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Nanostructured ZnO as a structural template for the growth of ZIF-8 with tunable hierarchical porosity for CO_2 conversion

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Electronic Supporting Information (ESI)

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1. Materials and Experimental methods

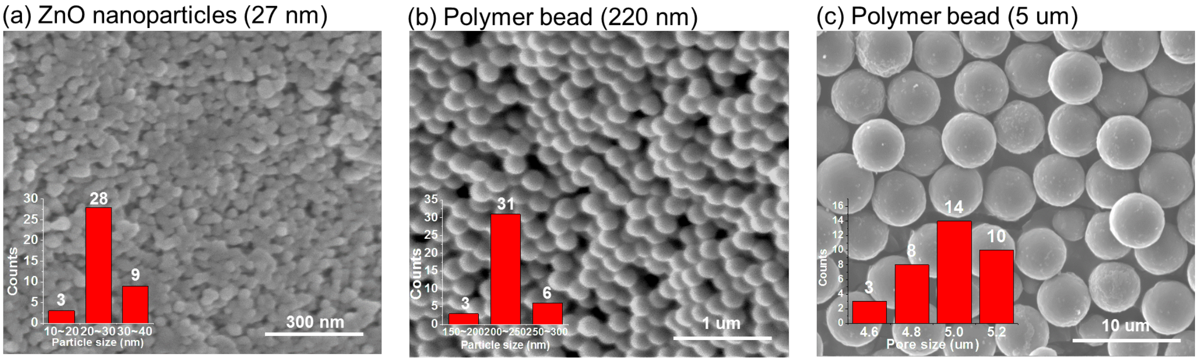
Materials: Styrene (99%, Sigma Aldrich), methyl methacrylate (MMA, 99%, Samchun), 3-sulfopropyl methacrylate potassium (SPMAP, 98%, Aldrich), ammonium persulfate (98%, Samchun), ammonium bicarbonate (95%, Samchun), $Zn(Ac)_2 \cdot 2H_2O$ (99%, Samchun), ethylene glycol (EG, 99.9%, Samchun), ethanol and acetone are purchased and used without further purification. Anionic alumina oxide (AAO) film with 200 nm pore size and 48 mm diameter was supplied from Whatman (Anodisc Inorganic membrane). Polymer beads with particles size of 5 μm were purchased from SUNJIN BEAUTY SCIENCE.

Characterization: Powder X-ray diffraction (PXRD) analysis was carried out using SmartLab (Rigaku) with CuK radiation (λ=1.5406Å) at a generator voltage of 40 kV and a generator current of 200 mA. For the scanning electron microscopy (SEM) analysis, all the samples were attached on carbon tapes and then coated with osmium. After the sample preparation, SEM images were obtained using Nova230 of FEI Company. Fourier transform infrared spectroscopy (FT-IR) data was obtained using Bruker Alpha with 64 scan-times and 4 cm^{-1} of resolution. Ar isotherms were measured using an ASAP 2020 physisorption analyzer (Micromeritics, USA) at 87 K. Prior to the measurements, all the samples were evacuated at 150˚C for 12 h. To analyze meso/macropore and micropore size distributions, Barret-Joyner-Halenda (BJH) with Halsey-Faas correction and NLDFT analyses were employed, respectively. TEM analysis was carried out using F30 ST (FEI Tecnai) operated at 300 kV. For TEM sample preparation, the diluted dispersion of ground ZIF-8/ZnO(S) in the ethanol was dropped onto the lacey-carbon-coated Cu grid. The STEM-EDS measurement was performed with scanning transmission electron microscopy (STEM) equipped with windowless EDAX spectrometer.

