Supporting Information For

$BiPO_4$ Oxygen Atom Self-Spillover Mechanism Promoting H_2O_2 Production via Piezoelectric Catalysis

Haiyan Wang[a], Xinhui Jiang[a], Jindou Hu[a]*, Hao Wang[a], Xiaoyan Lu[a], Zhenjiang Lu[a], Jing Xie[a], Junhong Li[a], Yong Wen[a] and Yali Cao[a]*

[a]*State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources; College of Chemistry, Xinjiang University, Urumqi, 830017, Xinjiang, P. R. China.*

*Corresponding author.

E-mail address: caoyali523@163.com. hujindu@xju.edu.cn

Experimental reagent

The following chemical reagents were used in the experiments: bismuth nitrate pentahydrate ($Bi(NO_3)_5 \cdot 5H_2O$) purchased from Shanghai McLean Biochemical Technology Co, Ltd. (99%, Shanghai, China), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) purchased from Shanghai Aladdin Bio-Chem Technology Co, Ltd. (99%, Shanghai, China), methanol, anhydrous ethanol, p-benzoquinone (PBQ) purchased from Shanghai Aladdin Bio-Chem Technology Co, Ltd. (97%, Shanghai, China), isopropanol (IPA), disodium ethylenediaminetetraacetic acid (EDTA-2Na), ammonium molybdate, and potassium iodide. KI from Wind Boat Chemical Reagent Technology Co, Ltd. (99.0%, Tianjin, China), and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was bought from Beilian Fine Chemicals Development Co, Ltd. (99.9%, Tianjin, China). All of the reagents do not require further purification.

Preparation of catalysts

First, 5 mmol of bismuth nitrate pentahydrate was accurately weighed and finely ground in a mortar. Subsequently, 10 mmol of ammonium dihydrogen phosphate was added. Thoroughly mixed the two reagents and ground them in a mortar for 30 min, until the white particles were reduced to a thin paste. The ground sample was placed into a beaker, seal it with cling film, then heat in a water bath at 80°C for 24 h. Then filtered and dried at 60°C for 5 h. Washed with distilled water and then filtered. Dried in a 60°C forced-air drying oven for 10 h. The dried white powder was placed in a muffle furnace for calcination. Set the temperature to rise at a rate of 5°C/min to 300°C, then maintained the temperature for 2 h. Samples fired at 0, 200, 300, 400, 500, and 600 degrees were named respectively as BPO-0, BPO-200, BPO-300, BPO-400, BPO-500 and BPO-600.

Piezoelectric catalytic H_2O_2 production experiment

The catalyst (50 mg) was dispersed in 100 mL of solution, consisting of 75 mL distilled water and 25 mL methanol solution. The piezoelectric-catalyzed H_2O_2

production was then tested in a 200 mL quartz reactor, which was kept protected from light during the entire experiment. Ultrasonically induced catalysis was performed using an ultrasonic device (240 W, 40 kHz) to generate mechanical vibration. Samples were taken at 30-minute intervals. 2 mL of the reaction solution was extracted from the suspension using a syringe and then filtered through a 0.22 μm filter. The filtrate was diluted three fold and 2 mL was transferred to a centrifuge tube. To this, 50 μL of 0.01 mol L^{-1} ammonium molybdate solution and 2 mL of 0.1 mol L^{-1} KI solution were added. The mixture was shaken well and left to stand for 10 minutes. Finally, absorbance was measured using a UV-visible spectrophotometer for quantitative analysis.

