Supporting Information

Floatable Porous BCZT@TPU Piezocatalytic Gels for Water Purification and Hydrogen Evolution

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1. Experimental section

1.1. Materials

Acetylacetone ($C_5H_8O_2$, 99%), tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, ⩾99.0%), barium acetate ($C_4H_6BaO_4$, 99.99%), calcium acetate monohydrate ($C_4H_8O_5Ca$, ⩾99.0%), and zirconium acetylacetone ($C_{20}H_{28}O_8Zr$, 98%) were all purchased from Shanghai Maclean Biochemical Technology Co., Ltd. (Shanghai, China). Glacial acetic acid (⩾99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were purchased directly from commercial suppliers without further purification.

1.2 Preparation of BCZT Nanowires

The barium calcium zirconate titanate (BCZT, $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$) nanowires were prepared via an electrospinning method. Firstly, stoichiometric amounts of calcium acetate monohydrate, barium acetate, and zirconium acetylacetonate were dissolved in a mixed solvent of acetic acid and ethylene glycol monomethyl ether. The solution was stirred at 300 rpm and 90 °C for 45 min to obtain solution A. Separately, acetylacetone and tetrabutyl titanate were mixed at 45 °C with stirring at 300 rpm for 20 min to obtain solution B.

Then, solution B was slowly added dropwise into solution A, and the mixed solution was stirred at 45 °C for 6 h to form a homogeneous light-yellow sol. After that, the sol was aged statically for more than 12 h. For electrospinning, 20 mL of the aged sol was mixed with 1.1 g of polyvinylpyrrolidone and stirred at 300 rpm and 25 °C for 4 h to obtain a spinnable precursor. The solution was loaded into a syringe and electrospun for 12 h. During the electrospinning process, the needle tip was 10 cm away from the collector, the applied voltage was 10 kV, the spinning rate was 1 mL h^{-1}, the roller rotation speed was 800 rpm, the ambient temperature was 40 °C, and the relative humidity was below 20%. The spun fibers were dried at 70 °C for 48 h and then calcined in a sintering furnace. First, the temperature was raised to 325 °C at a rate of 3 °C min^{-1} and held for 1 h, then raised to 800 °C at the same rate and held for 2 h. After natural

cooling to room temperature, the fibers were ground and crushed to obtain BCZT nanowires.

1.3 Preparation of BCZT@TPU gel

TPU powder was weighed according to the required mass fraction and dissolved in a mixed solvent of tetrahydrofuran and N,N-dimethylformamide in a mass ratio of 1:1. The solution was stirred continuously at 800 rpm for at least 6 hours at room temperature to obtain a uniform and transparent TPU solution. Subsequently, according to the required solid content, the TPU solution was mixed with BCZT nanowires and stirred at 300 rpm for 30 minutes at room temperature to ensure uniform dispersion of the BCZT nanowires in the polymer matrix. Finally, the mixed solution was coated into a film using a blade coating method at 80% relative humidity to prepare a porous BCZT@TPU gel; as a control, a dense BCZT@TPU gel was prepared in the same manner under conditions controlled at 40% relative humidity.

1.4 Characterization

The morphology of BCZT nanowires and their composite gel was characterized by scanning electron microscopy (SEM, TESCAN MIRA3, Czech Republic). The phase structure of BCZT nanowires was analyzed by X-ray diffraction (XRD, Rigaku SmartLab, Japan). The chemical composition in BCZT powder was determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher, ESCALAB 250, USA). The UV-Vis absorption spectra were recorded using a UV-Vis spectrophotometer (UV-2000i, Shimadzu, Japan).

1.5 Catalytic performance

To test the degradation performance of BCZT@TPU gel on organic pollutants, a 50 mm diameter BCZT@TPU gel was added to 100 mL of RhB aqueous solution (initial concentration = 5 mg L^{-1}). The solution was then stirred at 50 r/min for 45 min in the dark to allow the dye and catalyst to reach adsorption-desorption equilibrium. Periodic mechanical vibration was provided using an ultrasonic source (200 W, 45 kHz, KQ-200 VDE, China). During ultrasonic treatment, 6 mL of the reaction solution was

collected every 15 min, centrifuged, and the supernatant was collected. The change in dye absorbance was recorded using a UV-Vis spectrophotometer.

