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Supporting information for

Defect-Enhanced Photothermal Catalysis over ZnO for Efficient Depolymerization of Waste Polyester into High-Purity BHET

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Experimental section

Materials

Zinc oxide (ZnO), titanium dioxide (TiO_2), tantalum pentoxide (Ta_2O_5), molybdenum oxide (MoO_3), vanadium pentoxide (V_2O_5) and ferric oxide (Fe_2O_3) were purchased from Shanghai Titan Co., Ltd. Zinc acetate ($Zn(Ac)_2$) and Sodium borohydride ($NaBH_4$) were purchased from Aladdin Industrial Inc. (Shanghai, China). Tungsten oxide (WO_3), copper oxide (CuO), isophorone diisocyanate (IPDI) and N,N-dimethylformamide (DMF) were obtained from Shanghai Macklin Biochemical Co., Ltd. Dimethyl sulfoxide (DMSO), ethyl alcohol (EtOH) and ethylene glycol (EG) were bought from Sinopharm Chemical Reagent Co., Ltd. Polyethylene terephthalate (PET, 200 mesh) was purchased from Dongguan Guangyuan Plastic Co., Ltd. PTFE membrane (47 mm*0.22 μm) was bought from Longjin Membrane Industry Technology Co., LTD. All reagents were used as provided without further purification.

Method

Synthesis of ZnO nanosheets: The precursor Zn-EG-AC was prepared by dissolving 4.0 g of $Zn(Ac)_2$ in 40 mL of EG in a 100 mL round-bottom flask, followed by heating the solution at 160 °C under reflux for 1 h. After cooling naturally to room temperature, the white solid product was collected by centrifugation and washed three times with absolute ethanol. The obtained product was then stored under vacuum at 40 °C. The reaction scale can be expanded by proportionally increasing the amounts of zinc acetate and ethylene glycol. ZnO micro/nanostructures were synthesized via the hydrolysis of the Zn-EG-AC precursor in a water/ethanol solvent system (or in pure water). In a typical procedure for preparing ZnO, 4.0 g of Zn-EG-AC precursor was added to a mixed solvent consisting of 20 mL of deionized water and 20 mL of ethanol. After stirring at room temperature for 1 h, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 100 °C for 10 h. The resulting white product was separated by centrifugation, thoroughly washed multiple times with distilled water and ethanol, and finally dried at 60 °C[1].

Preparation of ZnO_{1-x}: The as-prepared ZnO was physically mixed with sodium borohydride ($NaBH_4$) at different mass ratios and manually ground in an agate mortar for 20 minutes. The resulting mixtures were then calcined in a tube furnace at 350 °C for 1 h under a continuous nitrogen flow. After cooling to room temperature under N_2, the obtained solids were thoroughly washed with copious amounts of deionized water to remove soluble residues, followed by vacuum drying at 60 °C for 12 h, obtaining black ZnO with oxygen vacancies (ZnO_{1-x}). According to the different mass ratios of ZnO and $NaBH_4$, the samples were named as ZnO_{1-x}-1:0.5, ZnO_{1-x}-1:1, ZnO_{1-x}-1:1.5 and ZnO_{1-x}-1:2.

General process of PET glycolysis: The experimental procedure was illustrated in Figure 1. A mixture of 2.0 g PET powder and 10 mL ethylene glycol was added into a 25 mL three-necked flask and stirred for 30 minutes. The flask was equipped with a thermometer, a magnetic stirrer, and a reflux condenser. After heating in an oil bath to the designated reaction temperature, a specified amount of catalyst was added to the flask (mass ratio of PET to catalyst = 50:1). The PET glycolysis reaction was conducted under atmospheric pressure within a temperature range of 170 to 210 °C, with reaction times varying from 15 to 60 minutes. For the photothermal catalytic glycolysis of PET, 0.5 g PET, 5 g EG, and 2 wt% catalyst were placed in a glass reactor, and the reaction was carried out under simulated sunlight irradiation from a xenon lamp. The internal temperature of the entire reaction system was measured by inserting a K-type thermocouple into the solution.

After a specified reaction time, the system was cooled to approximately 120 °C and immediately filtered while hot to separate the catalyst, any residual undegraded PET solids, and the liquid fraction. The recovered PET powder and catalyst were dried under vacuum at 70 °C for 12 h and then weighed. The liquid fraction was cooled to 4 °C and allowed to crystallize for 24 h. The resulting needle-like crystals of BHET were collected by vacuum filtration, dried in an oven at 80 °C for 24 h and weighed. The PET conversion rate was calculated using formulas (1) as follows:

$$Conversion\ of\ PET\ = \frac{m_0 - m_1}{m_0} \times 100\% \tag{1}$$

Where "m_0" refers to the initial weight of PET and "m_1" refers to the weight of undegraded PET. The BHET molar yield was calculated using formulas (2):

$$Yield\ of\ BHET = \frac{m_{BHET}/M_{BHET}}{m_0/M_{PET}} \times 100\% \tag{2}$$

Where "m_0" and "m_{BHET}" refer to the initial weight of PET and the weight of BHET obtained, respectively. M_{BHET} and M_{PET} correspond to the molar mass of BHET (254 $g \cdot mol^{-1}$) and the PET repeating unit (192 g·mol^{-1}), respectively[2].