Instrument reagent

X-ray diffraction (XRD) test was performed on a BRUKER D8 (Germany) diffraction system to investigate crystalline structures with monochromatic Cu Kα radiation (0.1541 nm) at a step size of 0.02°. The tube source was performed at 30 kV and 15 mA. Electron paramagnetic resonance (EPR) spectrometer (MEX-nano, Bruker) is used to detect hydroxyl (·OH) and superoxide ($\cdot O_2^-$) radicals via 5, 5-dimethyl-1-pyrroline N-oxide (DMPO). The morphology and microstructure of samples were revealed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscopes (HR-TEM) with an accelerating voltage of 200 kV (JEOL JEM-2010F electron microscope). The chemical composition was studied by energy-dispersive X-ray spectroscopy (EDS). Energy Dispersive Spectrometer (EDS), Raman spectroscope (Renishaw Micro-Raman), X-ray photoelectron spectrometer (XPS, Thermo Fischer, USA, ESCALAB Xi+) was used to analyze the chemical state and electronic structure. In this case, the vacuum of the analysis chamber was 8×10^{-10} Pa, the excitation source was Al Kα ray (hv = 1486.6 eV), the operating voltage was 12.5 kV, the filament current was 16 mA, and the signals were accrued according to the samples. Passing-energy was tested at 100 eV for the full spectrum, and 20 eV for the narrow spectrum with a step size of 0.05 eV and a dwell time of 40-50 ms. The samples were etched and thinned using an argon ion gun with an

etching spot size of 1.5 mm and an etching voltage of 3000 eV. Energy corrections for high-resolution scans were calibrated by referencing the C 1s peak to 284.8 eV. A Hitachi U-3010 spectrophotometer was utilized to measure the light absorption capacity of the sample and determine the band gap (Eg) of the catalyst.

Characterization of electrochemical properties

Tests were performed using the CHI-660E electrochemical workstation, including Mott-Schottky (M-S) curves, electrochemical impedance spectroscopy (EIS), and transient photocurrent response (i-t) curves. An open circuit voltage test was conducted prior to the main testing. A three-electrode system was set up, consisting of a conductive nickel foam (2.0 × 1.5 cm) coated with catalytic material as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl reference electrode. The electrolyte used was a 0.5 M Na_2SO_4 solution. Sample preparation: 5 mg of catalyst and 1 mg of acetylene black were weighed and thoroughly mixed with drops of anhydrous ethanol. Drops of PVDF were added as a binder and applied to the nickel foam, which was then folded in half for pressing. Finally, the sample was placed in a vacuum oven at 80°C for 10 h.

Fig. S1. Schematic representation of the synthesis of $BiPO_4$.

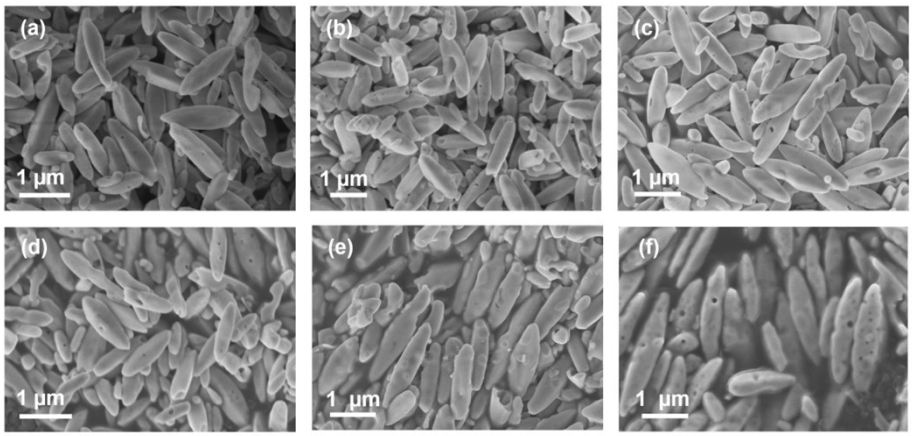

Fig. S2. SEM images of (a) BPO-0, (b) BPO-200, (c) BPO-300, (d) BPO-400, (e) BPO-500; (f) BPO-600.

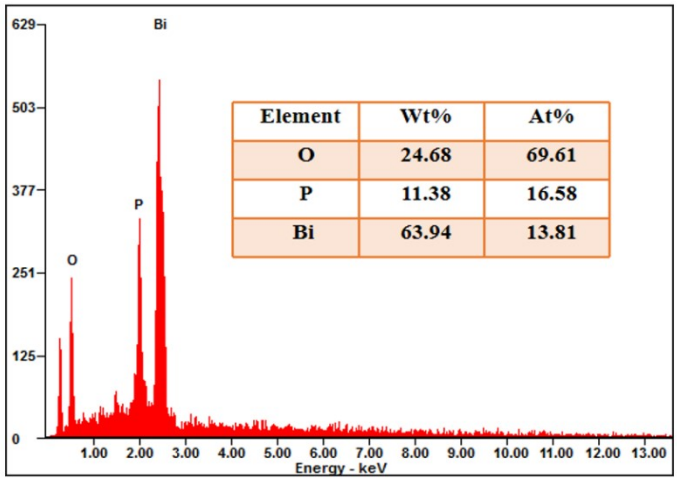

Fig. S3. EDS of BPO-300.