Electron paramagnetic resonance (ESR) was used to characterize the active free radicals generated during the reaction, with 5,5-dimethyl-1-pyrrolino-N-oxide (DMPO) as the spin trapping agent. A catalyst suspension with a mass concentration of 5 $g \cdot L^{-1}$ was prepared, with deionized water and dimethyl sulfoxide (DMSO) used as the ESR reaction media for detecting •OH and $\bullet O_2^-$, respectively. After treating the suspension with ultrasound for 15 min, 50 μL of the reaction solution was thoroughly mixed with 5 μL of DMPO solution and quickly sealed in a glass capillary tube. Subsequently, ESR measurements were performed on an electron spin resonance (Bruker A300, Germany).

To test the hydrogen production performance of BCZT@TPU porous gel, a ring-shaped sample with an outer diameter of 4 cm and an inner diameter of 1 cm was placed in a hydrogen production reaction vessel, and 160 mL of deionized water was added. After sealing the reaction vessel, high-purity nitrogen gas was first introduced through a gas valve for 10 min to fully displace the air in the system. The gas valve was then closed, and after ultrasonic stimulation, the concentration of the generated hydrogen gas was quantitatively analyzed using a gas chromatograph (UATEC-6600, China).

1.6 Finite Element Simulation

Finite element analysis (FEM) simulations of the piezoelectric potential distribution and deformation behavior of BCZT nanorods under ultrasonic excitation were performed using COMSOL Multiphysics software. The nanorod diameter in the model was set to 0.2 μm, with an aspect ratio of 20:1. During the simulation, the bottom surface of the nanorod was set as a grounded boundary condition, and a rigid constraint was applied to that end to suppress overall rigid motion. To simulate the ultrasonic-induced mechanical effects, an external load of 10^8 Pa was applied to the surface of the nanorods.

2. Supplemental figures

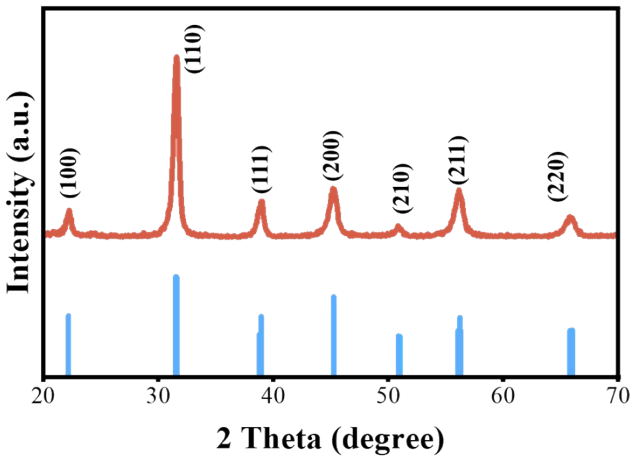

Fig. S1. XRD pattern of BCZT nanowires.