Catalyst recycling stability test: After each cycle, the solid residue was recovered by centrifugation, followed by washing three times with deionized water and ethanol. The washed catalyst was then dried at 60 °C under vacuum for 6 hours. After drying, the recovered catalyst was reweighed. The amount of PET added for each subsequent cycle was adjusted according to the recovered catalyst mass, maintaining the same catalyst-to-PET mass ratio as 1:50. No fresh catalyst was added.

Synthesis of aromatic-based PU: 0.02 mol of IPDI, 0.01 mol of PTMEG-2000 and 70 g DMF were added to the reactor. The reaction mixture was stirred and heated to 60 °C in a nitrogen atmosphere for 4 h. Then 0.01 mol of the chain extender (e.g., recovered BHET) was added to the homogenized mixture at 70 °C for about 2 h and cast in a polytetra fluoroethylene (PTFE) mold and cured at 70 °C for 48 h[3].

Characterization: The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD, D8 Advance) using Cu Kα radiation. Morphological features were examined by scanning electron microscopy (SEM, Regulus8230) and transmission electron microscope (TEM, Talos F200S). The ultraviolet–visible diffuse reflectance spectroscopy (UV-vis DRS) was performed using a spectrophotometer (UV3600 i Plus). Chemical states and surface compositions were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi), with energy calibration referenced to the adventitious C 1s peak at 284.8 eV and validated against the Au 4f$_{7/2}$ peak at 84.0 eV. Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C) were acquired on a Bruker AVANCE NEO 400 MHz spectrometer. Electron paramagnetic resonance (EPR) measurements were carried out on a JEOL JES-X320 spectrometer. Fourier transform infrared (FTIR) spectroscopy was conducted on a Nicolet iS50 spectrometer using KBr pellets over the range of 400-4000 cm^{-1}. Thermal properties were evaluated by differential scanning calorimetry (DSC) on a NETZSCH DSC 214 instrument from 20 to 250 °C under nitrogen atmosphere. The structure of the reaction intermediate was determined by liquid chromatography-mass spectrometry (LCMS, Xevo TQ-S cronos) and high performance liquid chromatography (HPLC).

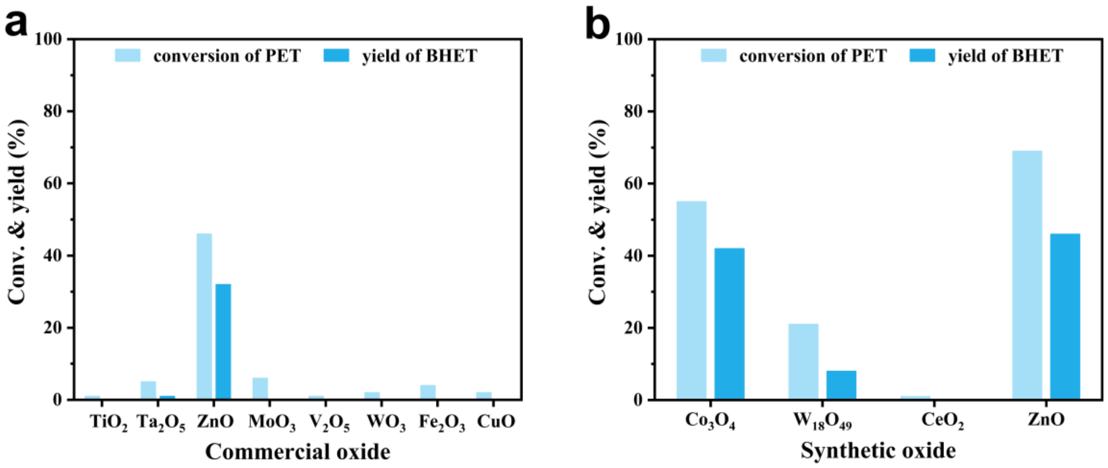


Fig. S1 PET conversion rate and BHET yield of (a) commercial oxides, (b) synthetic oxides after pyrolysis at 190 ℃ for 1 h.

