Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Engineering heterostructured $Ti_4O_5/BaTiO_3$ ferroelectric by surface reconstruction for enhanced photocatalytic CO_2 reduction

Ran Su[1#], Zhitong Sun[1#], Chao He[1#], Suna Wei[1], Lanju Chen[1], Dawei Zhang[2], Zhipeng Wang[3*], Xingtao An[1*], Fa-tang Li[1*],

[1]College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China

[2]School of Materials Science and Engineering, University of New South Wales Australia, Sydney, New South Wales 2052, Australia

[3]Frontier Institute of Science and Technology, State Key Laboratory for Mechanical behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

[#] These authors contributed equally: Ran Su, Zhitong Sun, Chao He.
[*] Corresponding authors
lifatang@126.com (F.T. Li); gstswzp@gmail.com; anxt2005@163.com

Additional Experimental.

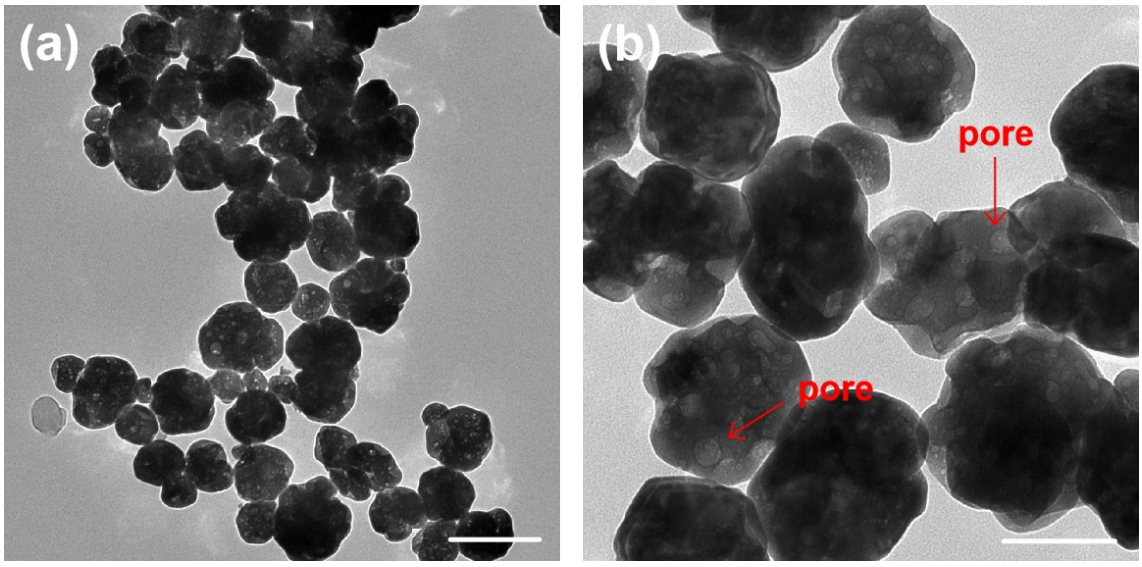

Fig. S1 TEM image of *b*-$BaTiO_3$ NPs showing lots of mesopores on the surface of nanoparticles.