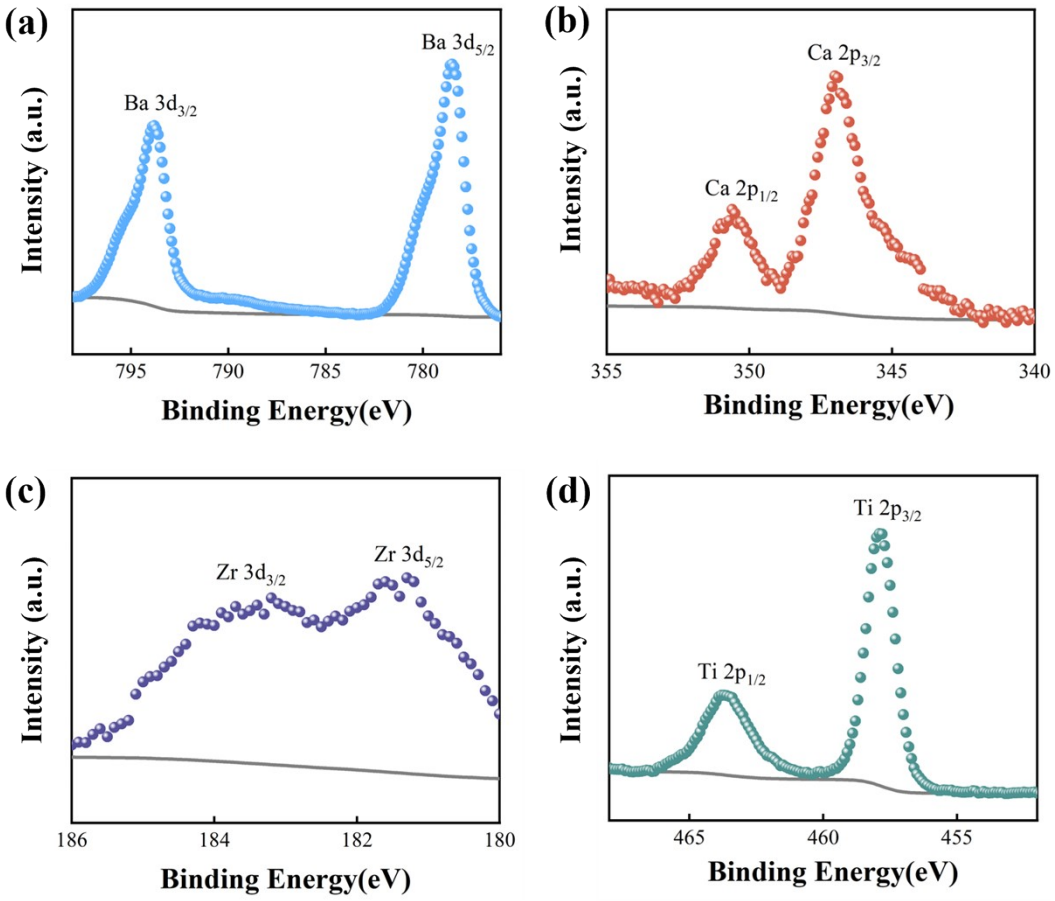

Fig. S2. XPS spectra of BCZT nanowires: (a) Ba, (b) Ca, (c) Zr, (d) Ti.

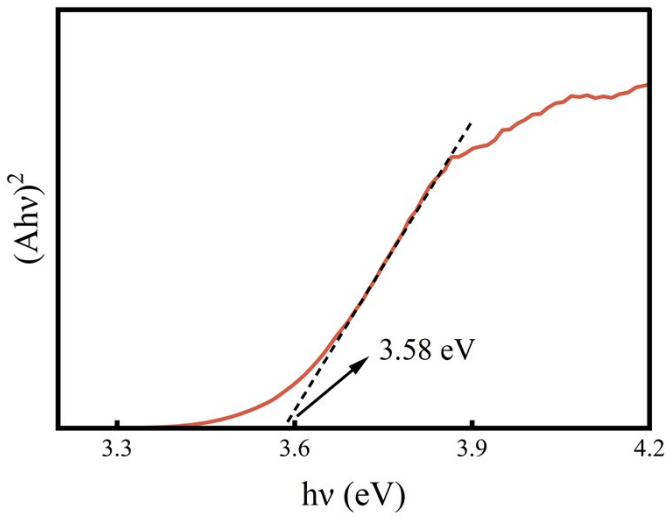

Fig. S3. Tauc curve of BCZT nanowires.