Synthesis of porous ZnO templates: The synthesis of ZnO template was conducted by following well-established methods reported in the literature.[S1] In our case, 0.17 g SPMAP are used to synthesize poly(styrene-methylmethacrylate-3-sulfopropylmethacrylate potassium) beads with the average particle size of 220 nm. Aqueous suspension of the polymer beads (0.25 wt%, 5 mL) and ZnO nanoparticles (0.01g mL^{-1}, ZnO(S): 5mL, ZnO(L): 15 mL) were mixed under magnetic stirring for 1–2 h. The dispersion of ZnO nanoparticles and polymer beads was slowly vacuum filtered and dried at 40ºC for 8 h. The polymer/ZnO structures were calcined at 450ºC under air for 4 h to remove polymer beads.

Synthesis of hierarchical ZIF-8/ZnO nanostructures: As-prepared 0.08 g ZnO templates were mixed in 1 mL MIM MeOH solution (1 M) and then MeOH was completely dried at room temperature. The mixtures of MIM and ZnO templates were kept at 150ºC for 1 h. After the completion of the reaction, the resulting ZIF-8/ZnO nanostructures were washed thoroughly with MeOH.

Catalytic CO_2 conversion reaction: The reactions were conducted by using 50 mL glass lined stainless-steel reactor equipped with a pressure gauge. Catalyst (100 mg, ca. 6 wt%) and epichlorohydrin (1.6 g, 18 mmol) were placed in the vessel and charged with CO_2 (1 MPa). After heating for 24 h at 80ºC, the reactor was cooled down to room temperature and the remaining CO_2 was vented. The resulting materials were immersed in $CDCl_3$ and filtrated to collect liquid phase. The liquid samples were directly analyzed by ^{1}H NMR spectroscopy.



(a) ZnO nanoparticles (27 nm)

(b) Polymer bead (220 nm)

(c) Polymer bead (5 um)

Figure S1. SEM images of (a) ZnO nanoparticles and polymer beads with average particle diameters of (b) ~220 nm and (b) ~5 ⌠m. The insets represent particle size distribution for each sample.

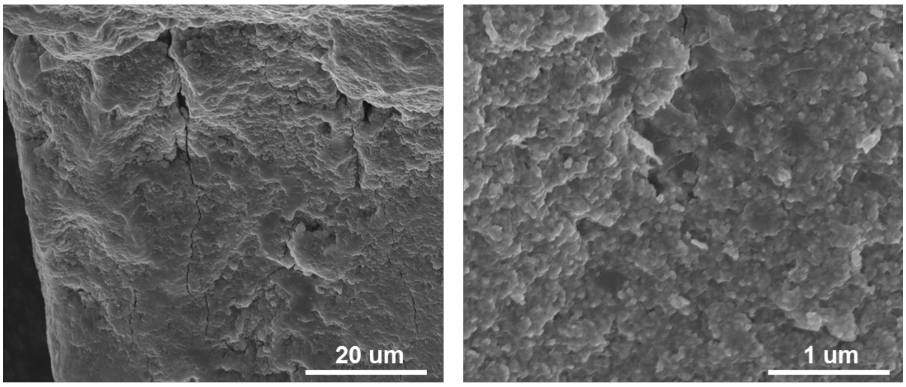


Figure S2. SEM images of porous ZnO templates after their reaction with 2-methylimidazole powder at 160˚C.

