Electronic Supplementary Material (ESI) for ChemComm.

Ligand-assisted formation of mesoporous Zn-N-C to realize superior catalytic activity in solvent-free CO_2 cycloaddition reaction

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Experimental

Materials

Tetrabutylammonium bromide (TBAB) and 1,10-phenanthroline monohydrate were purchased from Innochem (Beijing, China). 2-Methylimidazole and styrene oxide were purchased from Aladdin Reagent Crop. (Shanghai, China), methanol (CH_3OH) and Zinc nitrate hexahydrate (Zn $(NO_3)_2$•$6H_2O$) were purchased from Sinopharm Chemical Reagent (Shanghai, China). All the reagents in this experiment were of analytical grade and used as received without further purification.

Synthesis of ZIF-8

Dissolve 13.39 g of Zn $(NO_3)_2$ • $6H_2O$ in 375 ml of methanol and ultrasound to form solution A. Dissolve 14.78 g of 2-methylimidazole in 375 ml of methanol and ultrasound to form solution B. Pour solution A into solution B, sonicate for 10 min, stir at room temperature for 12 h, centrifuge, wash with methanol at 50 ^oC, and dry for 12 h to obtain white solid powder.

Synthesis of m-Zn-N-C

Dissolve 1g of ZIF-8 and 200mg of 1,10-phenanthroline monohydrate in 50ml of methanol in a round bottom flask. Stir at 50 ° C for 12 h, wash three times with methanol, and dry at 50 °C for 12 h to obtain white solid powder. White powder is calcined at different temperatures to obtain different Zn-N-C, named m-Zn-N-C. Calcine ZIF-8 pure sample to obtain Zn-N-C.

CO_2 cycloaddition reaction.

For a typical reaction, 2.5 ml of styrene oxide, 300 mg of TBAB, and 40mg of catalyst are mixed in a test tube, placed on a heated magnetic stirrer, and connected to a CO_2 balloon. The conversion and selectivity of the reaction were determined by gas chromatography (GC) (Thermo Scientific Trace 1300 series) and GC mass spectrometry (MS) (Thermo Scientific Trace 1300 series ISQ LT).

Characterization.

The samples were tested by X-ray diffraction (XRD) using smartlab 9 kW system equipped with cu-k α Radiation source. Shape and structure product dimensions work at 100 kV through Hitachi ht-7700 transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS, thermo escalab 250xi) was used to analyze the chemical composition and valence state of the samples. High resolution transmission electron microscope (HRTEM) images and corresponding EDS mapping images were obtained using Feitf20 system. Fourier transform infrared spectroscopy was recorded using Bruker Invenio-R instruments. Raman spectra were collected on an inVia (Renishaw) micro-Raman spectrometer using a 532 nm laser.

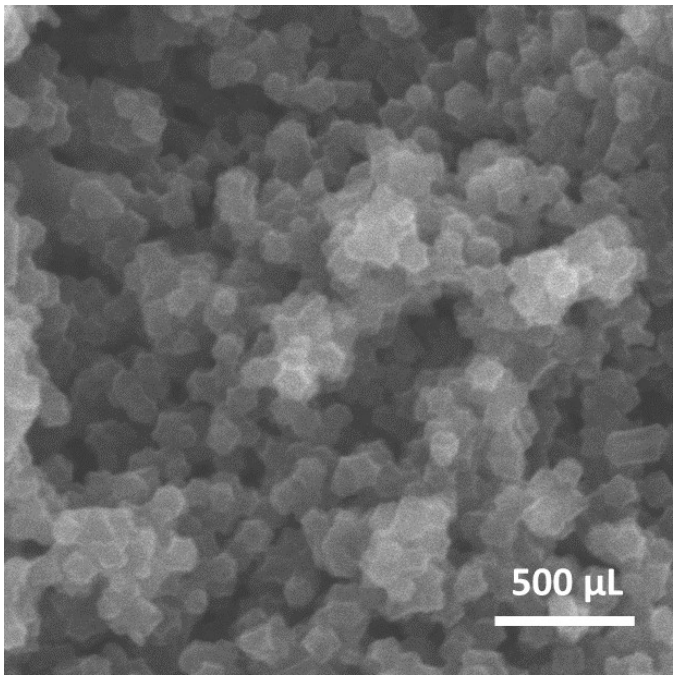

Fig. S1 SEM images of ZIF-8.

