

Electronic Supporting Information

Zinc oxide rod/peanut shell-derived porous carbon composites for cooperative CO₂ chemical fixation

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S1 Materials and Instrumentation

All chemicals were purchased from commercial sources and used without further treatment: Peanut shells were collected from a local farm in Henan Province, China. Zinc chloride (ZnCl_2 , Nanjing Chemical Reagent Co. Ltd, 98%), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Nanjing Chemical Reagent Co. Ltd, AR) epichlorohydrin (Aladdin Industrial Inc., 99.5%), epobromopropane (Aladdin Industrial Inc., 99.5%), 1,2-epoxybutane (energy chemical, 99%), glycidyl phenyl ether (energy chemical, 99%), 1,2-epoxyoctane (energy chemical, 99%), tetrabutylammonium bromide (TBAB, Sinopharm Chemical Reagent Co., Ltd., AR), acetonitrile (Sinopharm Chemical Reagent Co., Ltd., AR), ethyl acetate (Sinopharm Chemical Reagent Co., Ltd., AR), *N,N*-Dimethylformamide (Sinopharm Chemical Reagent Co., Ltd., AR), methanol (Sinopharm Chemical Reagent Co., Ltd., AR), hydrochloric acid (Nanjing Chemical Reagent Co. Ltd, AR), hydrofluoric acid (HF, Nanjing Chemical Reagent Co. Ltd, AR).

The crystalline phase of the samples was determined by X-ray diffraction (XRD, Ultima IV, Rigaku). Scanning electron microscopy (SEM) images were recorded by a field emission scanning electron microscope (FESEM, JEOL JSM-7600F). Thermo Electron Nicolet-360 spectrometer was utilized to record their Fourier transform infrared (FT-IR) spectra, with KBr discs between 4000 and 400 cm^{-1} . The contents of zinc ions in samples were determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES) on a PerkinElmer 8300 atomic emission spectrometer. The conversion and yield were determined by using a gas

chromatograph (GC, HF-901A, Shandong Huifen Instrument Co., Ltd., China), which has an FID detector and high purity nitrogen as the carrier gas. The CO₂ and N₂ sorption isotherms were measured by an automatic volumetric adsorption equipment (Micromeritics TriStar 3020). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a AXIS UltraDLD (Shimadzu, Kyoto, Japan) with Al K α as the excitation source. The content of chloride ion was quantified by a Dionex 7680 ion chromatography upon combustion in oxygen bomb. Thermogravimetric analyses (TGA) were conducted on a Netzsch STA 449C thermal analyzer at a ramp rate of 10 °C/min under nitrogen.

S2 Experimental Section

2.1 Preparation of catalysts

Synthesis of ZnO/PSC composites: ZnO/PSC composites were prepared based on a previous report with minor modifications.^{S1} Typically, peanut shells were first washed with deionized water several times and dried at 120 °C overnight. The dried peanut shells were crushed and then shifted through a 60-mesh sieve. The peanut shell powder was mixed with 2 mol L⁻¹ ZnCl₂ aqueous solution at different mass ratios of ZnCl₂/peanut shell (3:1, 4:1, and 5:1). The mixture was then transferred to a 100 mL Teflon-lined autoclave and placed in a preheated oven at 120 °C for 10 h. Upon cooling down to room temperature, the mixture was dried overnight at 80 °C. The resultant product was obtained by heating at 550 °C for 2 h at a heating rate of 5 °C min⁻¹ with argon (Ar) flow rate of 8 mL min⁻¹.

Synthesis of PSC: Typically, peanut shells were first washed with deionized water several times and dried at 120 °C overnight. The dried peanut shells were crushed and then shifted through a 60-mesh sieve. The resultant product (PSC) was obtained by heating at 550 °C for 2 h at a heating rate of 5 °C min⁻¹ with Ar flow rate of 8 mL min⁻¹.

Synthesis of PSC-4: Typically, ZnO/PSC-4 (1.0 g) was introduced and stirred in 1.5 mol L⁻¹ HF aqueous solution at room temperature for 24 h. The resultant product (PSC-4) was obtained by filtration, then washed with 1 mol L⁻¹ hydrochloric acid,

water and methanol several times, and dried at 60 °C in vacuum.

Synthesis of ZnO: Typically, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 g) was placed in a crucible and calcined in air at 550 °C for about 2 h in a muffle furnace. ZnO powder was then obtained after cooling down to room temperature naturally.