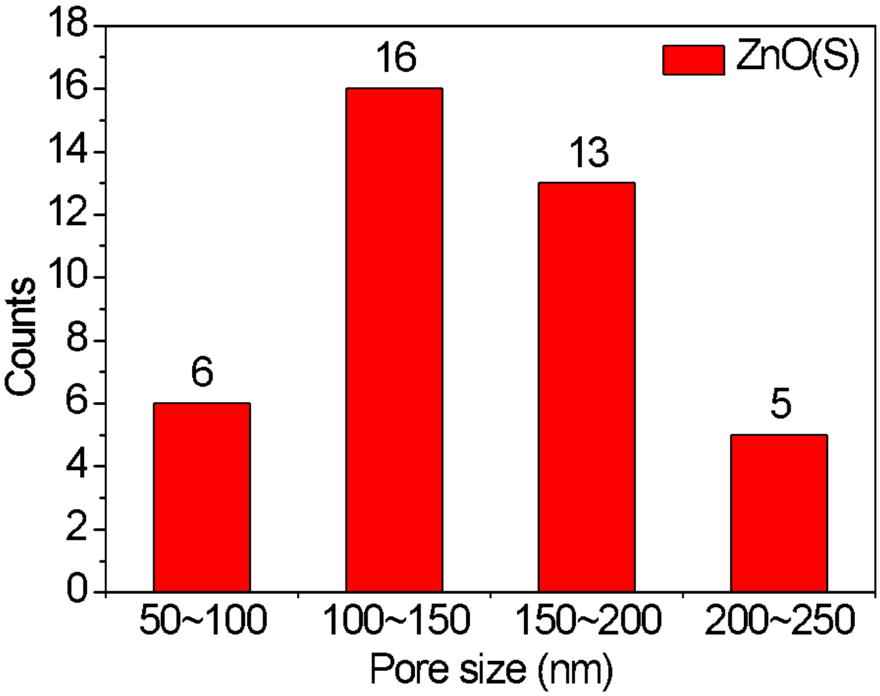


Figure S3. Pore size distribution histogram of ZnO(S)

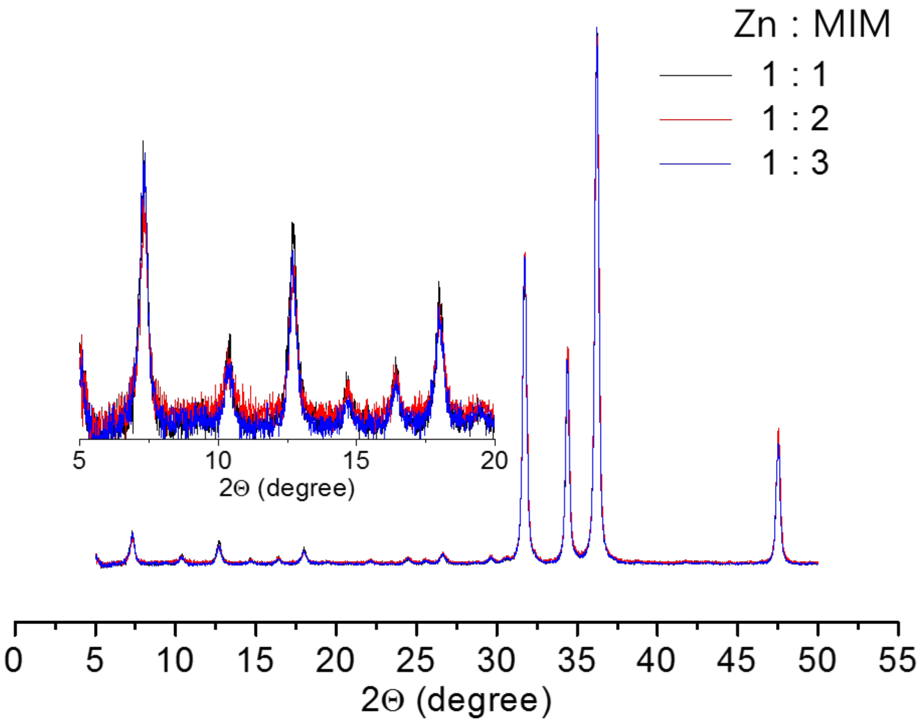


Figure S4. PXRD spectra of ZIF-8/ZnO(S) obtained by the reaction of ZnO(S) with equimolar, 2 and 3 times of MIM.