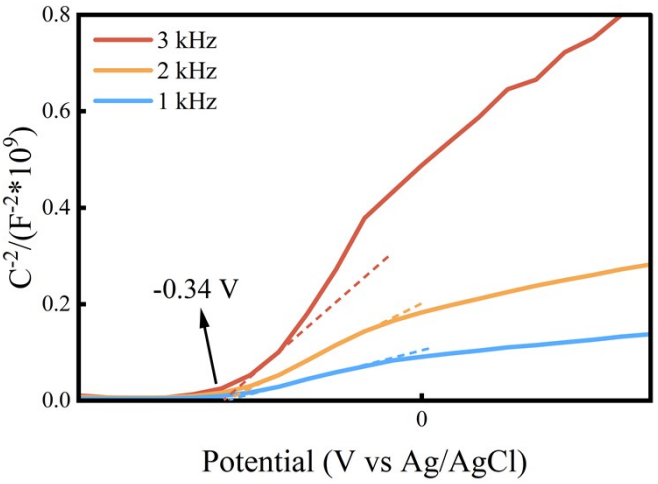

Fig. S4. Mott-Schottky plots of BCZT nanowires at different frequencies.

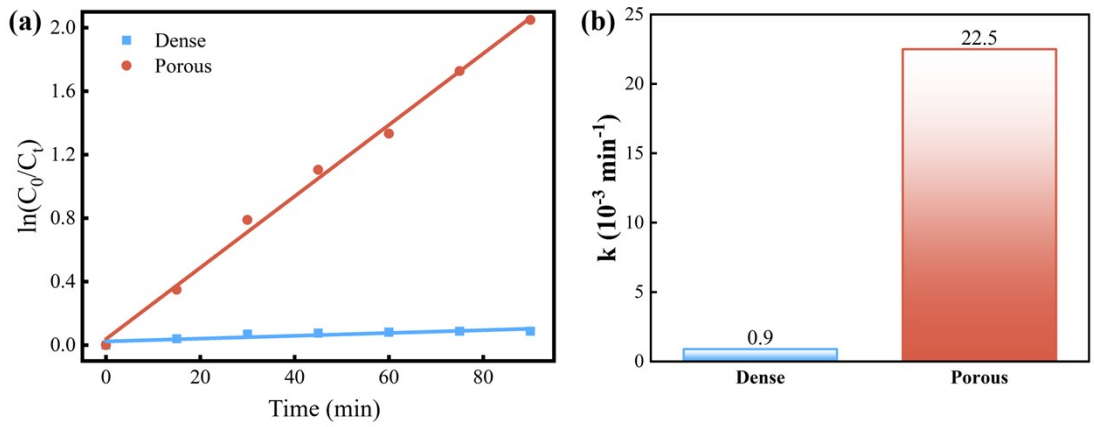

Fig. S5. (a) First-order kinetic plots and (b) corresponding rate constants (*k*) of dense and porous BCZT@TPU composite gel.