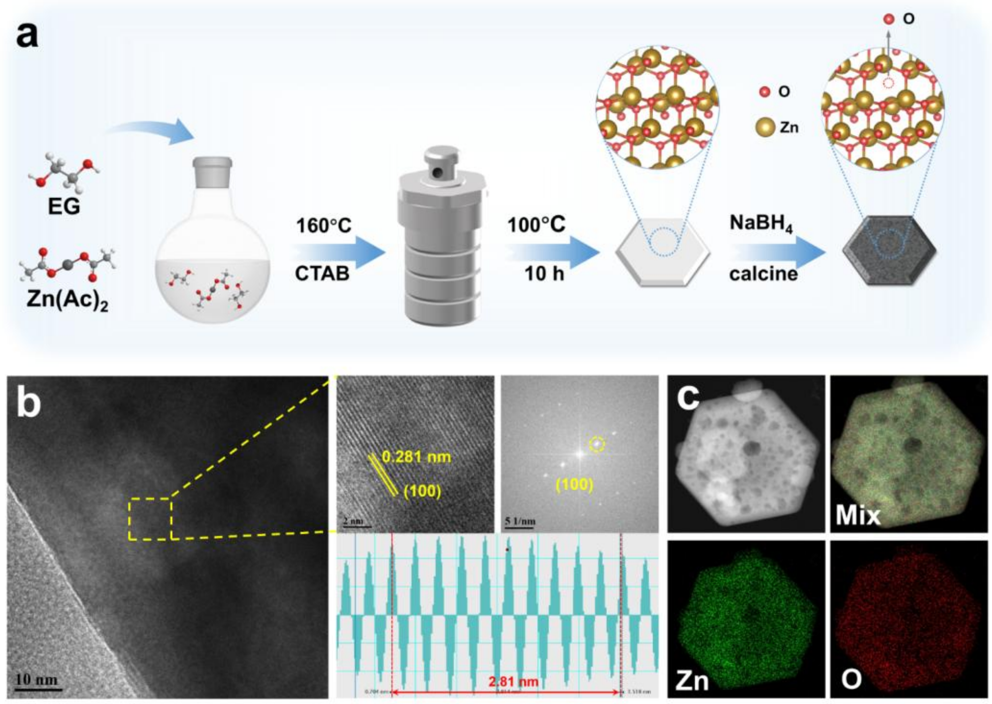


Fig. S2 (a) Schematic diagram of the synthesis procedure of ZnO$_{1-x}$. (b) HRTEM image of ZnO$_{1-x}$-1:1. (c) EDS-mappings of ZnO$_{1-x}$-1:1.

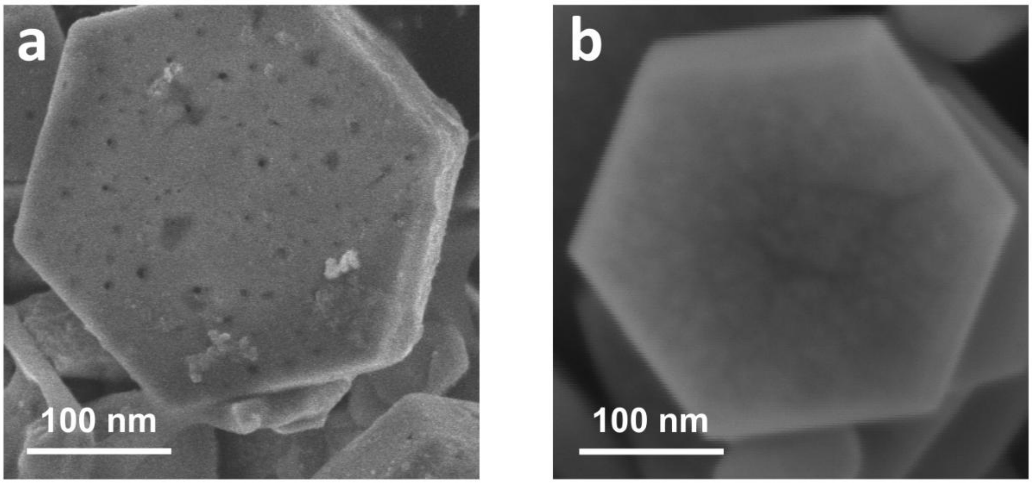


Fig. S3 SEM images of (a) ZnO_{1-x}-1:1 and (b) ZnO.

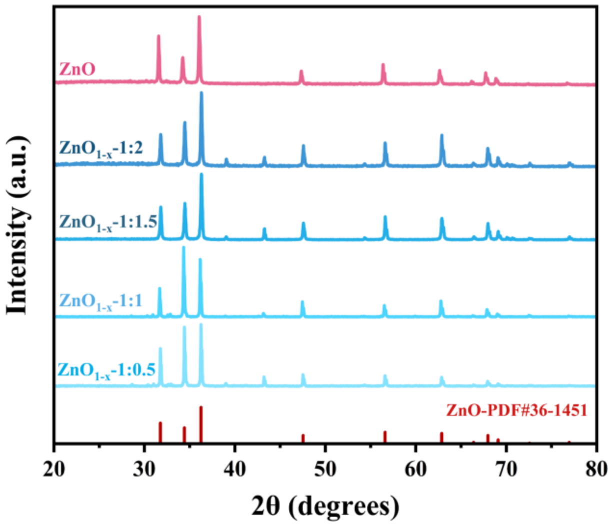


Fig. S4 XRD patterns of ZnO, ZnO_{1-x}-1:0.5, ZnO_{1-x}-1:1, ZnO_{1-x}-1:1.5 and ZnO_{1-x}-1:2.

