Supporting information

Mars-van-Krevelen mechanism-based blackening of nano-sized white semiconducting oxides for synergetic solar photo-thermocatalytic degradation of dye pollutants

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1. Computational details

The computational calculations were performed within DFT method. The general gradient approximation (GGA) with Perdew-Burke-Enzerhoff (PBE) functional and ultrasoft pseudo-potentials were used to describe the exchange correlation effects and electron-ion interactions, respectively, with kinetic energy cutoffs of 340.0 eV. The k-points were set to $4 \times 4 \times 1$, Structure optimization was performed by minimizing the total energy and the ionic force, until all the components of the residual forces were less than 0.03 eV/Å. The energy and the displacement tolerances were set to 1.0×10^{-5} eV/atom, and 1.0×10^{-3}Å, respectively. All the calculations have been performed in CASTEP codes.

The optimized bulk lattice parameters were a=3.78904 Å, b=3.78904 Å, c=8.3475 Å. The (001) surface were modeled by vacuum slabs with a thickness of 15 Å and the number of the atom layers is 4.

2 Synthesis of the ZnO nanocrystal powder

The synthesis of nano sized ZnO nanocrystal was prepared by direct precipitation method, according to a previous work [S1].

In details, firstly, 50 mL of $Zn(NO_3)_2$ aqueous solution with concentration of 1 wt% was

added into 50 mL of NaOH aqueous solution with concentration of 1.5 wt%. Afterwards, white $Zn(OH)_2$ precipitate was formed. After 3 times of centrifugation (5 min, 800 rpm) for collection and cleaning, the $Zn(OH)_2$ precipitate was dried at 80 ^oC for 1 h, forming $Zn(OH)_2$ powder. Then the $Zn(OH)_2$ powder was annealed at 300 ^oC for 2.5 h. After that the ZnO powder was thus prepared.

3 Synthesis of the SnO_2 nanocrystal powder

The synthesis of nano sized SnO_2 nanocrystal was also prepared by direct precipitation method, according to a previous work [S2].

In details, firstly, 50 mL ammonia aqueous solution (1 M) was added directly to 50 mL $SnCl_4$ aqueous solution (0.2 M) to form white $Sn(OH)_4$ precipitate. The $Sn(OH)_4$ precipitate was collected by 3 times of centrifugation (5 min, 800 rpm). The precipitates were then dried at 80 ^oC for 1 h. The dried precipitates were annealed at 300 ^oC in the air for 2.5 h, forming the SnO_2 powder.

Reference

S1 J. R. Huffman and B. F. Dodge, *Ind. Eng. Chem.*, 1929, **21**, 1056-1061.

S2 K. C. Song and Y. Kang, *Mater. Lett.*, 2000, **42**, 283-289.

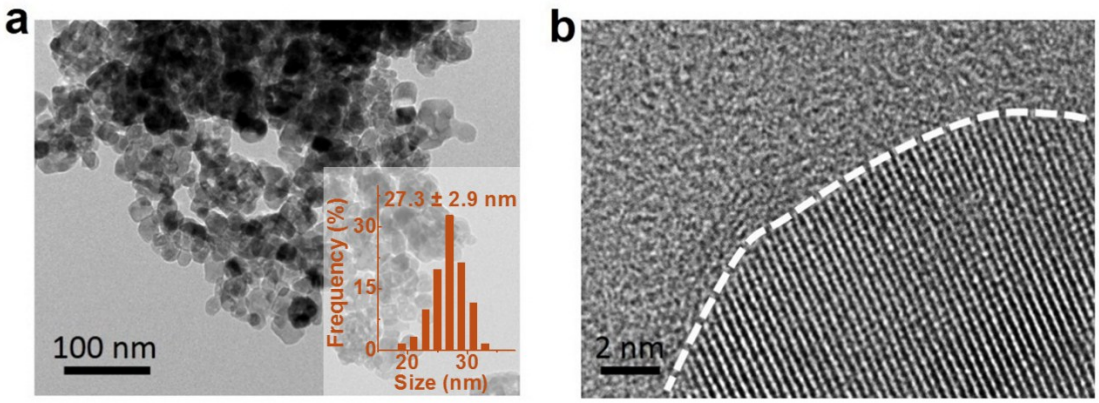

Fig. S1 (a) The low magnification of TEM image of the pristine TiO_2 nanocrystals. (b) The HRTEM image of the pristine TiO_2 nanocrystals.