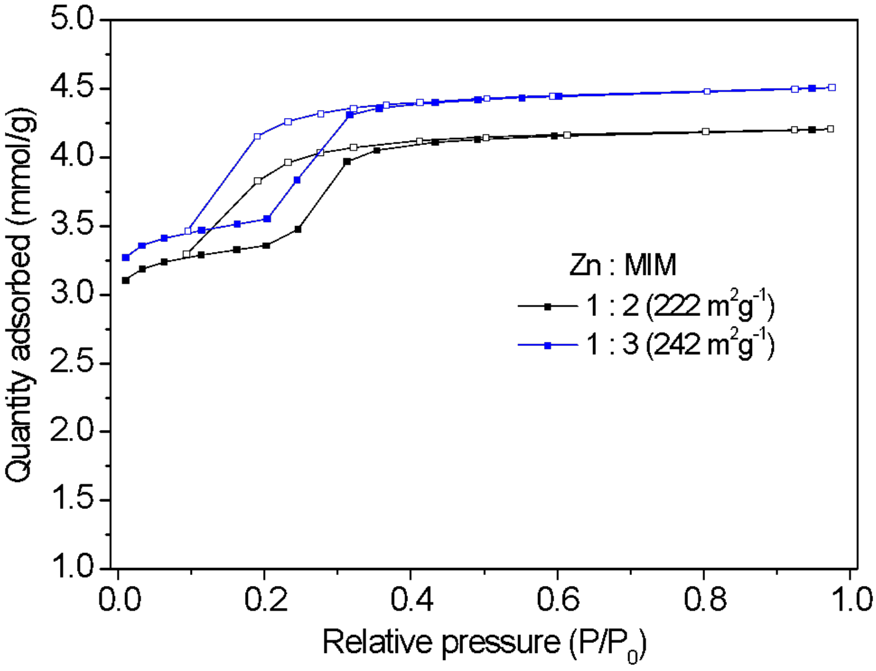


Figure S5. Ar adsorption-desorption isotherms of ZIF-8/ZnO(S) obtained by the reaction of ZnO(S) with 2 and 3 times of MIM at 77 K.

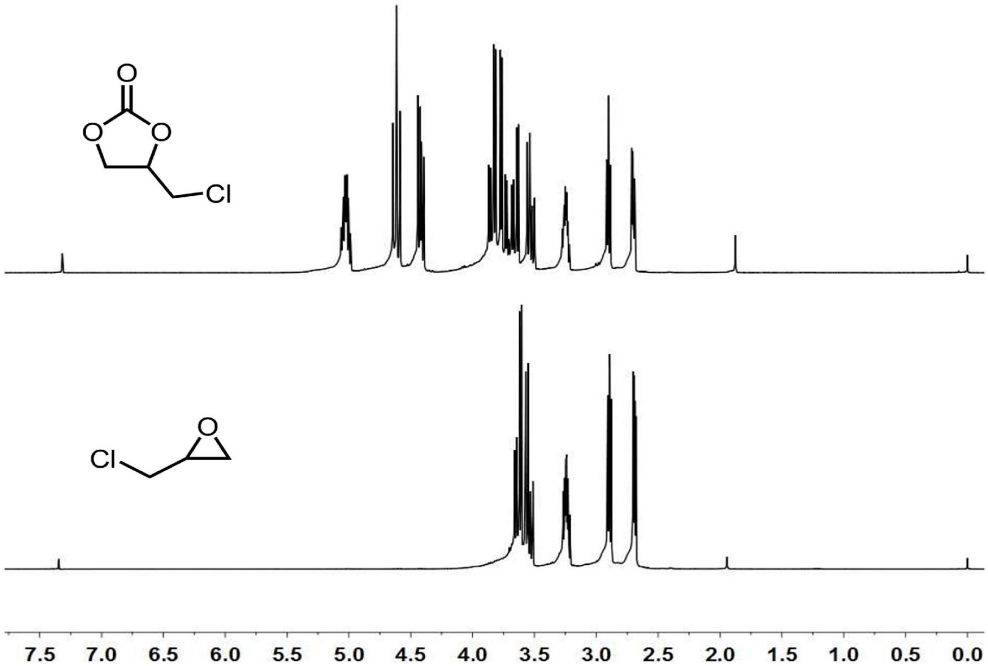


Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra of epichlorohydrin and its catalytic conversion to the corresponding cyclic carbonate. ^{1}H NMR spectrum was obtained from the crude sample after reaction of epichlorohydrin with CO_2 at 10 bar 80 ºC by using **ZIF-8/ZnO(S)** as a catalyst.

