Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting information

Effect of oxygen vacancies and crystal symmetry on piezocatalytic properties of Bi_2WO_6 ferroelectric nanosheets for wastewater decontamination

Zihan Kang, Enzhu Lin, Ni Qin*, Jiang Wu, Baowei Yuan and Dinghua Bao*

State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China

Corresponding Authors

*E-mail: qinni2@mail.sysu.edu.cn (N.Q.).

*E-mail: stsbdh@mail.sysu.edu.cn (D.B.).

Fig. S1

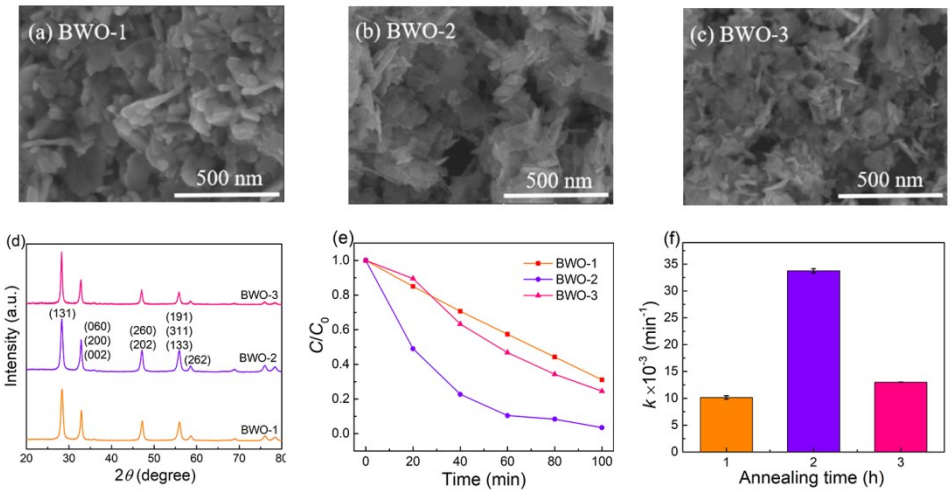

Fig. S1. (a)-(c) SEM patterns of BWO annealed at 400°C for (a) 1 h; (b) 2 h; (c) 3 h. (d) X-ray Diffraction patterns of BWO samples. (e) The piezocatalytic degradation of RhB under ultrasonic vibration by the different BWO samples. (f) Reaction kinetics rate constant *k* as a function of the annealing time.

The crystal size of BWO nanosheets can be changed independently by controlling annealing time. The XRD patterns of BWO nanosheets annealed at 400 °C for 1 h (BWO-1), 2 h (BWO-2) and 3 h (BWO-3) are shown in **Fig. S1a**, all the diffraction peaks can be clearly indexed to the orthorhombic phase of BWO crystals, and the diffraction peaks become slightly stronger with the extension of the annealing time. The crystallite size of BWO-1, BWO-2 and BWO-3 is calculated by Scherrer equation as 47.9, 49.8 and 67.3 nm, respectively. This is due to the grain boundary migration with the increase of annealing time, resulting in the increase of crystallite size. As shown in **Fig. S1d-f,** surface morphology of the BWO nanosheets annealed for different times are different. The grain boundaries of the BWO-1 and BWO-3 are not clear, and no distinct flaky boundaries can be seen, while the grains of BWO

nanosheets possess a quadrilateral structure with obvious edges, and the grain size of BWO-3 is rather large. This is because the grain boundary diffusion occurs first and then grain boundary migration occurs in the annealing process. Grain boundary diffusion is a densification process driven by the decrease of surface energy, which makes the grain boundary more regular. However, excessive grain boundary will be activated and migrated at the later stage of annealing, resulting in the increase of grain size.[33]

According to **Fig. S1b-c**, the piezocatalytic activity of BWO nanosheets is enhanced firstly and then weakened by extending the annealing time. After 100 min reaction, less than 2 % of RhB molecules are left for BWO-2, while these for BWO-1 and BWO-2 are nearly 22 % and 25 %, respectively. In **Fig. S1c**, the rate constant *k* for BWO-1, BWO-2 and BWO-3 is calculated as 10.1, 33.7 and 13.0 min^{-1}, respectively. These results indicated that crystallites with appropriate crystal size, clear boundary and regular shape are beneficial to piezocatalytic performance.

Table S1

Table S1. The atomic concentration on different catalyst surface.

Sample	Atomic %		
	Bi 4f	W 4f	O 1s
O_2-BWO	0.17	0.07	0.41
N_2-BWO	0.16	0.05	0.38

Fig. S2

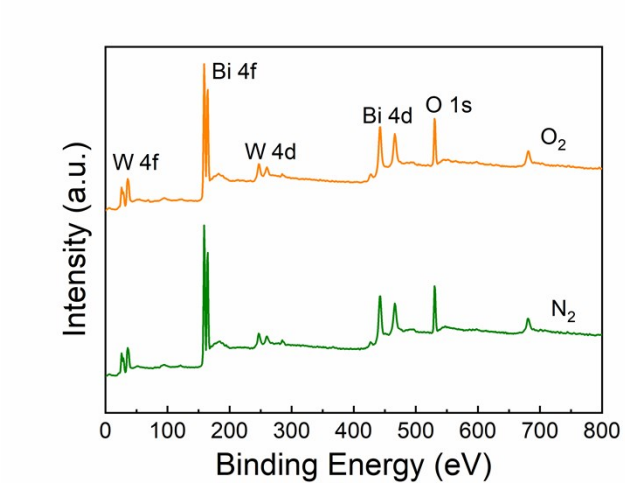

Fig. S2. The XPS survey spectra of BWO samples annealing in O_2 and N_2 atmosphere.