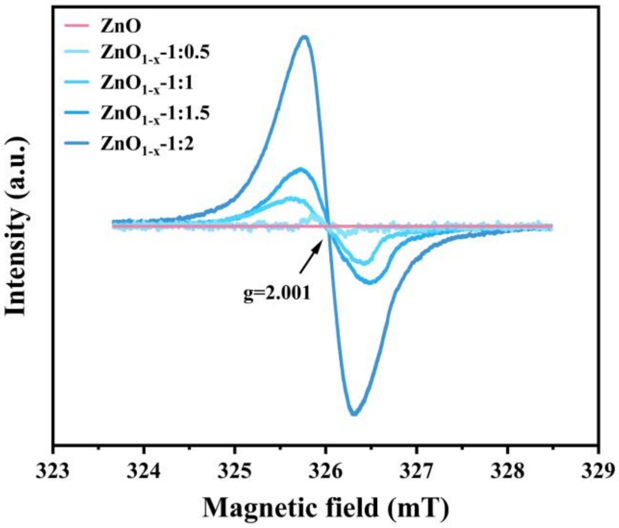


Fig. S5 EPR spectra of ZnO, ZnO$_{1-x}$-1:0.5, ZnO$_{1-x}$-1:1, ZnO$_{1-x}$-1:1.5 and ZnO$_{1-x}$-1:2.

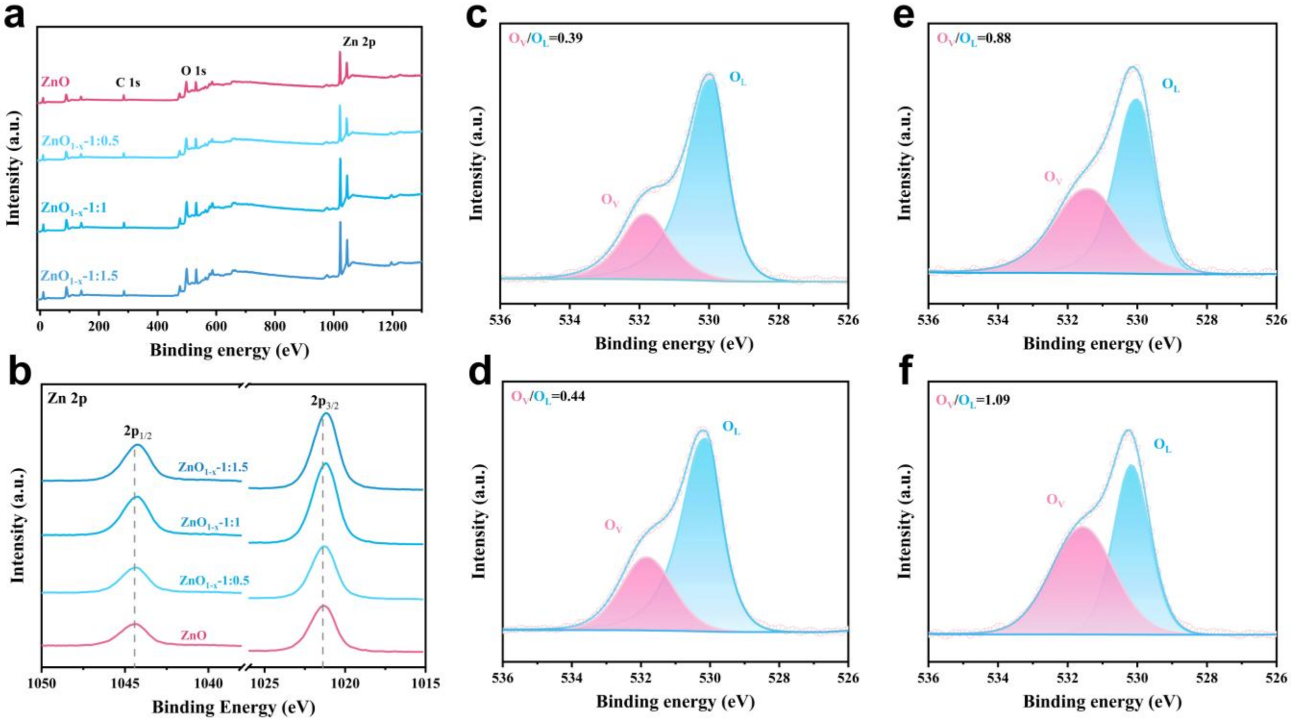


Fig. S6 (a) Full XPS spectra, (b) Zn 2p spectra of ZnO and ZnO_{1-x}. O 1s spectra of (c) ZnO, (d) ZnO_{1-x}-1:0.5, (e) ZnO_{1-x}-1:1, (f) ZnO_{1-x}-1:1.5.