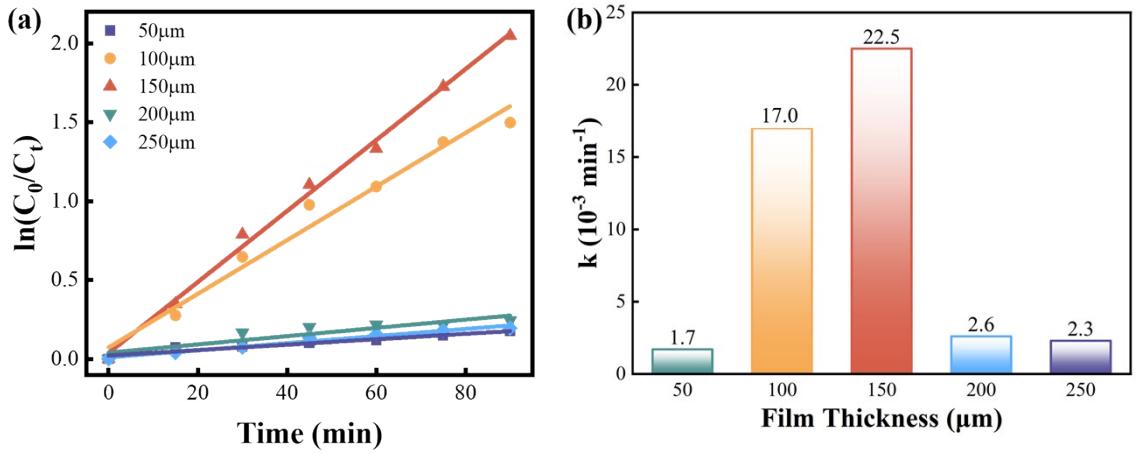

Fig. S6. Effect of film thickness on piezocatalytic performance of porous BCZT@TPU gels: (a) first-order kinetic plots and (b) corresponding rate constants.

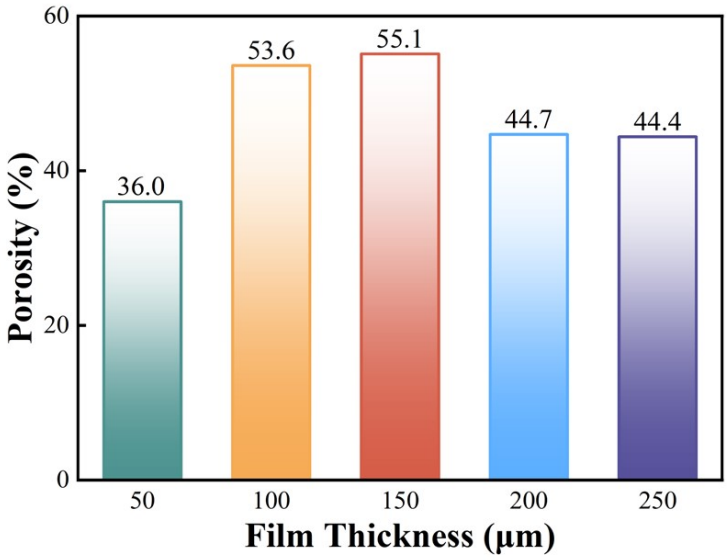

Fig. S7. Porosity of porous BCZT@TPU gels of different thicknesses.

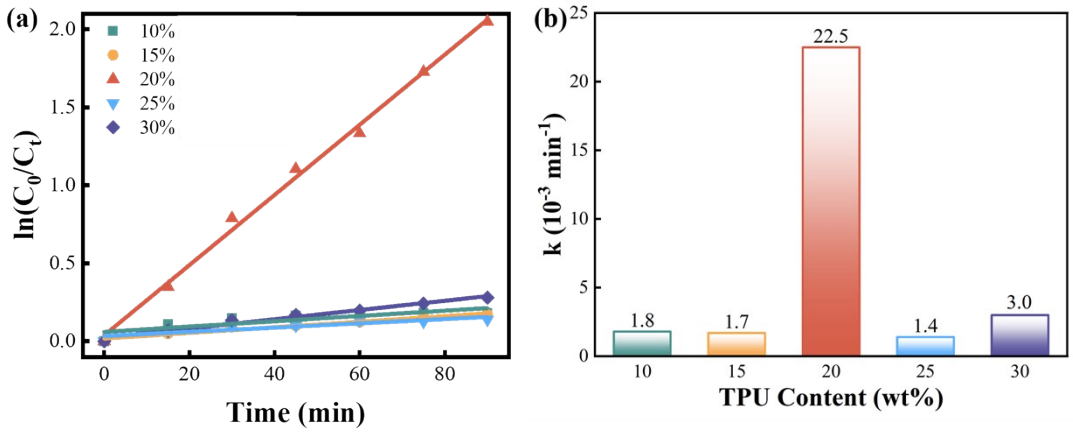

Fig. S8. (a) First-order kinetics and (b) corresponding rate constants of porous BCZT@TPU gels with different TPU mass fractions.