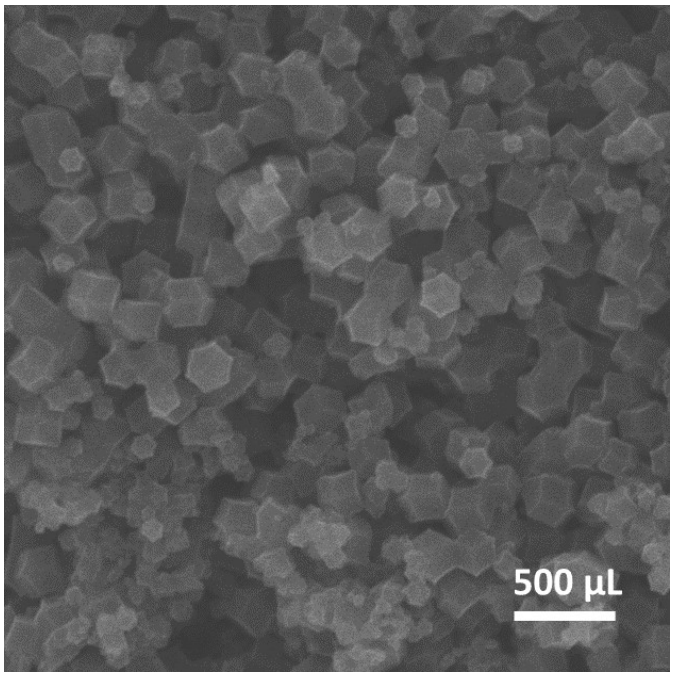

Fig. S2 SEM images of phen-ZIF-8.

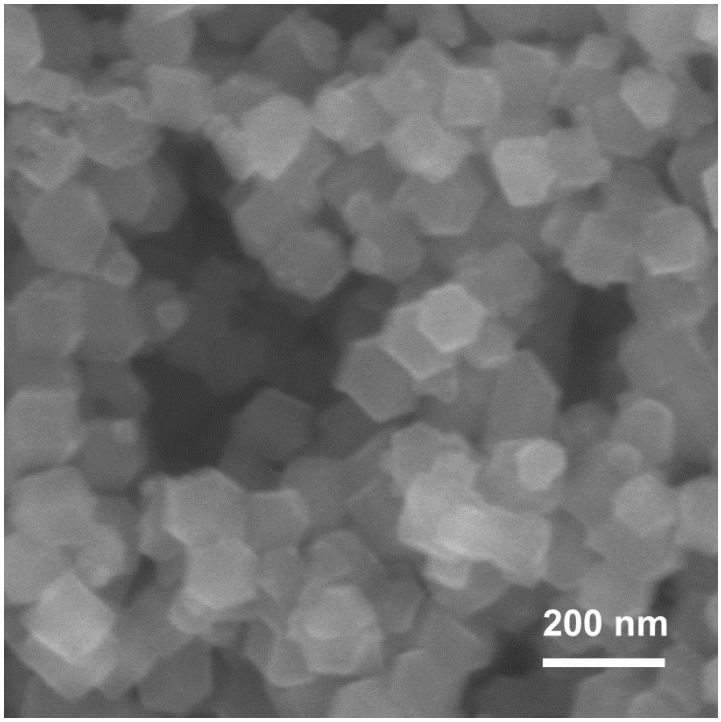

Fig. S3 SEM images of m-Zn-N-C.