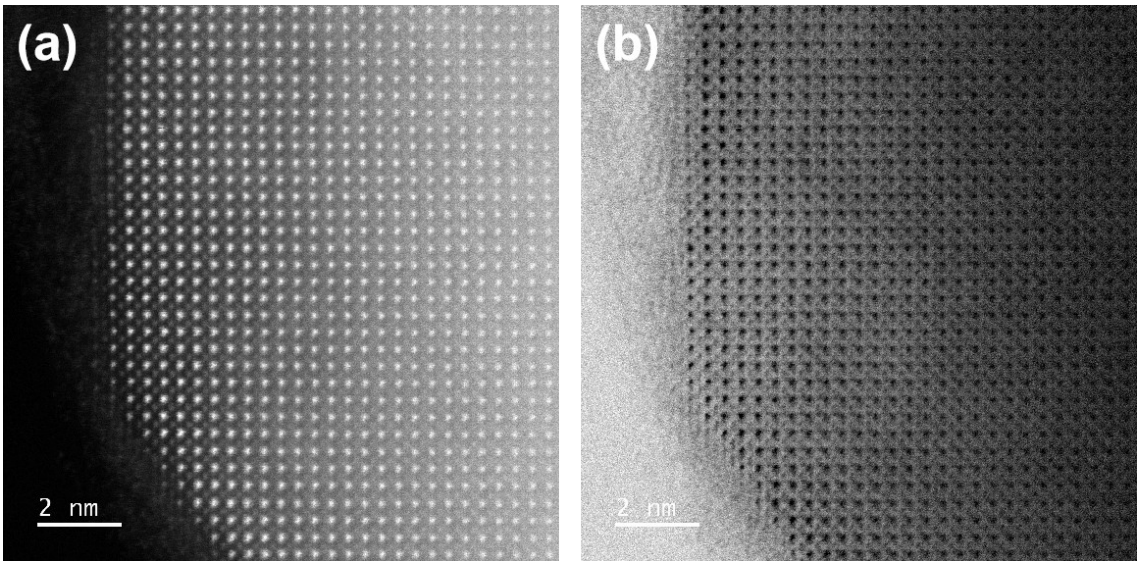

Fig. S2 HAADF-STEM (a) and HAADF-STEM ABF (b) images of the surface region of pristine $BaTiO_3$.

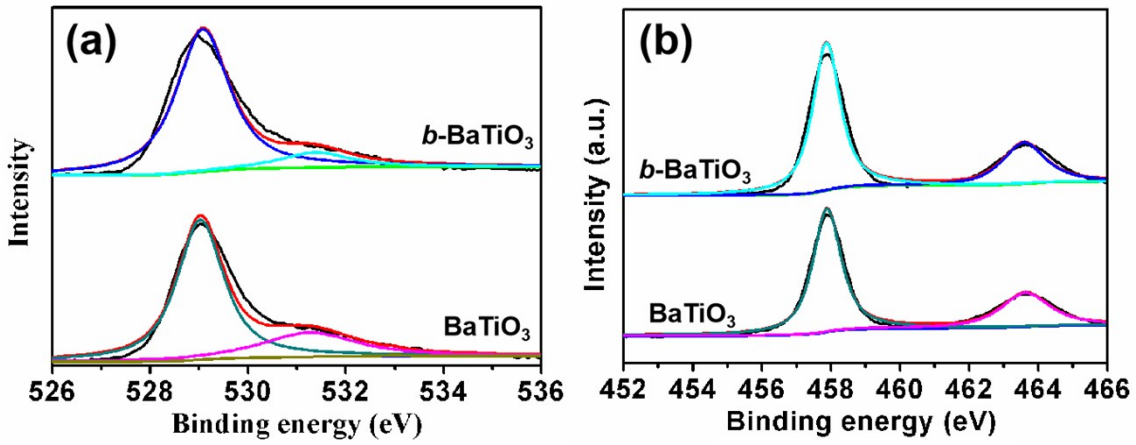

Fig. S3 O 1s spectra (a) and Ti 2p spectra (b) of the *b*-$BaTiO_3$ and pristine $BaTiO_3$. The XPS data reveal that the pristine $BaTiO_3$ and *b*-$BaTiO_3$ show almost no signal from oxygen vacancies and Ti^{3+}.