2.2 Catalytic Performance Evaluation

Cycloaddition of epoxides with CO_2 : Typically, the mixture of catalyst (50 mg), TBAB (54.8 mg, 0.17 mmol), acetonitrile (2 mL) and epoxide (1 mmol) was loaded into a 5 mL round-bottom flask, which was connected to a balloon that filled with CO_2 by T-piece. Afterwards, the mixture was stirred at 60 °C for 24 h. The reaction was monitored by GC analysis.

Recyclability investigation for catalysts: After the cycloaddition reaction of epichlorohydrin and CO_2 for 24 h, the catalyst (ZnO/PSC-4) was collected by centrifugation, washing with methanol several times and drying overnight in a vacuum oven at 60 °C. After that, the catalyst was used for the subsequent cycloaddition reaction of epichlorohydrin and CO_2 . The same procedure was conducted for five times to examine the recyclability performance of ZnO/PSC-4.

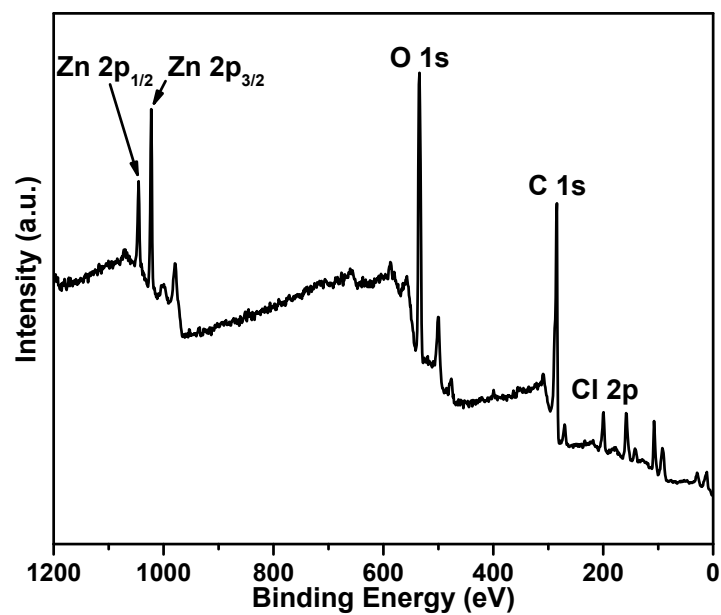


Fig. S1 XPS survey spectrum for ZnO/PSC-4.

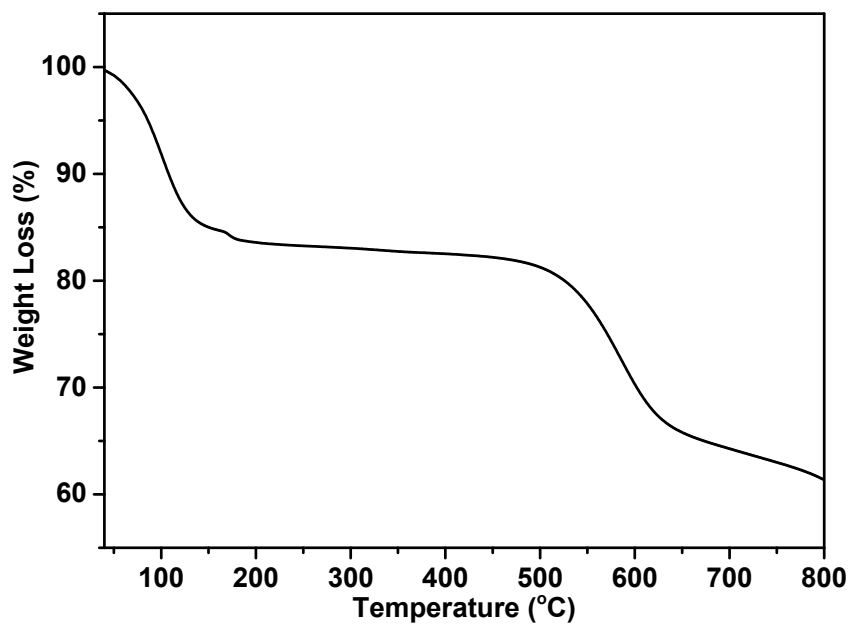


Fig. S2 TG curve of ZnO/PSC-4 in N₂ atmosphere. The weight loss in the range of 40-200 °C could be attributed to removal of water. The de-solvated ZnO/PSC-4 started to collapse from 500 °C.