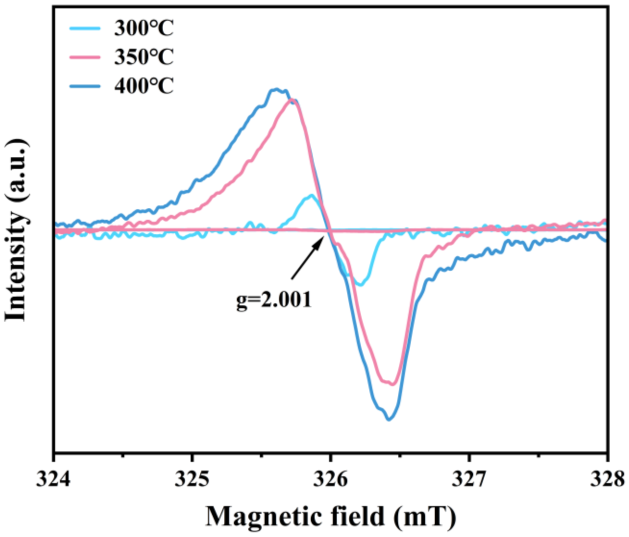


Fig. S7 (a) EPR spectra of samples obtained at different calcination temperatures.

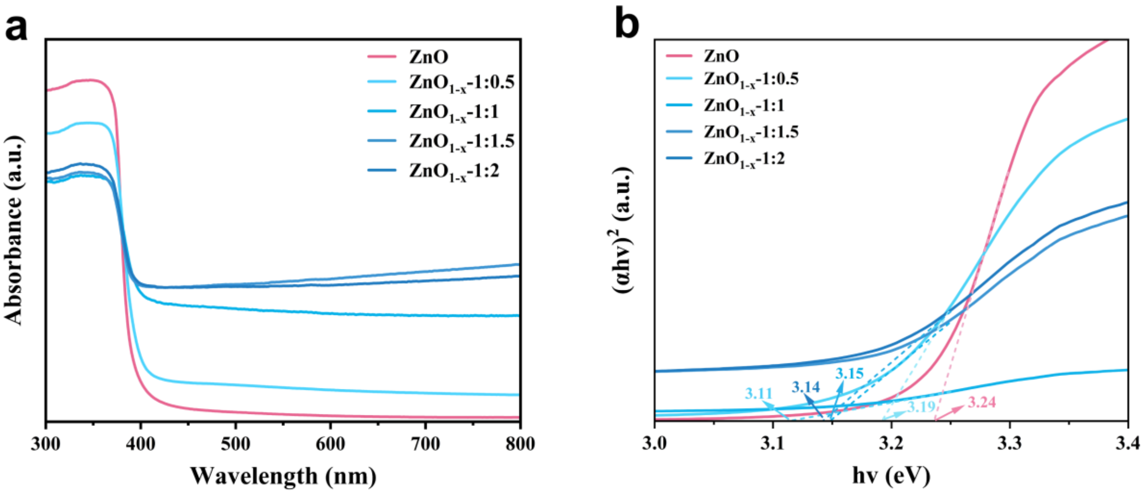


Fig. S8 (a) UV-vis spectra, (b) Tauc plots of ZnO and ZnO_{1-x}.

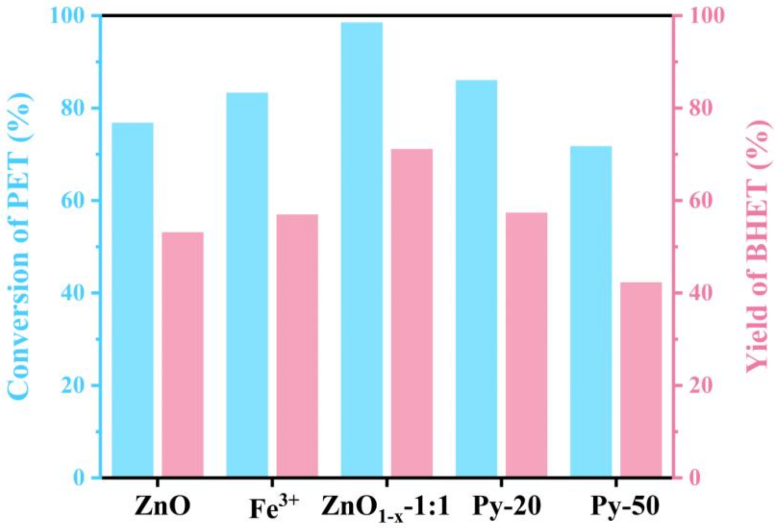


Fig. S9 Comparison of PET conversion and BHET yield over different catalytic systems.

To provide direct evidence for the Lewis acid site activity of oxygen vacancies, we conducted the following control experiments: (1) using pristine ZnO (without oxygen vacancies) as the catalyst, (2) soaking pristine ZnO in a 5 mol% $FeCl_3$ ethanol solution to introduce Lewis acid site onto its surface, (3) using ZnO_{1-x}-1:1 as the catalyst; (4) using ZnO_{1-x}-1:1 as the catalyst with the addition of 20 μL of pyridine (a Lewis base to block the effect of the Lewis acid) to the solvent as a Lewis acid inhibitor; and (5) using ZnO_{1-x}-1:1 as the catalyst with the addition of 50 μL of pyridine to the solvent.