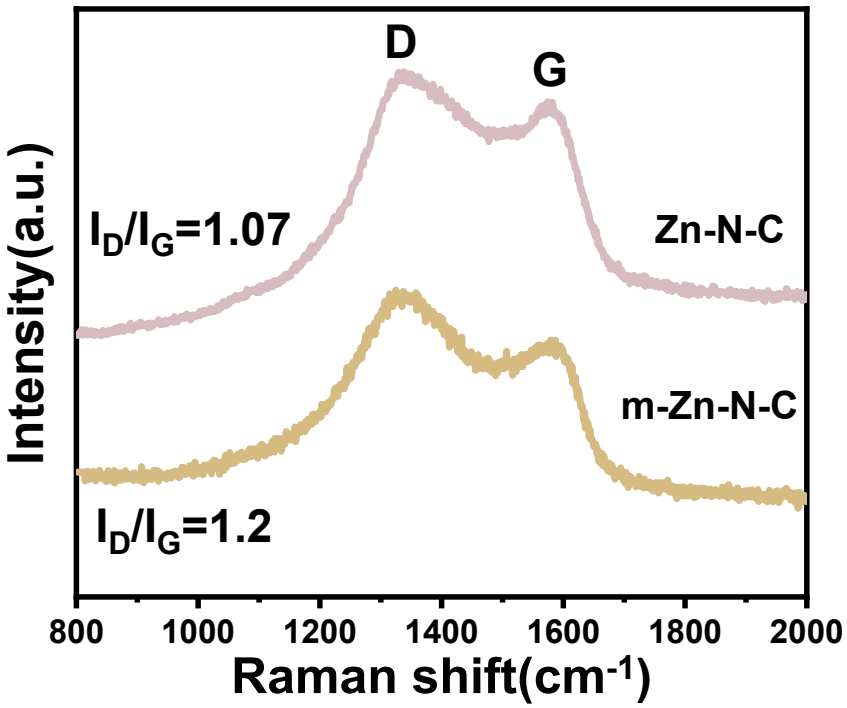

Fig. S4 Raman spectra of m-Zn-N-C and Zn-N-C

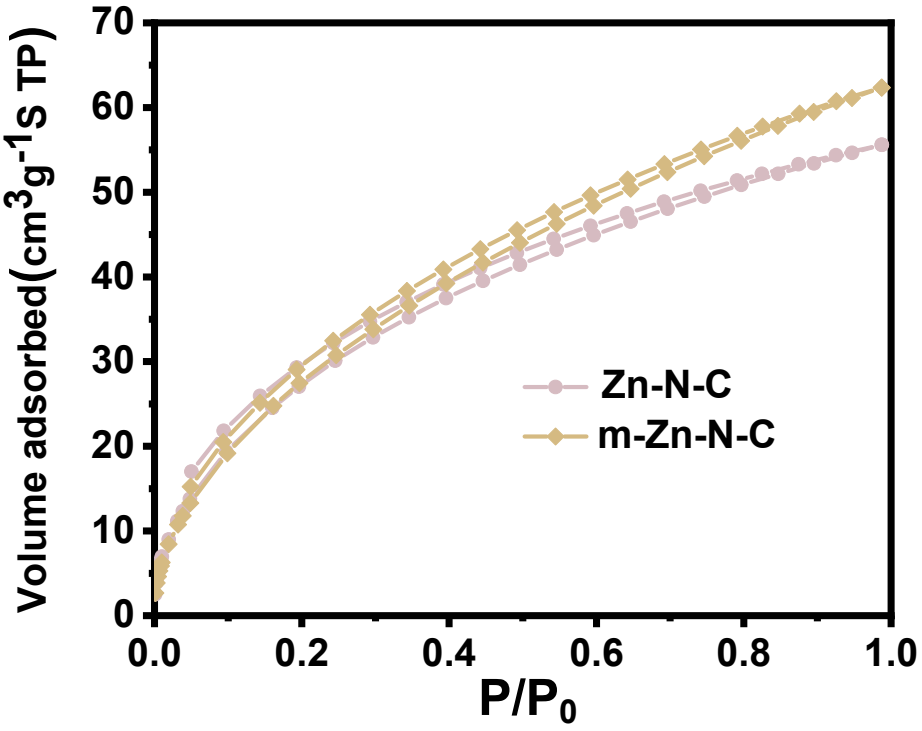

Fig. S5 The CO_2 sorption isotherms of m-Zn-N-C and Zn-N-C.