Table S1 The content of Zn in ZnO/PSC-X (X=3, 4, 5) determined by ICP-OES.

	Zn (wt%)
ZnO/PSC-3	17.4
ZnO/PSC-4	27.1
ZnO/PSC-5	21.4

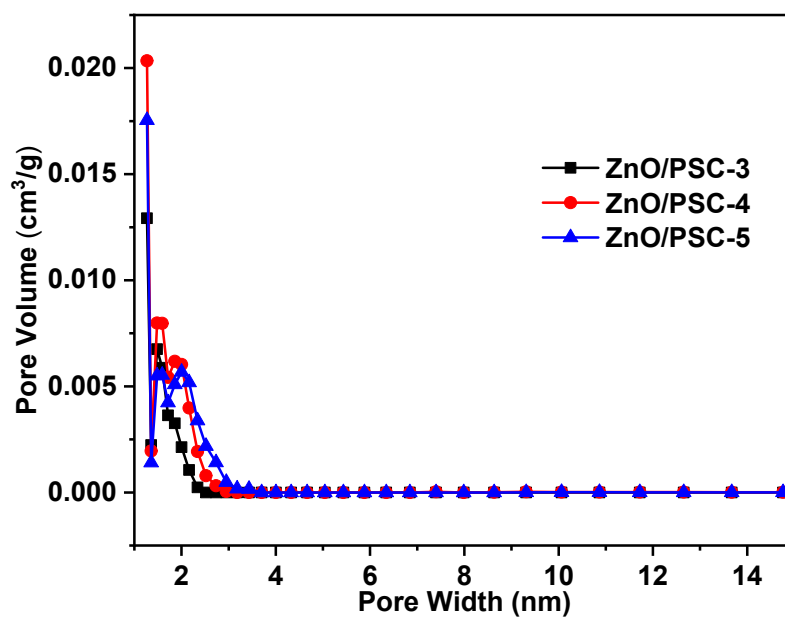


Fig. S3 Pore size distribution analyses based on the density functional theory (DFT) method for ZnO/PSC-X (X=3, 4, 5).

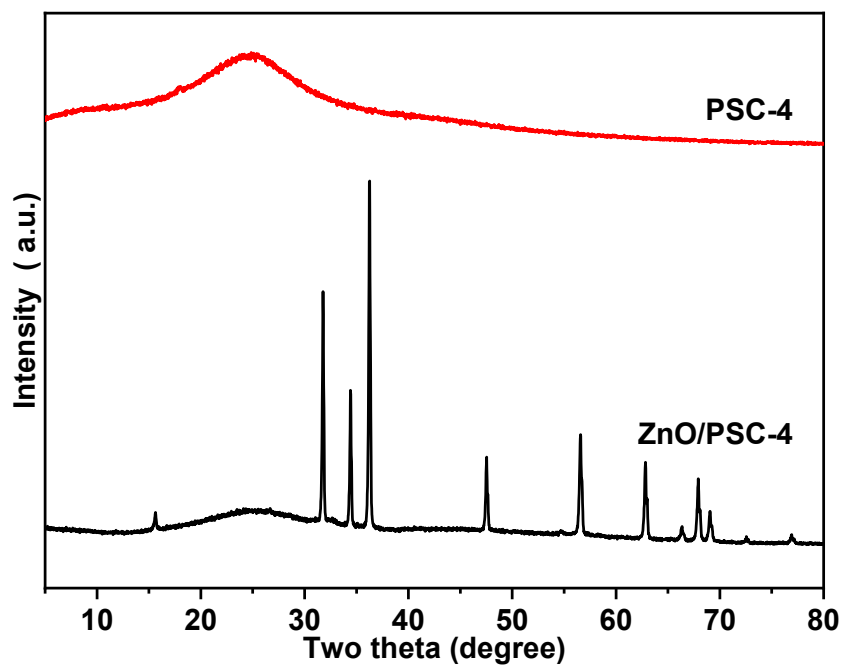


Fig. S4 Powder XRD patterns of ZnO/PSC-4 and PSC-4 obtained by acid etching.