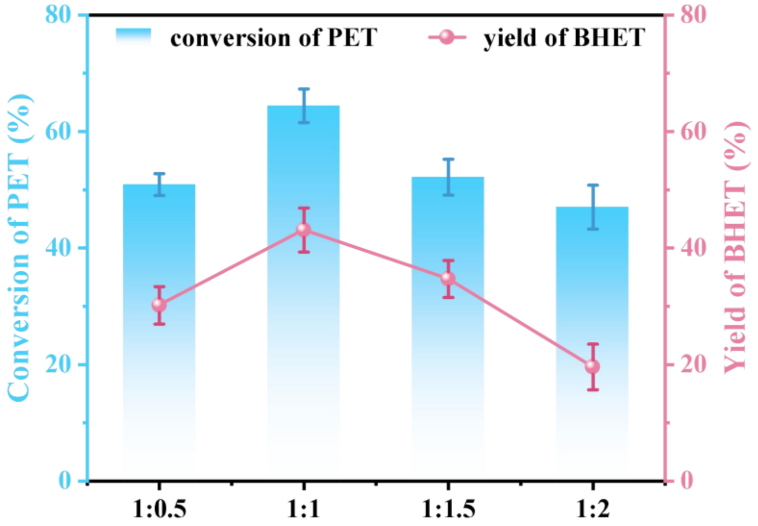


Fig. S10 PET conversion and BHET yield rate of ZnO_{1-x} thermocatalytic reaction at 190 ℃ for 0.5h.

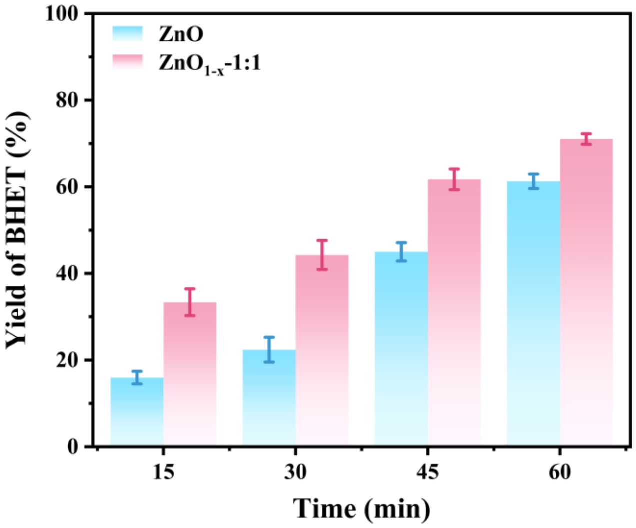


Fig. S11 BHET yield rate for ZnO and ZnO_{1-x}-1:1 thermocatalytic reaction at 190 °C for different durations.

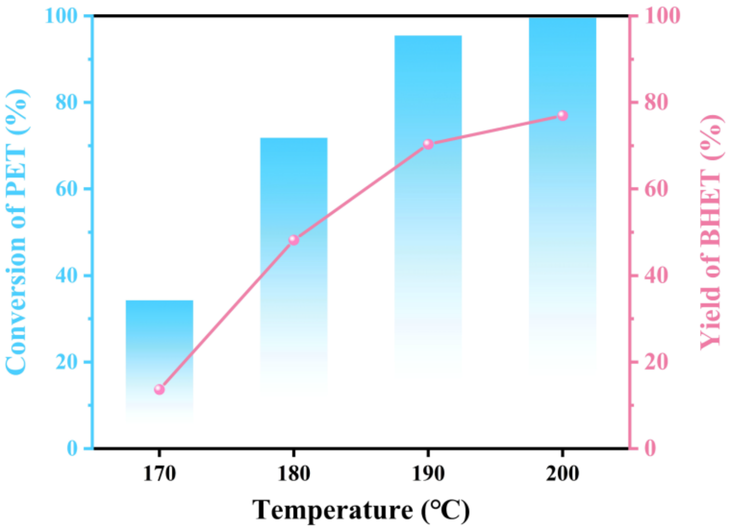


Fig. S12 PET conversion and BHET yield of ZnO_{1-x}-1:1 thermocatalytic reaction at various temperatures for 1 h.