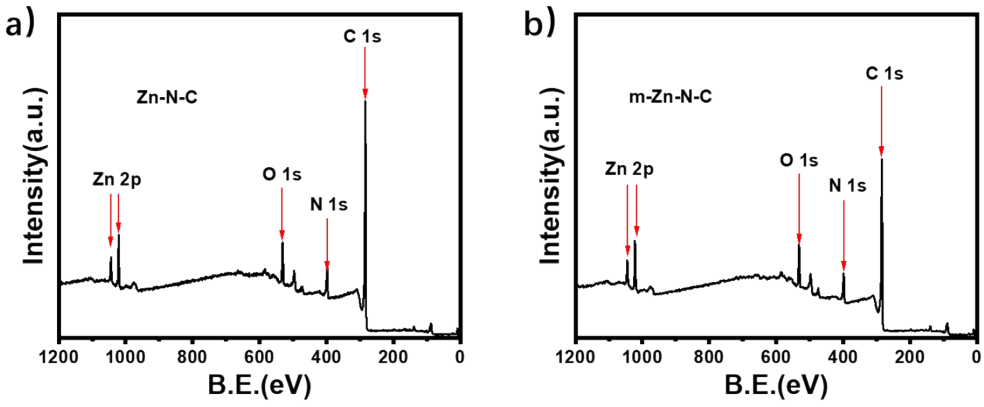

Fig. S6 a) The XPS spectra of Zn-N-C; b) The XPS spectra of m-Zn-N-C.

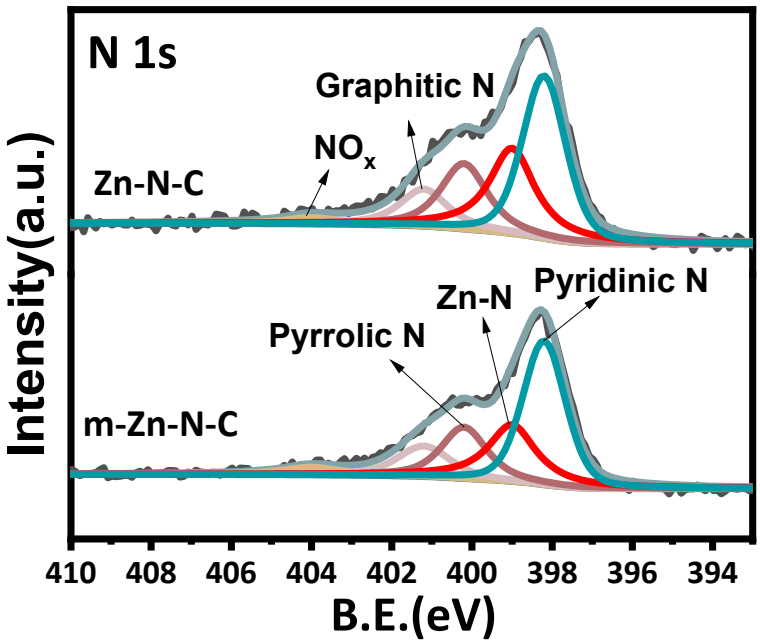

Fig. S7 High-resolution N 1s spectra of m-Zn-N-C and Zn-N-C.

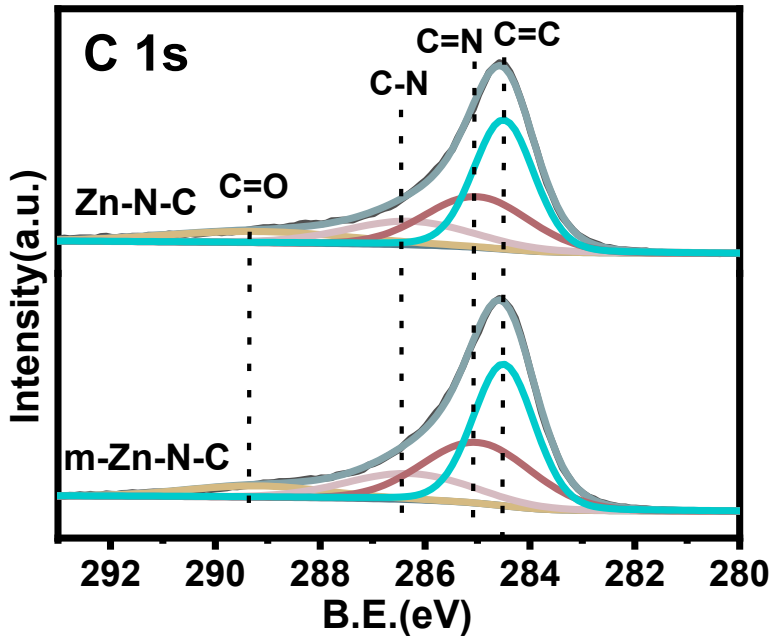

Fig. S8 High-resolution C 1s spectra of m-Zn-N-C and Zn-N-C.