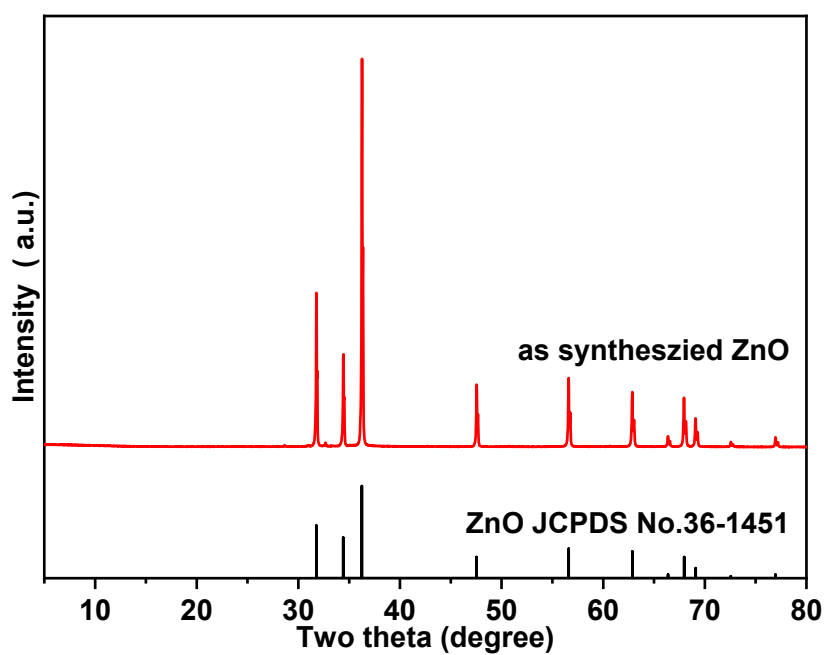


Fig. S5 Powder XRD pattern ZnO obtained by the pyrolysis of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in air.

Table S2 Comparison of ZnO/PSC-4 with other porous carbon catalysts for the cycloaddition of epichlorohydrin with CO₂.

entry	catalyst	carbon source	reaction condition	yield (%)	refs.
1	ZnO/PSC-4 + TBAB	peanut shell	60 °C, 1 bar CO ₂ , 24 h	99	this work
2	HPC-800 + TBAB	ZIF-8	light irradiation, 1 bar CO ₂ , 10 h	96	S2
3	ZnO@NPC-Ox-700 + TBAB		60 °C, 1 bar CO ₂ , 24 h	94	S3
4	C600-ZIF-9 + TBAB	ZIF-9	80 °C, 0.6 Mpa CO ₂ , 6 h	98	S4
5	ox-bc _{hw} + TBAB	hardwood	110 °C, 10 bar CO ₂ , 6 h	97	S5
6	Co@N-HPC-40 + TBAB	chitosan + g-C ₃ N ₄	80 °C, 0.15 Mpa CO ₂ , 48 h	93	S6
7	ZnS/NPC-2 + TBAB	bovine serum albumin	light irradiation, 1 bar CO ₂ , 12 h	98	S7
8	ZnO/CPre + TBAB	triazine-based MOP	25 °C, 0.1 Mpa CO ₂ , 48 h	91	S8
9	AA-950	alginic acid	150 °C, 40 bar CO ₂ , 16 h	84	S9
10	CNFWs-600-2	polypyrrole	150 °C, 20 bar CO ₂ , 12 h	86	S10
11	Co/CMC-A-1 + TBAB	waste cow manure	80 °C, 1 bar CO ₂ , 48 h	69	S11
12	CSAC-[APTS][Br]	coconut shell	130 °C, 1.4 Mpa CO ₂	44	S12
13	TW-900 + TBAB	tea waste	100 °C, 1 bar CO ₂ , 8 h	90	S13