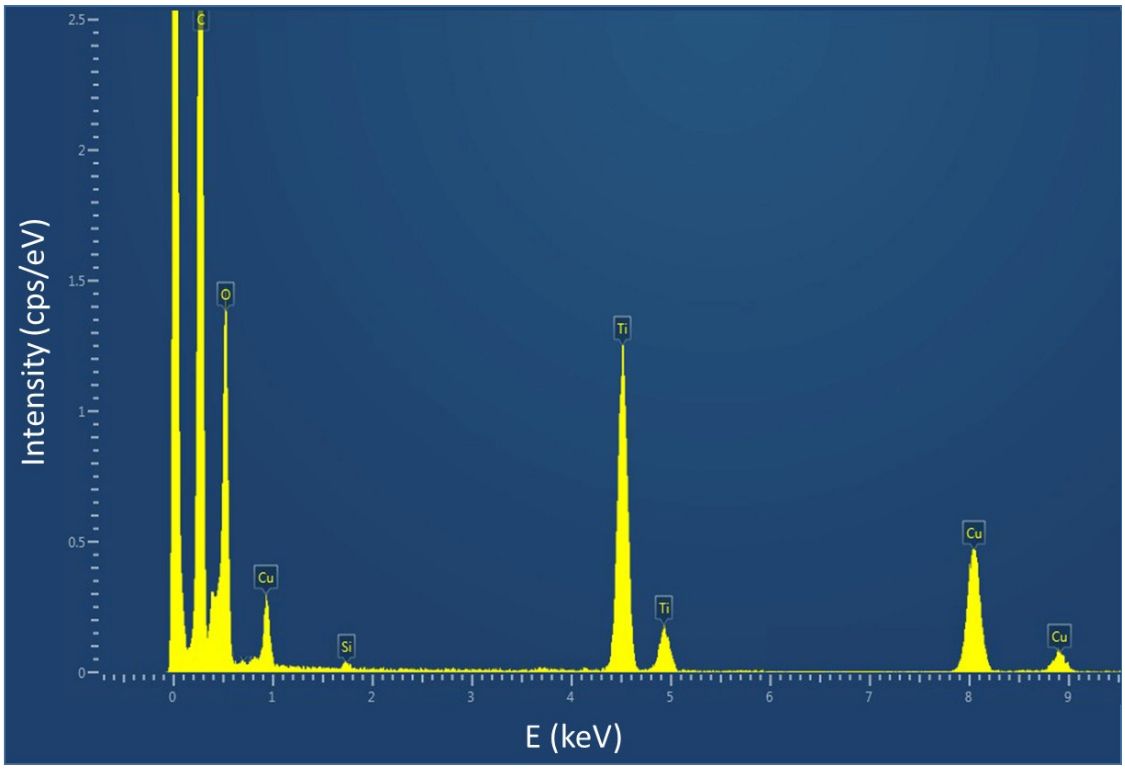

Fig. S2 The EDS spectrum of the B-TiO_2 corresponding to Fig. 2b.