Fig. S3

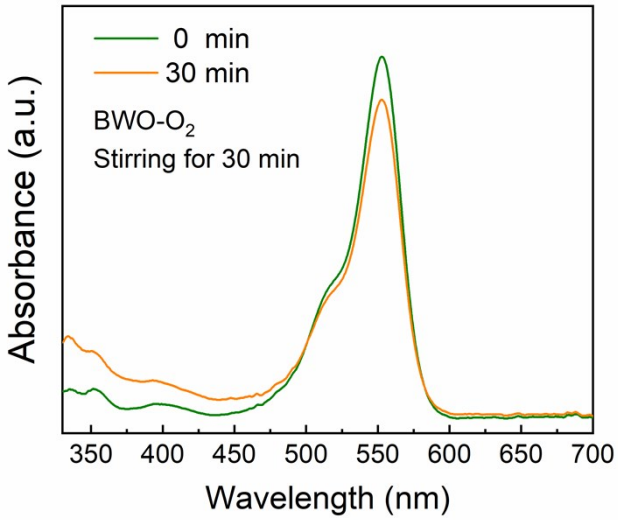

Fig. S3. Adsorption of RhB dye solutions on the BWO nanosheets annealed in O_2 atmosphere when the pH of dye solution was adjusted to 10.

Fig. S4

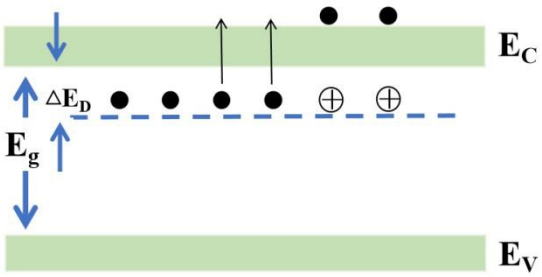

Fig. S4. Band structure of BWO with oxygen vacancy. The donor energy level is represented by a short line segment, and the small black dot on the donor level represents the electron bound by the donor impurity

Fig. S5

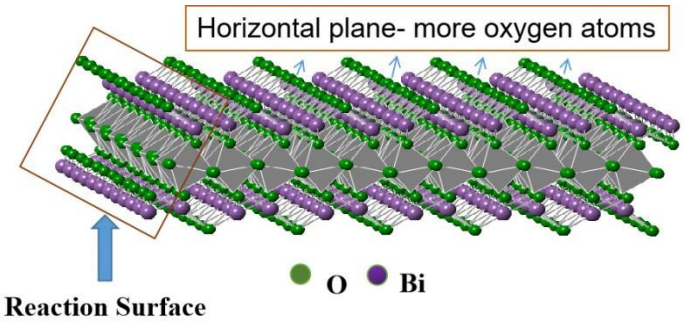

Fig. S5. The atomic structure diagram of BWO nanosheet. Two sides are reactive active surfaces and two horizontal surfaces are non-reactive active surfaces.

Equation (S1-S7)

$$O_2 + e^- \rightarrow \cdot O_2^-$$

（S1）

$$\cdot O_2^- + H_2O \rightarrow HO_2 \cdot + OH^-$$

（S2）

$$2HO_2 \cdot \rightarrow H_2O_2 + O_2$$

（S3）

$$H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2$$

（S4）

$$h^+ + H_2O \rightarrow \cdot OH + H^+$$

（S5）

$$OH^- + h^+ \rightarrow \cdot OH$$

（S6）

$$\text{Pollutants} + (\cdot O_2^-, \cdot OH, h^+, H_2O_2) \rightarrow CO_2 + H_2O$$

（S7）

Fig. S6

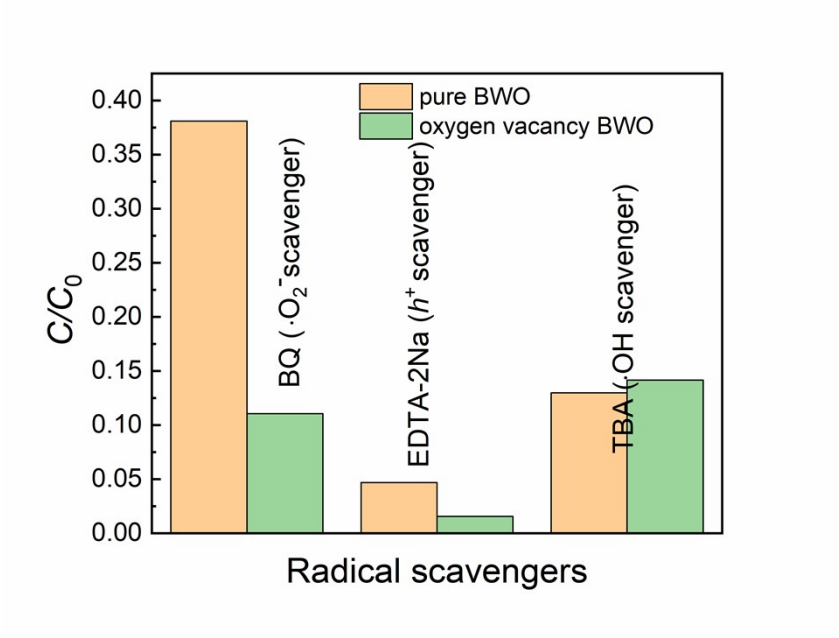

Fig. S6. Inhibition ratio of different free radical scavengers on piezocatalytic activity in pure and oxygen vacancy BWO nanosheets.