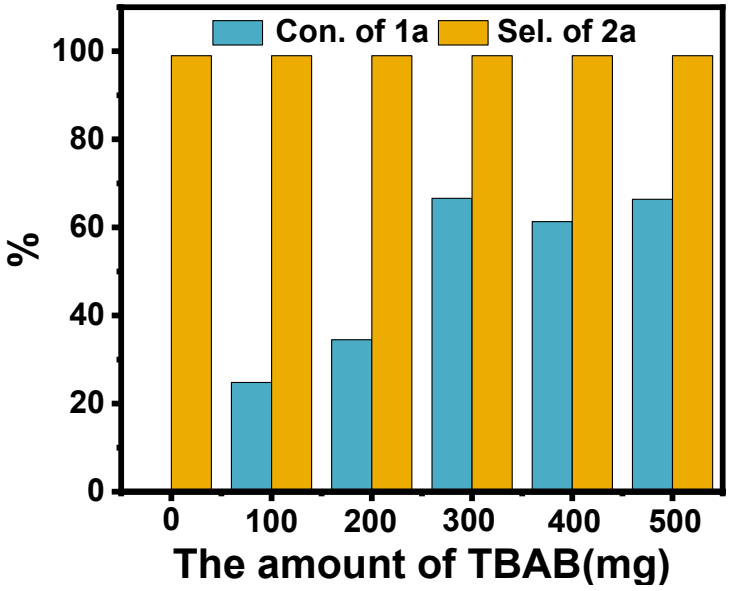

Fig. S9 The styrene oxide and CO_2 cycloaddition TBAB-dependent tests.

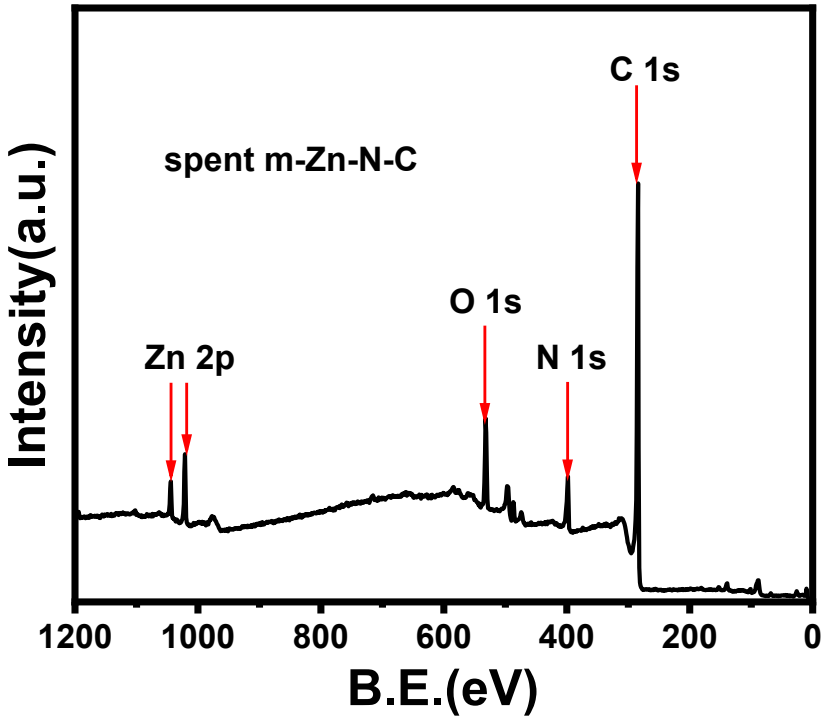

Fig. S10 The XPS spectra of spent m-Zn-N-C.