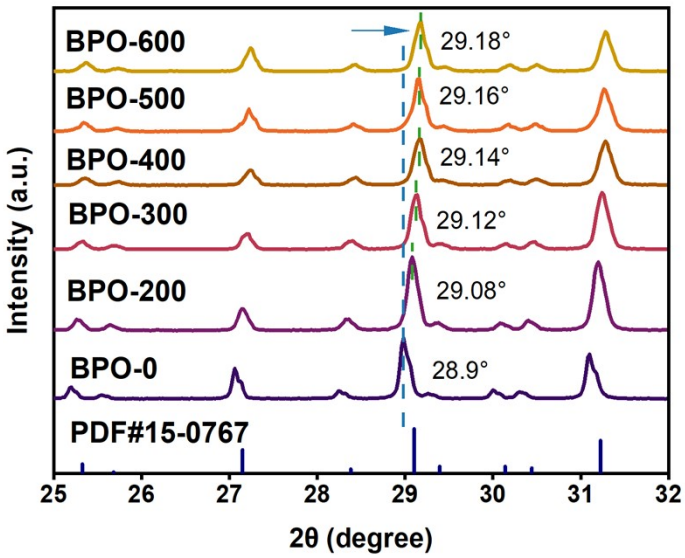

Fig. S4. Locally magnified XRD spectra of BPO-0, BPO-200, BPO-300, BPO-400, BPO-500 and BPO-600.

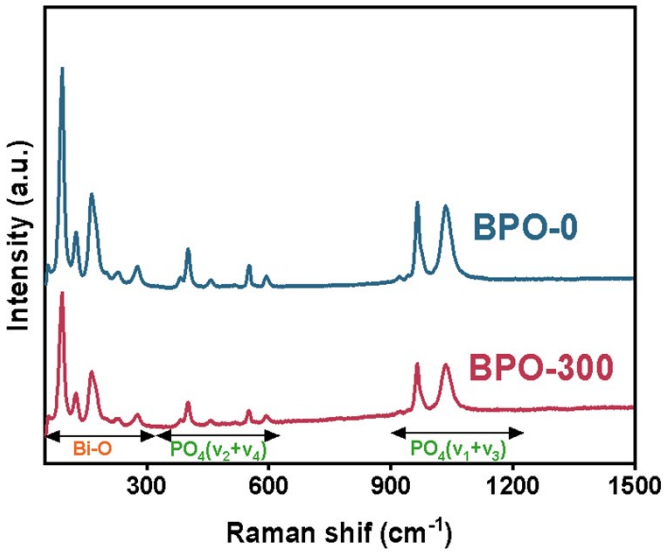

Fig. S5. Raman spectra of BPO-0 and BPO-300.

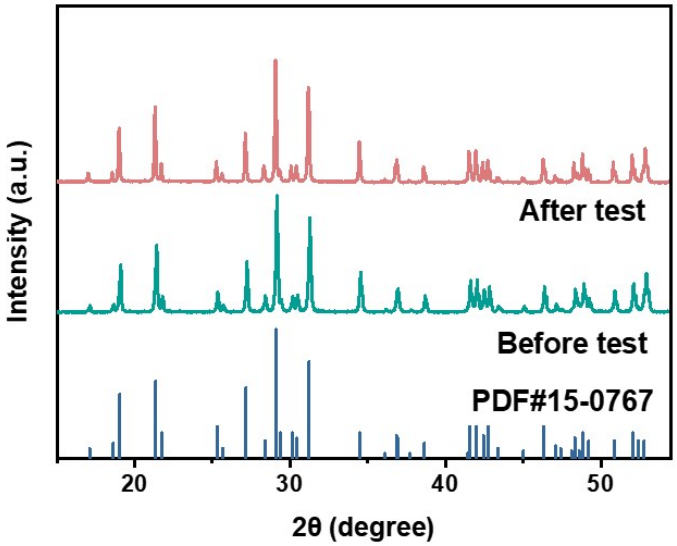

Fig S6. The XRD spectra of BPO-300 before and after the test.