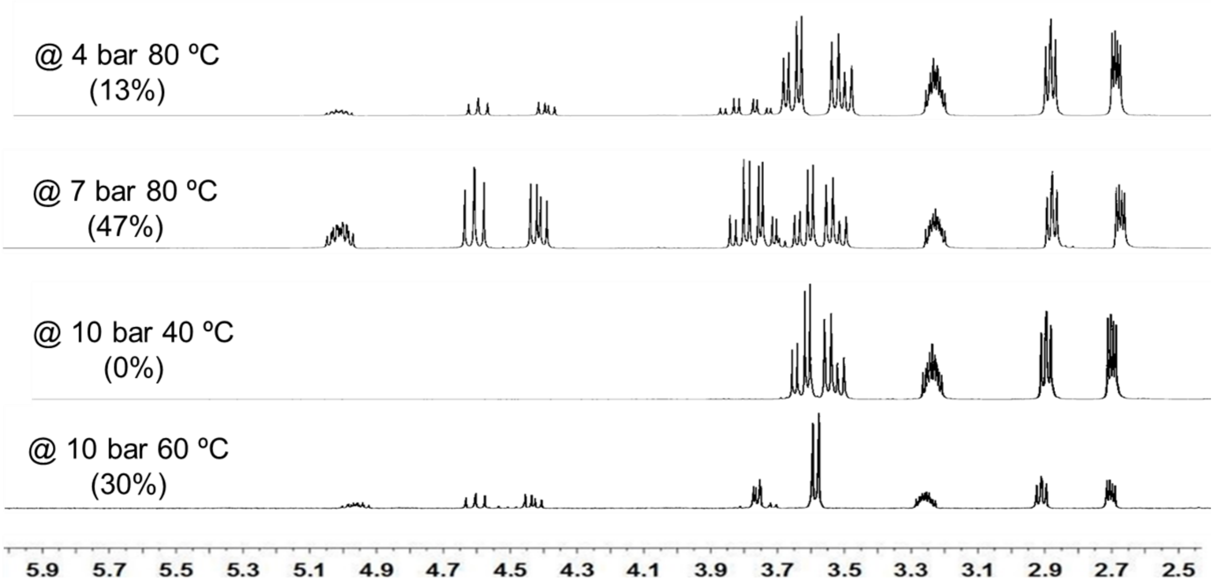


Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra for the catalytic conversion of epichlorohydrin to chloropropene carbonate in the presence of CO_2 under different reaction conditions by using **ZIF-8/ZnO(S)** as a catalyst. ^{1}H NMR spectra were obtained from the crude samples.