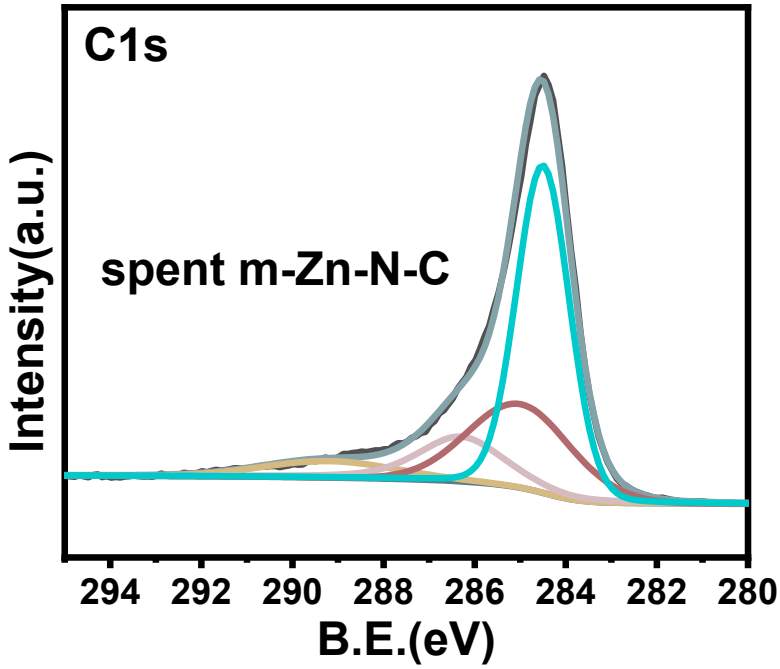

Fig S11 The C 1s spectra of spent m-Zn-N-C sample.

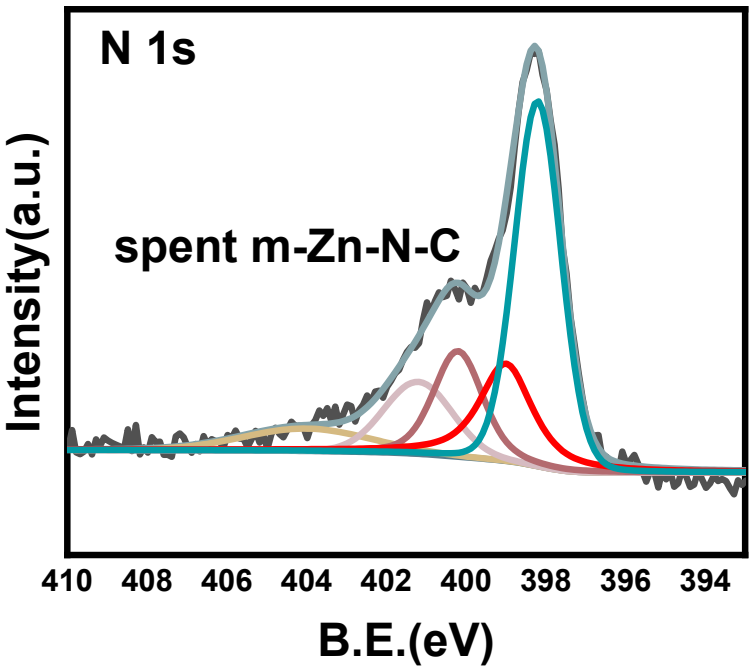

Fig S12 The N 1s spectra of spent m-Zn-N-C sample.