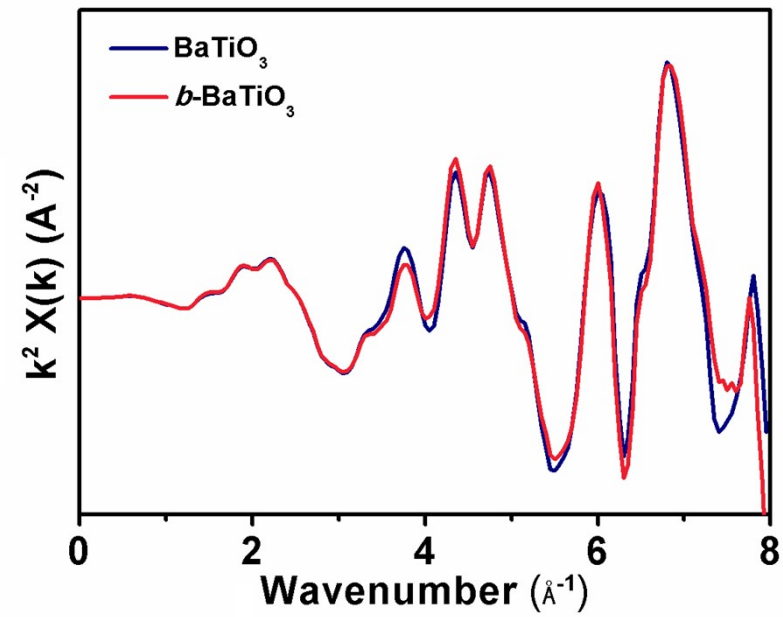

Fig. S4 Ti K-edge EXAFS oscillation function k2χ(k) for pristine $BaTiO_3$ and *b*-$BaTiO_3$.

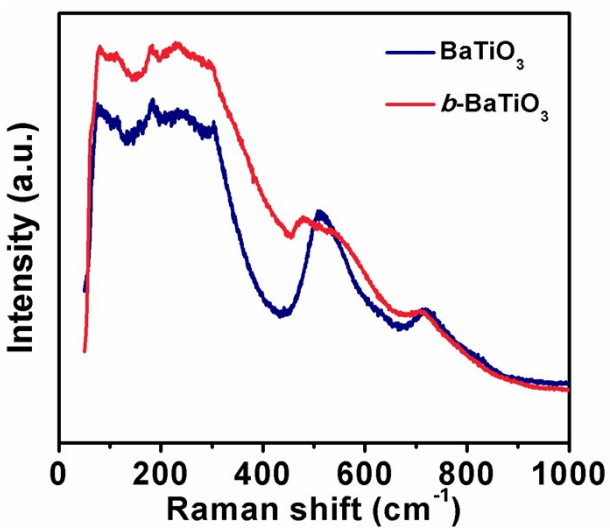

Fig. S5 Room temperature Raman spectra of the pristine $BaTiO_3$ NPs and *b*-$BaTiO_3$.