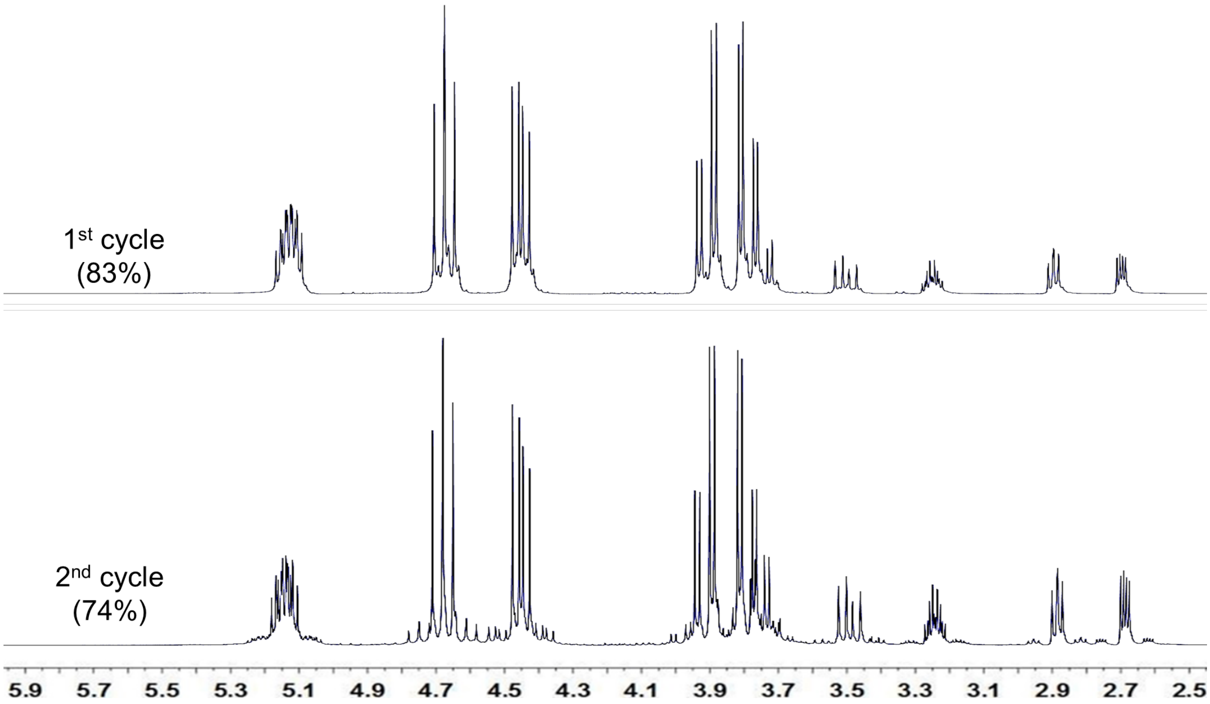


Figure S8 ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra for the catalytic conversion of epichlorohydrin to chloropropene carbonate in the presence of CO_2 (10 bar) at 100°C by using **ZIF-8/ZnO(S)** as a catalyst up to two catalytic cyles. ^{1}H NMR spectra were obtained from the crude samples.

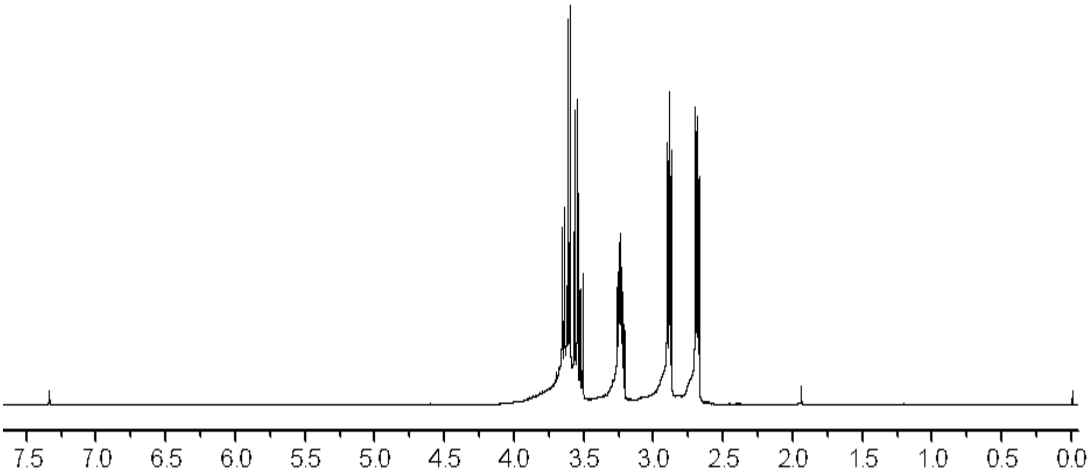


Figure S9 ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of catalytic conversion of epichlorohydrin to the corresponding cyclic carbonate. ^{1}H NMR spectrum was obtained from the crude sample after reaction of epichlorohydrin with CO_2 by using **ZnO** as a catalyst. Importantly, ZnO did not show any catalytic activity.