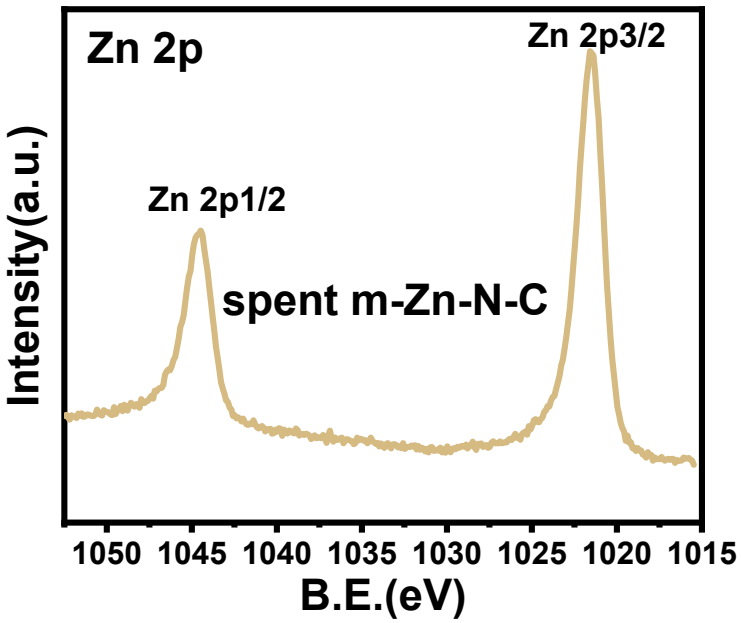

Fig S13 The Zn 2p spectra of spent m-Zn-N-C sample.

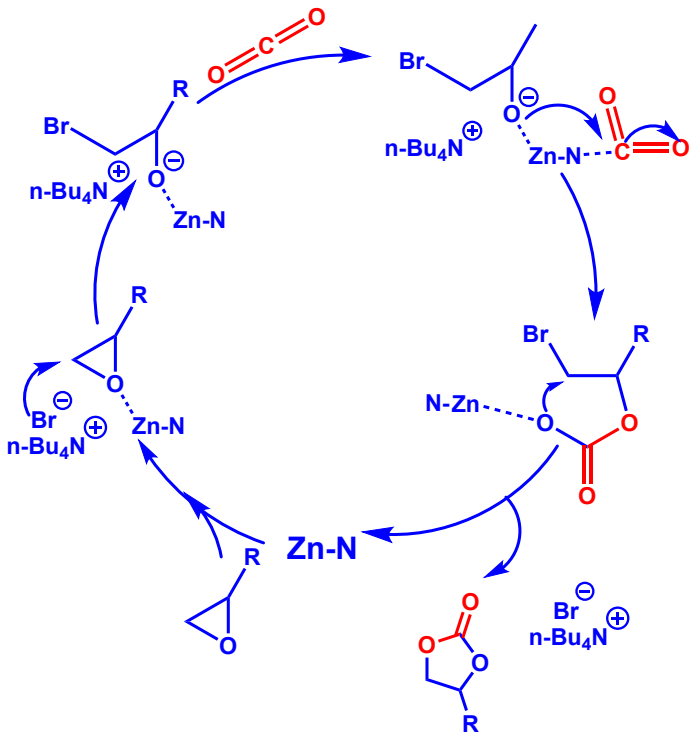

Fig S14 The proposed mechanism of m-Zn-N-C catalyzed cycloaddition of oxidized styrene with CO_2.

Table S1 Analysis of metal elements in m-Zn-N-C and Zn-N-C.

Samples	metal	Sample element content W (%)
Zn-N-C	Zn	18.8996
m-Zn-N-C	Zn	11.7420

Table S2 The specific surface area, pore Size and pore volume of different samples

Samples	**SBET (m^2/g)**	**Pore Volum（cm^3/g）**	**Pore Size(nm)**
Zn-N-C	560.3798	0.047402	5.0835
m-Zn-N-C	952.4501	0.265814	7.8664

Table S3. Structural parameters extracted from the EXAFS fitting. (S_0^2 = 0.85)

Sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}Å^2)$	ΔE_0(eV)	R factor
Zn-N-C	Zn-N	4.0	1.88	0.00553	-6.896	0.0252
	Zn-C	4.0	2.56	0.00839	-8.218	
m-Zn-N-C	Zn-N	3.9	1.88	0.00568	-5.357	0.0286
	Zn-C	**4.1**	**2.56**	**0.0081**	**-7.504**	

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is

interatomic distance (the bond length between Zn central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

Table S4 Analysis of metal elements in reaction solution

Sample	Element	Element concentration of test solution C0 (mg/mL)
m-Zn-N-C	Zn	0.004875