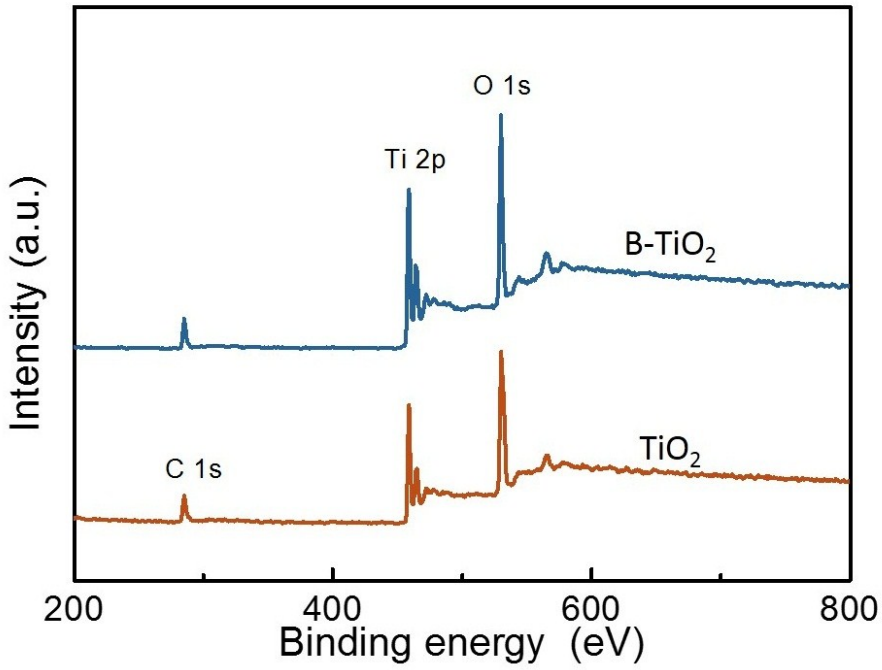

Fig. S3 The XPS full survey spectra of the pristine TiO_2 and the B-TiO_2 powders.

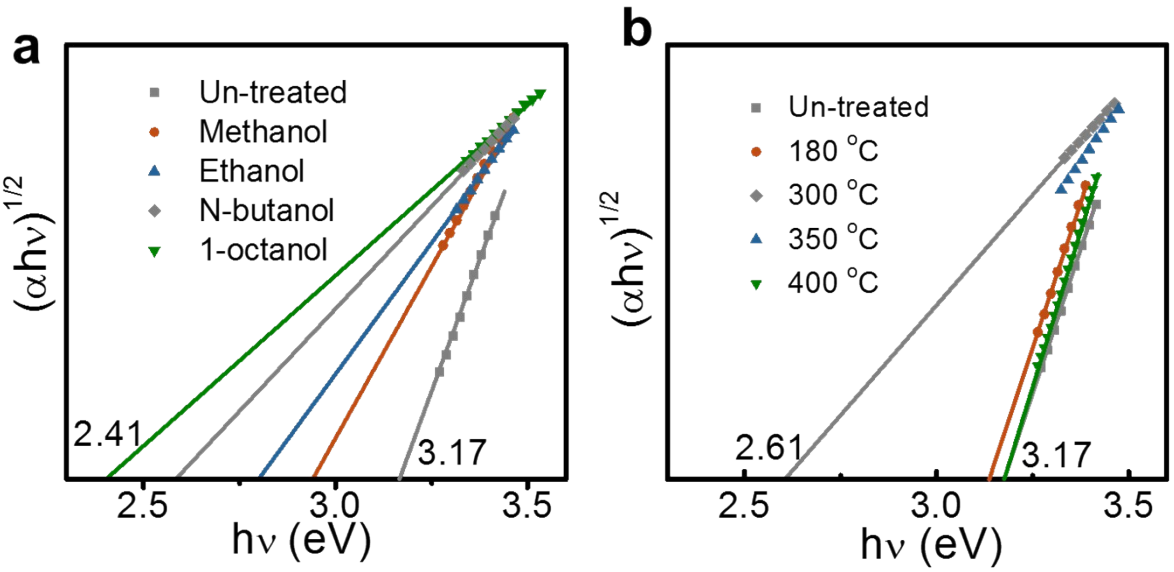

Fig. S4 The plots of photon energy (hυ) versus the $(\alpha h\upsilon)^{1/2}$ corresponding to the data in Fig. 3.