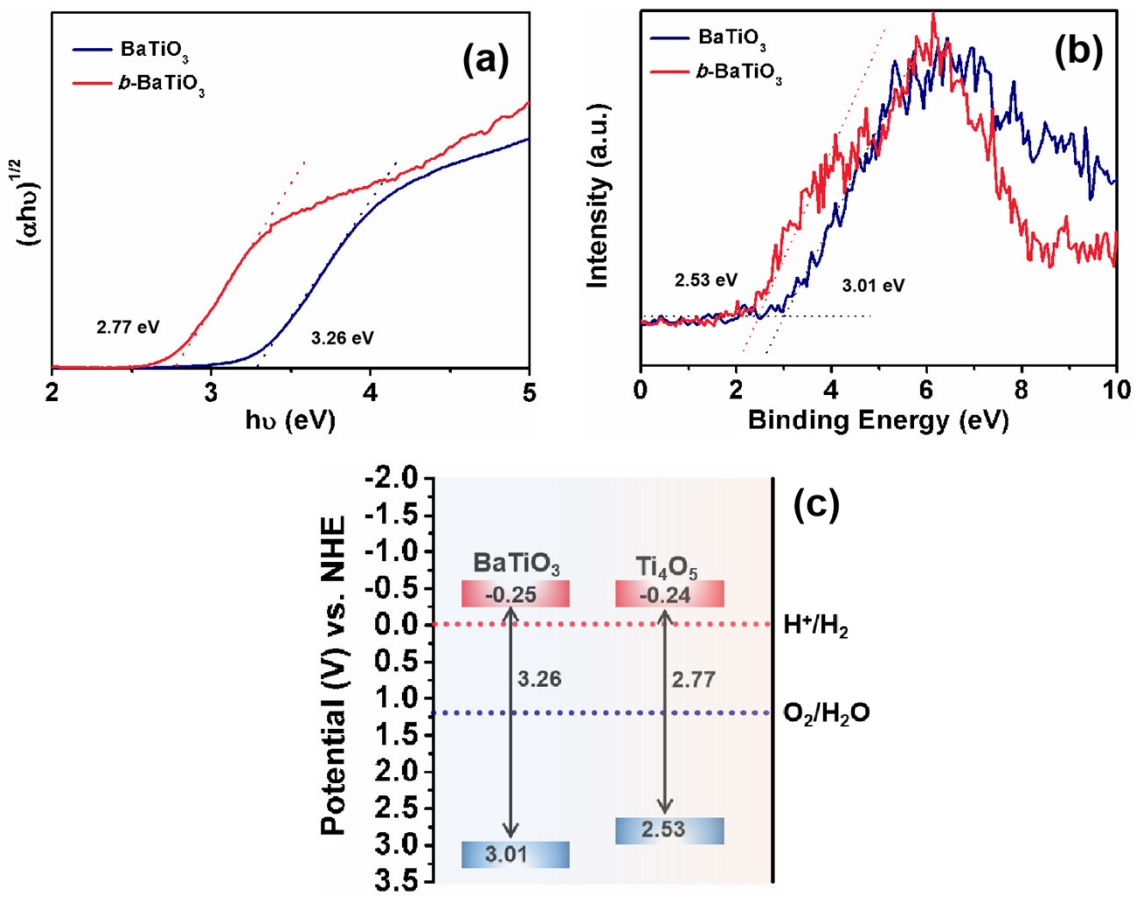

Fig. S6 (a) Tauc plot of the samples for determining bandgap. (c) Valence band XPS of the pristine $BaTiO_3$ NPs and *b*-$BaTiO_3$. (d) Band energy diagram of *b*-BaTiO3.

The band gap (Eg) values of the pristine $BaTiO_3$ and *b*-$BaTiO_3$ nanoparticles are calculated to be 3.26, and 2.77 eV, respectively. The The band gap (Eg) value of the pristine $BaTiO_3$ is equivalent to the $BaTiO_3$ bulk in ferroelectric heterostructure (*b*-$BaTiO_3$).The valence band values are determined to be 3.01 eV and 2.53 eV for the pristine $BaTiO_3$ and Ti_4O_5 in *b*-$BaTiO_3$ nanoparticles, respectively. Based on the UV-vis absorbance and XPS valence band, the positions of the valence band and conduction band of ferroelectric heterostructure (*b*-$BaTiO_3$) are presented.

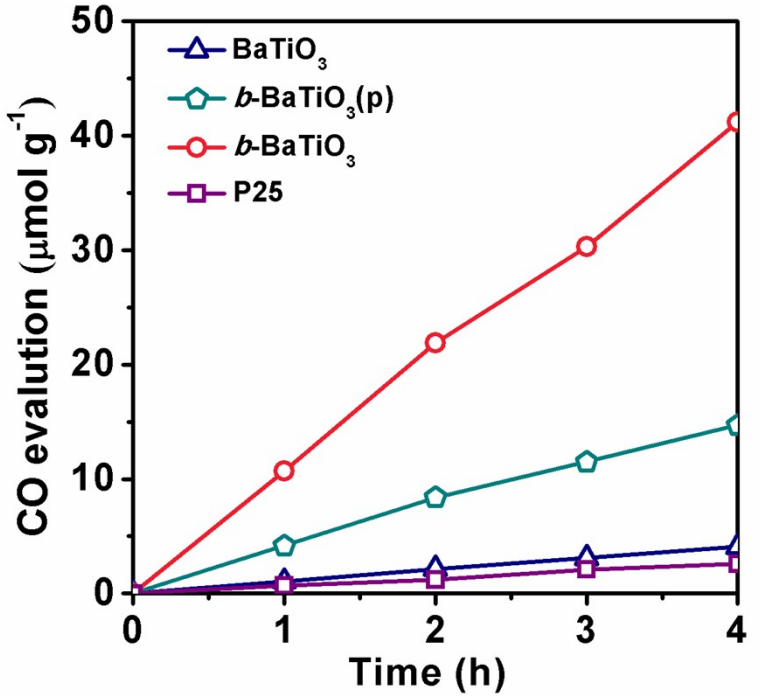

Fig. S7 Time courses of photocatalytic CO evolutions for $BaTiO_3$, *b*-$BaTiO_3$(b), $BaTiO_3$ and P25.