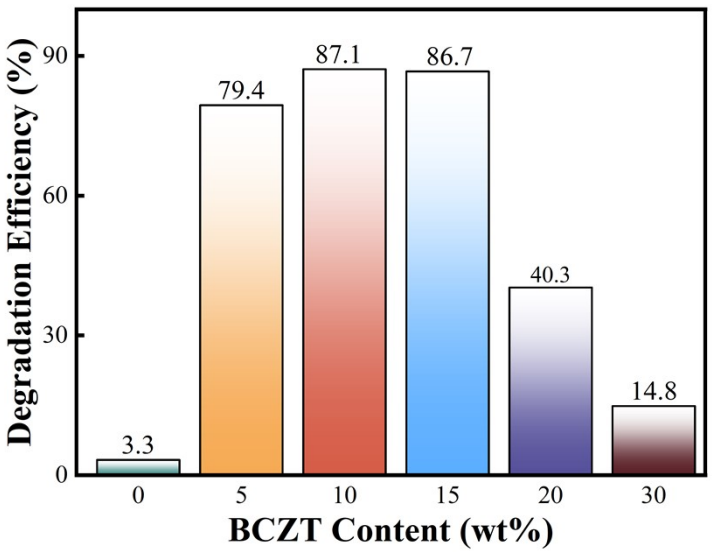

Fig. S9. Degradation efficiency of RhB as a function of BCZT content in the porous BCZT@TPU gels.

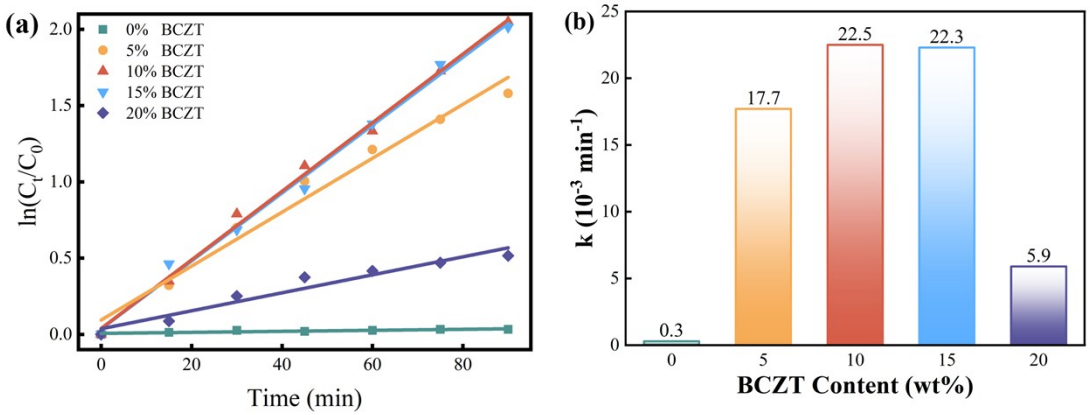

Fig. S10. (a) First-order kinetics and (b) corresponding rate constants of porous BCZT@TPU gels with different BCZT mass fractions.

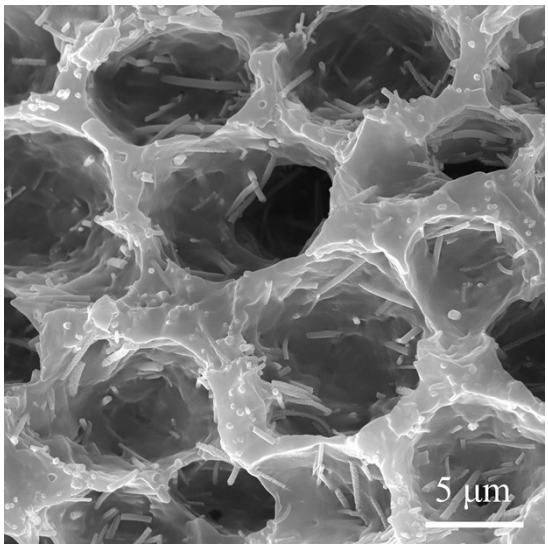

Fig. S11. SEM images of the porous BCZT@TPU gel after hydrogen evolution.