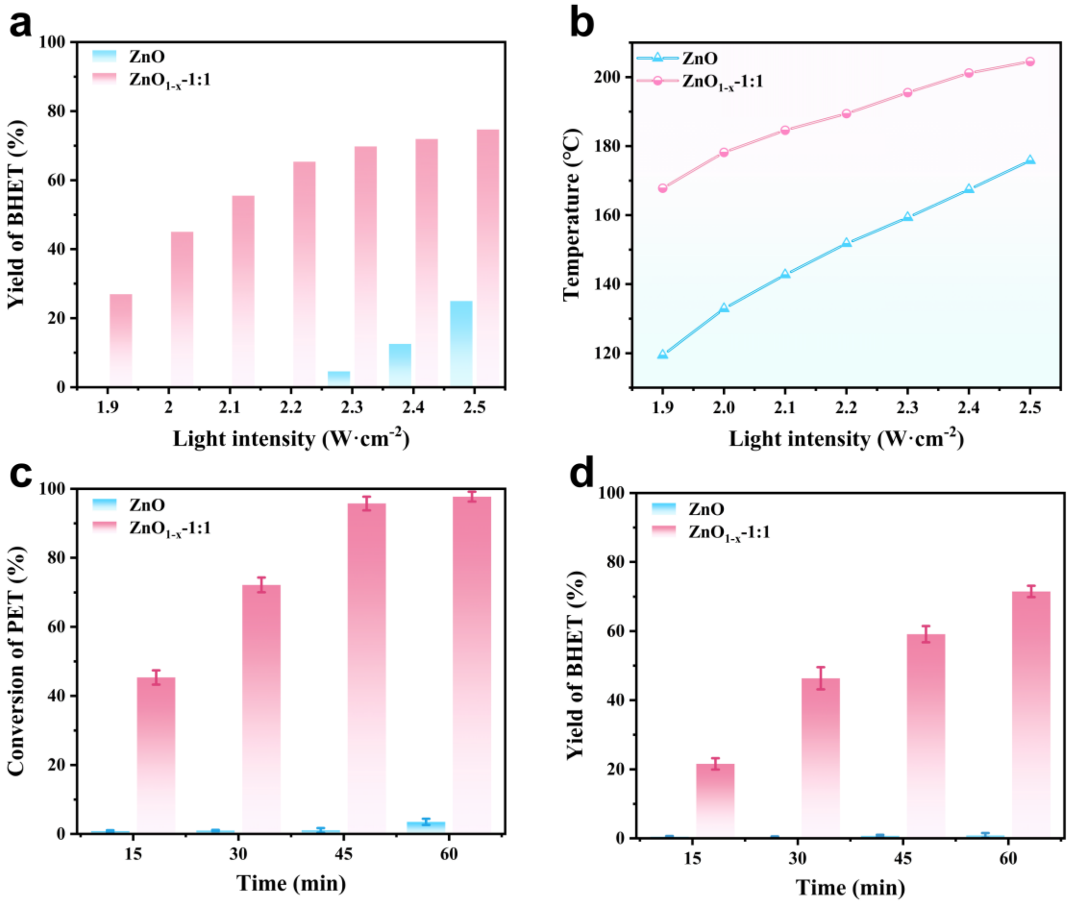


Fig. S13 (a) BHET yield for ZnO and ZnO_{1-x}-1:1 reacted for 1 h under different light intensities. (b) The system temperature reached at different light intensities for ZnO and ZnO_{1-x}. (c) PET conversion rate, (d) BHET yield for ZnO and ZnO_{1-x}-1:1 under 2.2 W cm^{-2} light intensity for different durations.

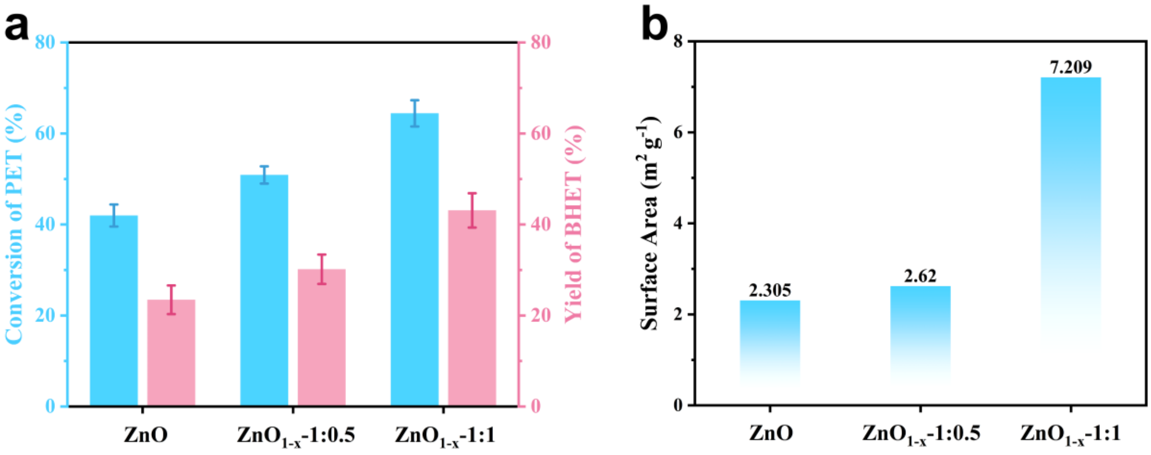


Fig. S14 (a) PET conversion and BHET yield rate, (b) Surface area of ZnO, ZnO_{1-x}-1:0.5 and ZnO_{1-x}-1:1.

