of Ti 2p (a), Ba 3d (b), O 1s (c) and C 1s (d) reference for BaTiO<sub>3</sub>/BaTiO<sub>3-x</sub>/CdS composite sample.



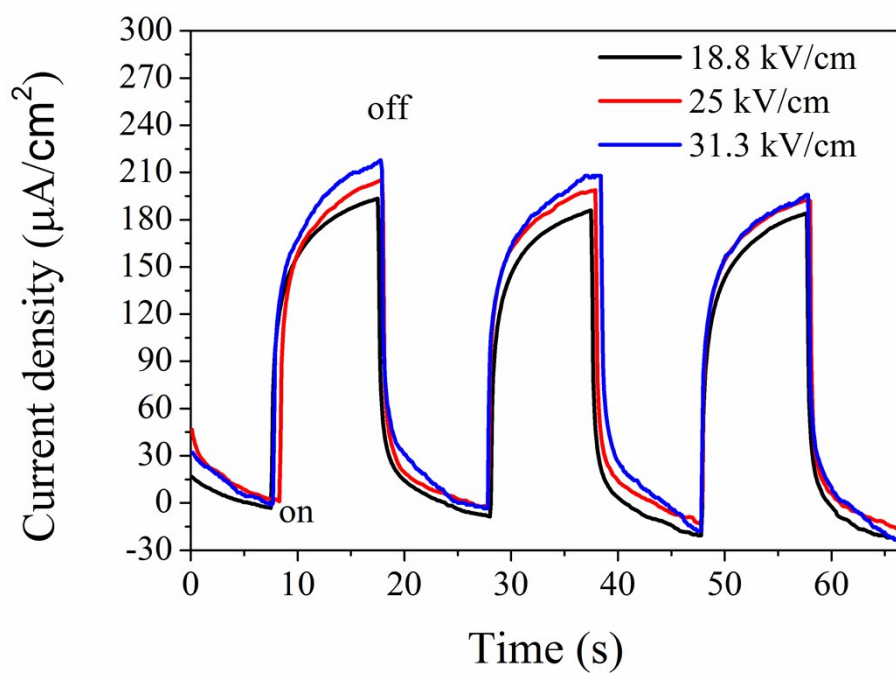
**Fig. S2.** Optical photographs of film electrodes



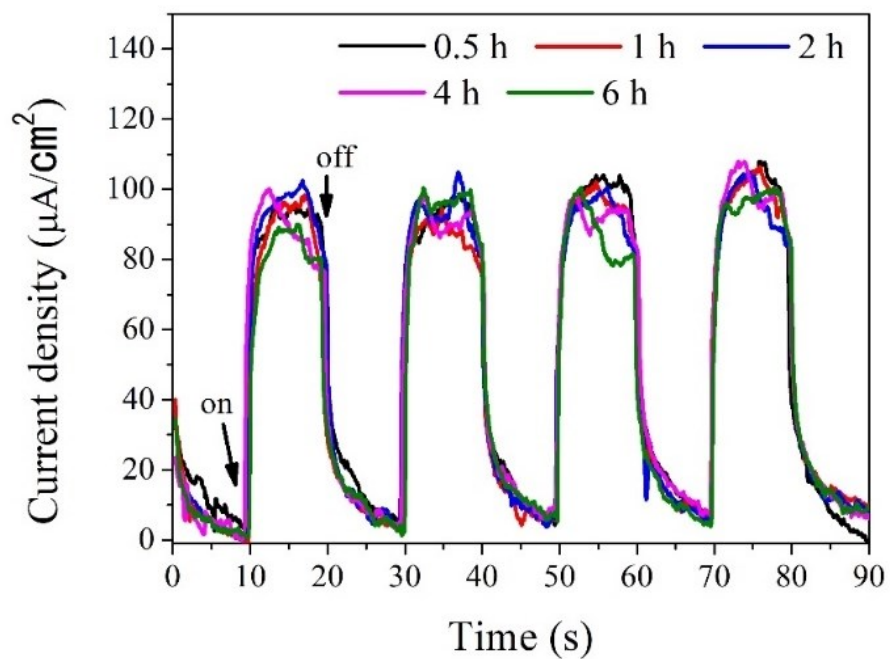
**Fig. S3.** EDS spectra with element ratio table of an individual particle of BaTiO<sub>3</sub>/BaTiO<sub>3-x</sub>/CdS composite sample.