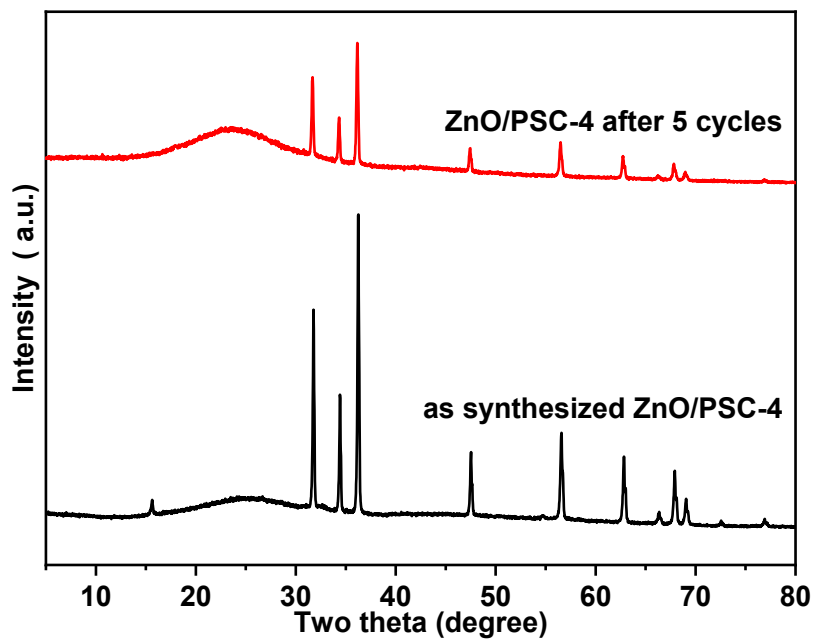
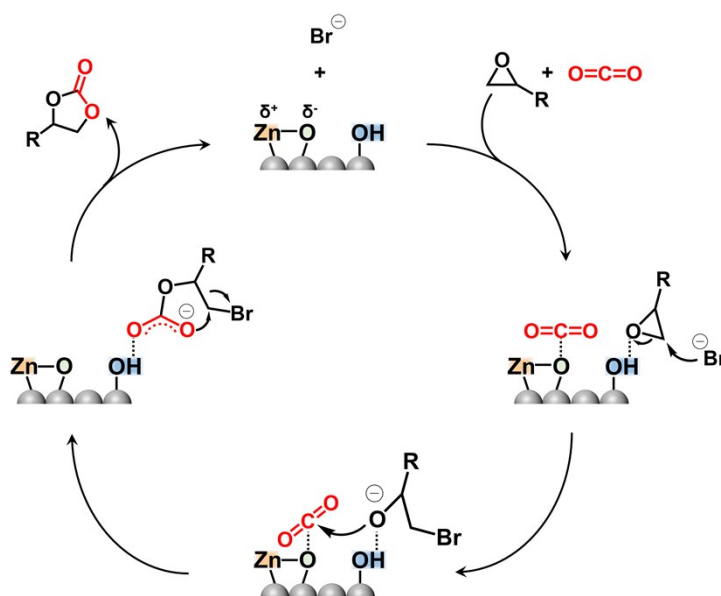
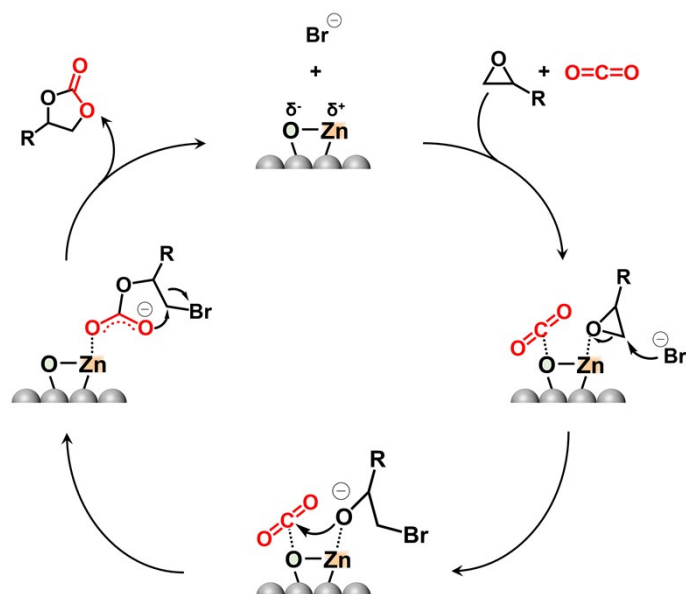


Fig. S6 Powder XRD patterns of ZnO/PSC-4 before and after five catalytic cycles.



Scheme S1 Proposed reaction mechanism for cycloaddition of epoxides with CO₂ catalyzed by ZnO/PSC-4 involving ZnO and hydroxyl species, in the presence of bromide ion from TBAB.



Scheme S2 Proposed reaction mechanism for cycloaddition of epoxides with CO₂ catalyzed by ZnO species of ZnO/PSC-4, in the presence of bromide ion from TBAB.

References

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