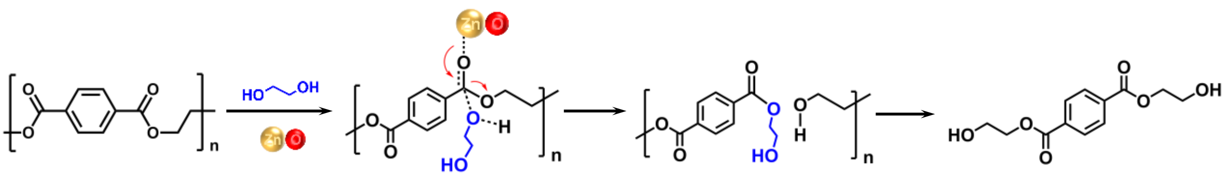
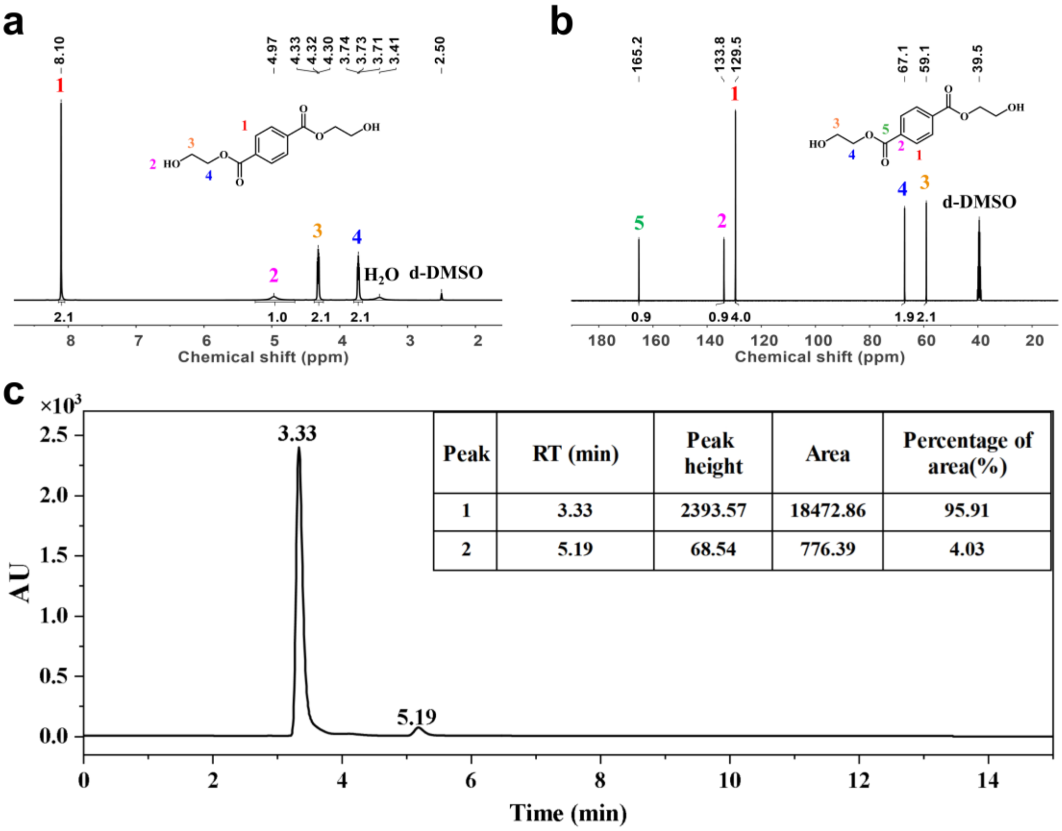


Fig. S15 The photothermal catalytic mechanism of PET glycolysis.



Peak	RT (min)	Peak height	Area	Percentage of area(%)
1	3.33	2393.57	18472.86	95.91
2	5.19	68.54	776.39	4.03

Fig. S16 (a) ^{1}H NMR spectrum of BHET, (b) ^{13}C NMR spectrum of BHET, (c) HPLC spectrum of BHET.

Table S1 The catalytic activities of PET glycolysis with different catalysts.

Entry	Catalyst	Temp.(°C)	Time(min)	C_{PET}(%)	Y_{BHET}(%)
1	TiO_2-comm.	190°C	60	1	0
2	Ta_2O_5-comm.	190°C	60	5	1
3	ZnO-comm.	190°C	60	46	32
4	MoO_3-comm.	190°C	60	6	0
5	V_2O_5-comm.	190°C	60	1	0
6	WO_3-comm.	190°C	60	2	0
7	Fe_2O_3-comm.	190°C	60	4	0
8	CuO-comm.	190°C	60	2	0
9	Co_3O_4-syn.	190°C	60	55	42
10	ZnO-syn.	190°C	60	55	38
11	$W_{18}O_{49}$-syn.	190°C	60	21	8
12	CeO_2-syn.	190°C	60	1	0

Table S2 Fitting results of O 1s from XPS for ZnO_{1-x}.

	ZnO	ZnO_{1-x}-1:0.5	ZnO_{1-x}-1:1	ZnO_{1-x}-1:1.5
O_L (Lattice O)	72.12%	69.48%	53.21%	47.78%
O_V (O vacancy)	27.88%	30.52%	46.79%	52.22%
O_V/O_L	0.39	0.44	0.88	1.09

Reference

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[3] F. Li, X. Yao, R. Ding, et al., Directional Glycolysis of Waste PET Using Deep Eutectic Solvents for Preparation of Aromatic-Based Polyurethane Elastomers. *Green Chem.* **2024**, 26, 9802-9813.