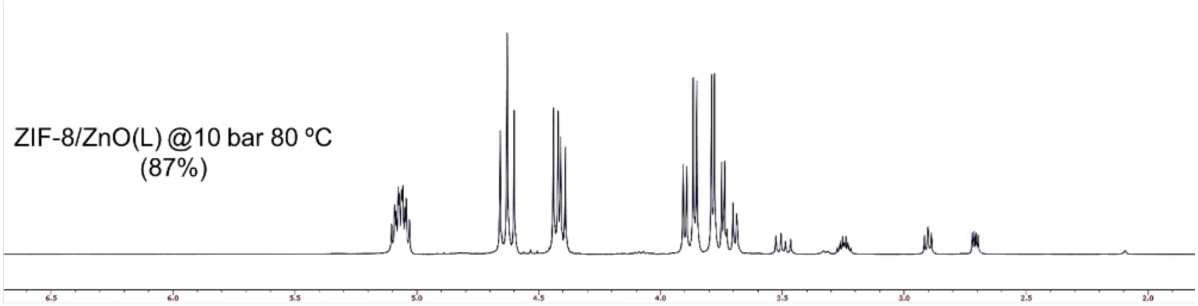


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum for the catalytic conversion of epichlorohydrin to chloropropene carbonate in the presence of CO_2 (10 bar) at 80°C by using ZIF-8/ZnO(L) as a catalyst. ^{1}H NMR spectrum was obtained directly from the crude sample.