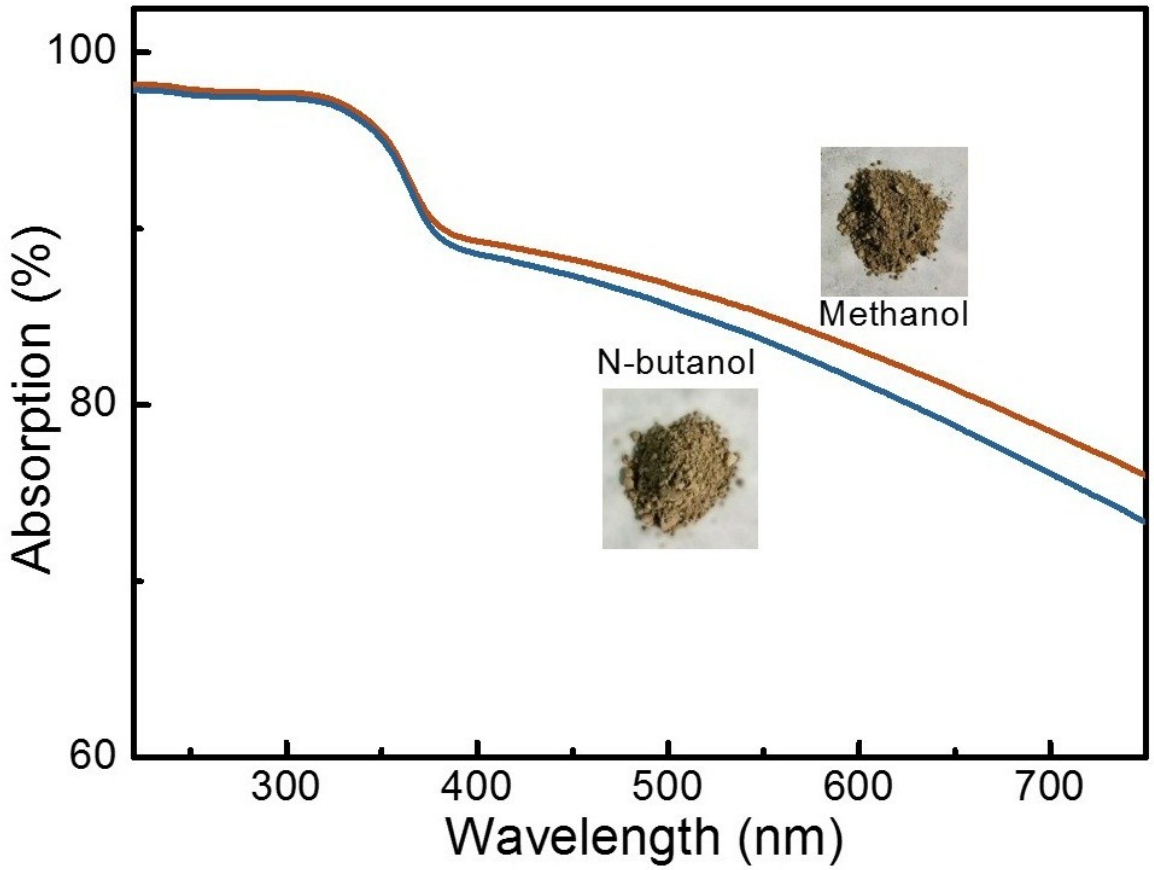

Fig. S5 The optical absorption spectra of the B-TiO_2 powders obtained with argon-loaded methanol and N-butanol vapor flow. The insets are the photos of the corresponding B-TiO_2 powders.

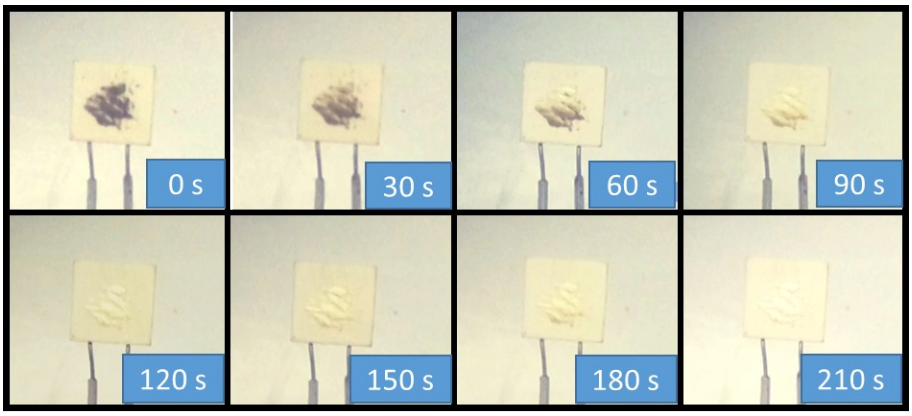

Fig. S6 The pictures of color evolution of B-TiO_2 during heating at 400 ^{o}C.