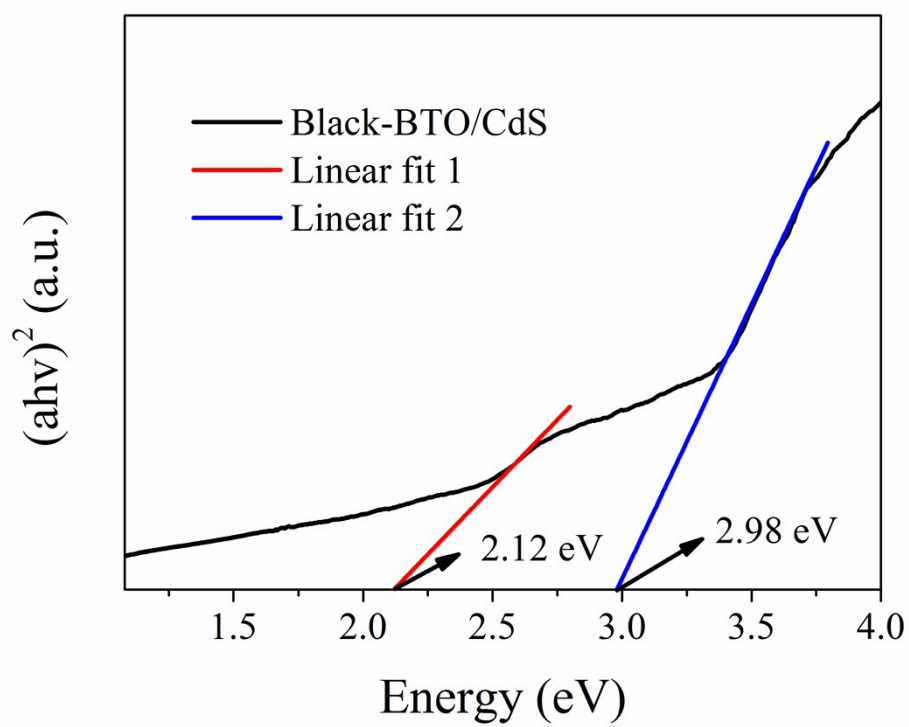
**Fig. S4.** The element mapping images of an individual particle of  $\text{BaTiO}_3/\text{BaTiO}_{3-x}/\text{CdS}$  composite sample.



**Fig. S5.** Photocurrent transient responses of the composite film after poling at positive polarization electric field  $> 18.8$  kV/cm.