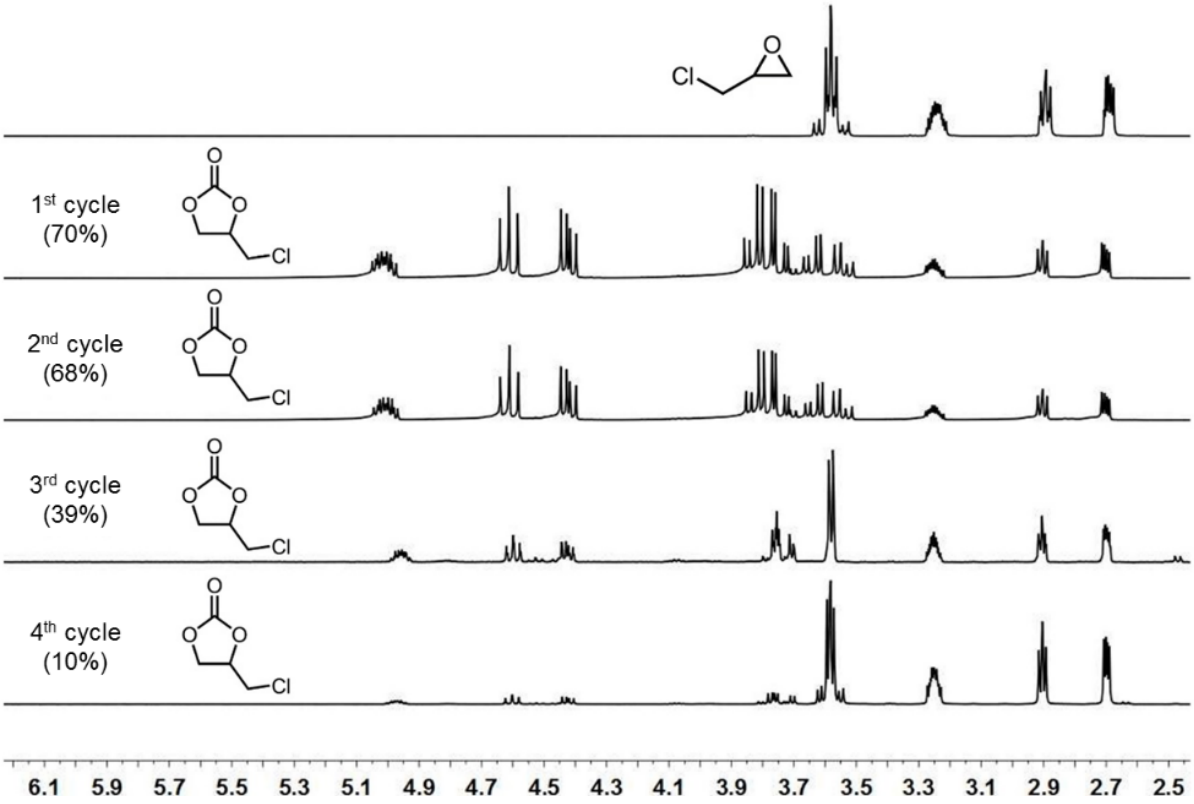


Figure S11. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra of epichlorohydrin and its catalytic conversion to corresponding cyclic carbonate in the presence of CO_2 (10 bar, 80°C) by using ZIF-8/ZnO(S) as a catalyst up to four catalytic cycles. ^{1}H NMR spectra were obtained from the crude samples.

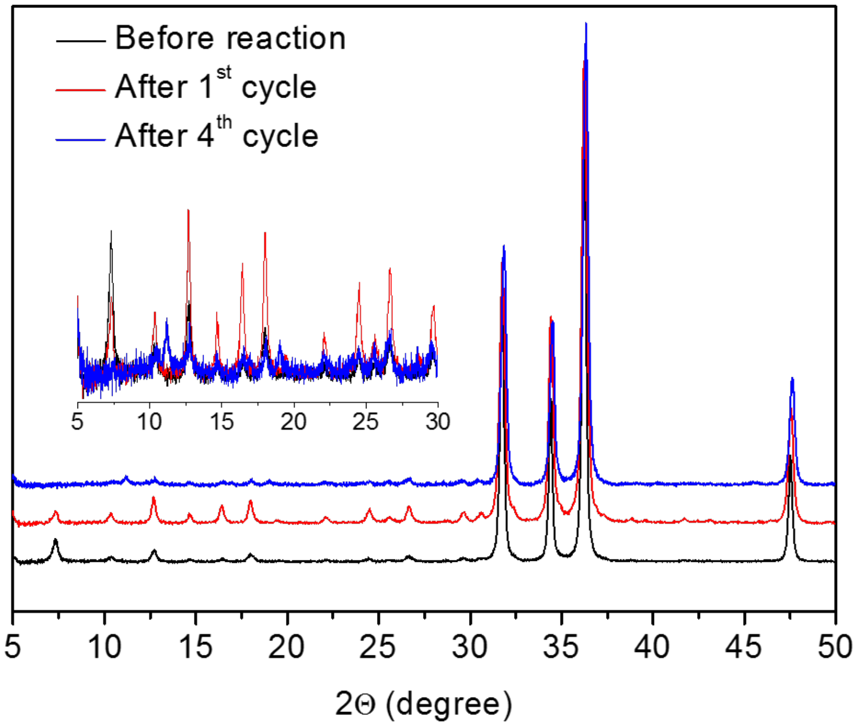


Figure S12 PXRD spectra of ZIF-8/ZnO(S) before (black), after the first cycle (red) and the fourth cycle (blue).

Table S1 Catalytic performance of ZnO and ZIF-8/ZnO(S) in the reaction of CO_2 with epichlorohydrin.

Catalyst	Temperature (C°)	Pressure (bar)	Epichlorohydrin Conversion (%)
ZnO	80	10	0
ZIF-8/ZnO(S)	80	4	13
ZIF-8/ZnO(S)	80	7	47
ZIF-8/ZnO(S)	80	10	70
ZIF-8/ZnO(S)	40	10	0
ZIF-8/ZnO(S)	60	10	30
ZIF-8/ZnO(L)	80	10	87

3. References

[S1] H.-W. Huang, J. Liu, G. He, Y. Peng, M. Wu, W.-H. Zheng, L.-H. Chen, Y. Li, B.-L. Su, *RSC Adv.*, 2015, **5**, 101910–101916