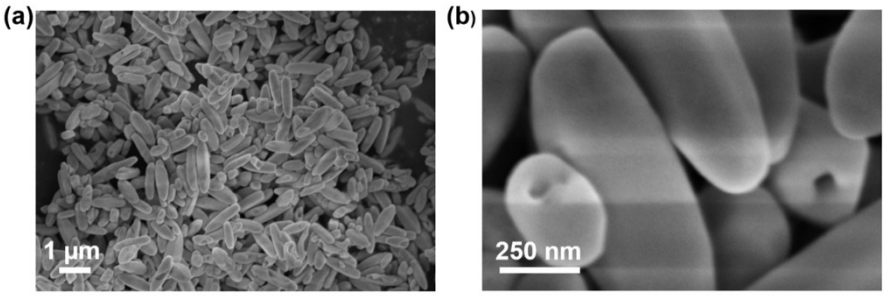

Fig S7. The SEM images of BPO-300 after cycle test.

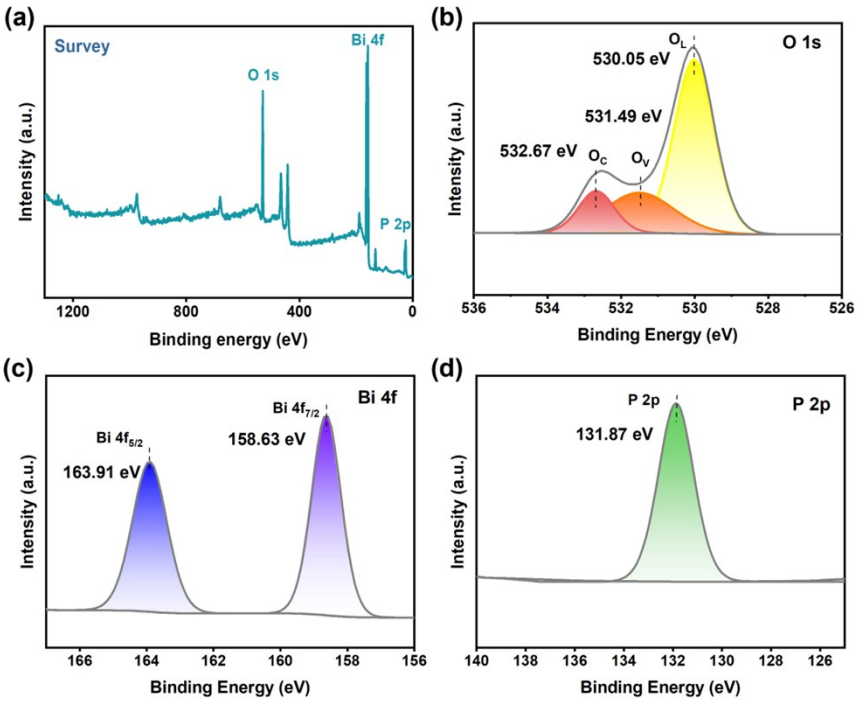

Fig. S8. (a) XPS survey spectra of BPO-300 after cycle test, and (b) high-resolution spectra of O 1s, (c) Bi 4f, and (d) P 2p.

Acknowledgement

This research was financially supported by the National Natural Science Foundation of China (22568047, 22278348), Scientific Research Program of Higher Education Institution of Xinjiang (XJEDU2024P014), Technology Innovation Leading Talent Project of Xinjiang (2024TSYCLJ0003), Central Guidance Local Science and Technology Development Project of Xinjiang (ZYYD2025JD09), Natural Science Foundation of Xinjiang Autonomous Region (2022D01D05).