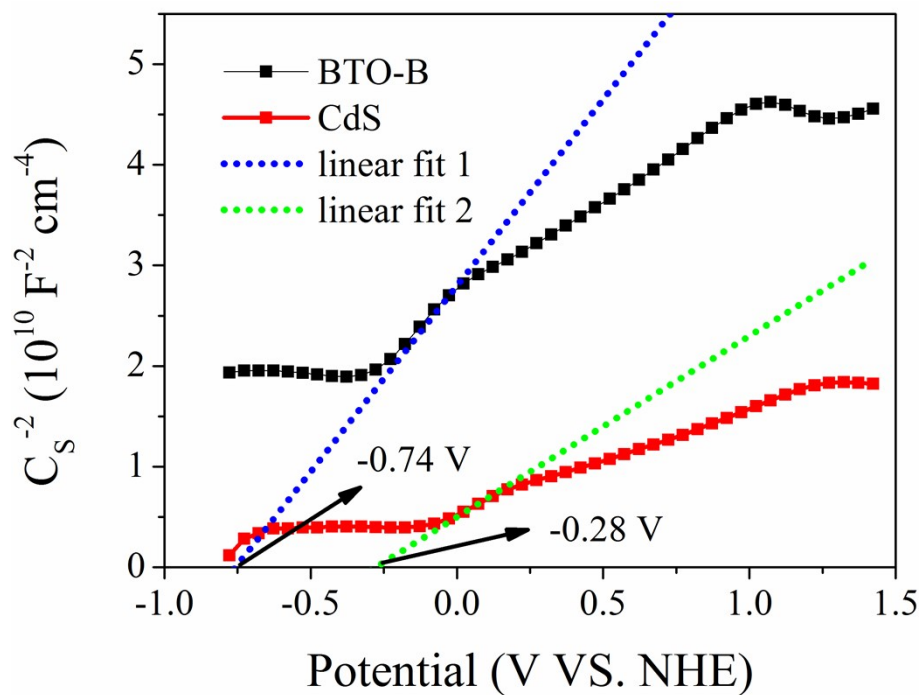


**Fig. S6.** Photocurrent transient responses of BaTiO<sub>3</sub>/BaTiO<sub>3-x</sub>/CdS composite films after exposing at different radiation time.

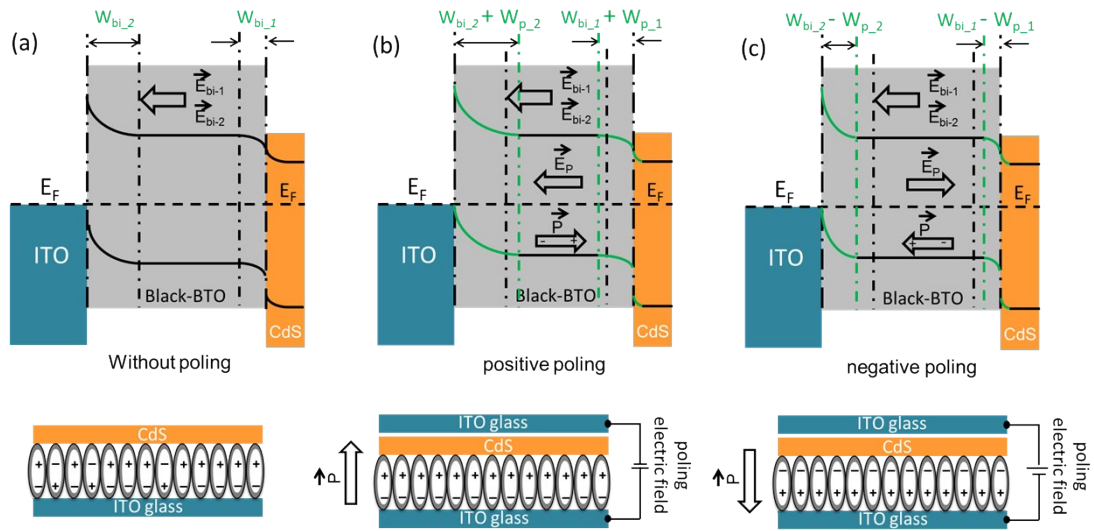


**Fig. S7.** UV-vis-NIR diffuse reflectance spectrum and bandgap of  $\text{BaTiO}_3/\text{BaTiO}_{3-x}/\text{CdS}$  composite sample after longtime illumination (6 h).





**Fig. S8.** The Mott-Schottky plots of BaTiO<sub>3</sub>/BaTiO<sub>3-x</sub> and CdS (electrolytes: [Na<sub>2</sub>SO<sub>4</sub>] = 0.5 M).



**Fig. S9.** Schematic and band diagram of the composite films under different poling conditions: (a) without poling, (b) positive poling, and (c) negative poling.