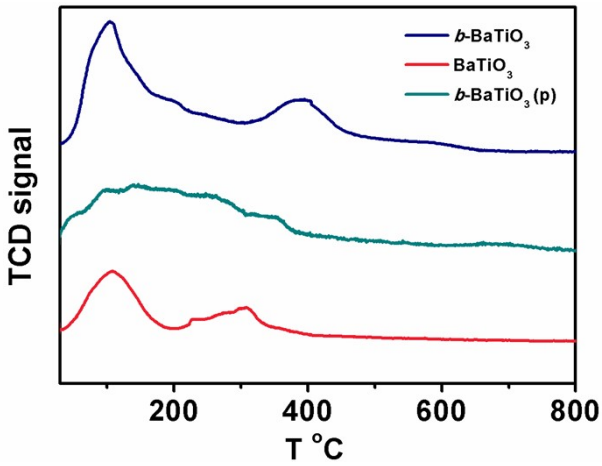

Fig. S8 CO_2-TPD profiles of the pristine $BaTiO_3$, *b*-$BaTiO_3$ and *b*-$BaTiO_3$(p), respectively.

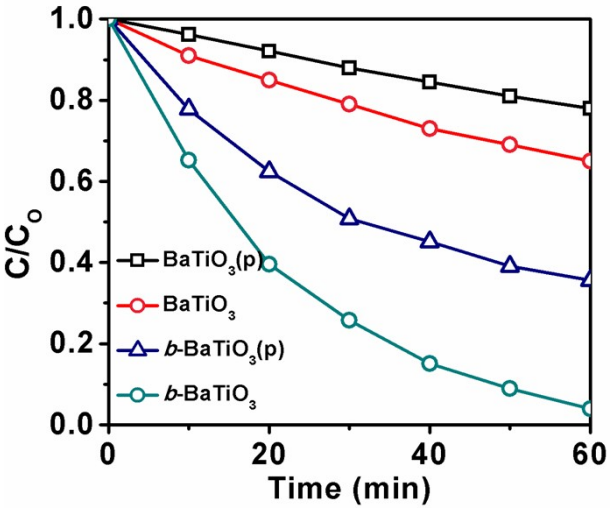

Fig. S9 Decomposition of Rh B by $BaTiO_3$(p) NPs, $BaTiO_3$ NPs, *b*-$BaTiO_3$(p) NPs and *b*-$BaTiO_3$ NPs, respectively.

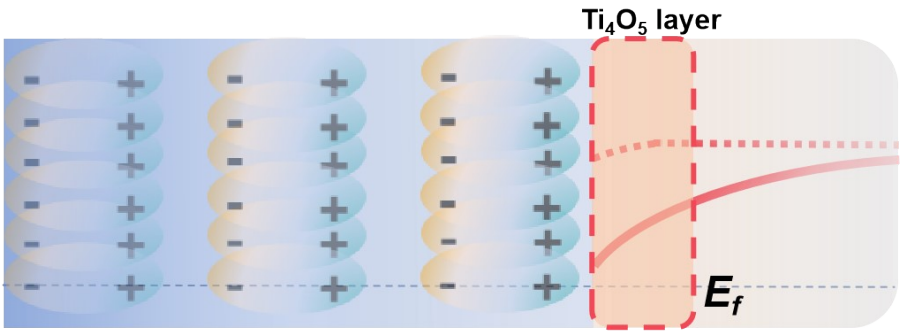

Fig. S10 Schematic band diagrams of semiconductor/ferroelectric heterojunction.