

## Supplementary Information

### **Stable Single-atom Zn Catalyst Synthesized by Ligand-stabilized Pyrolysis Strategy for Selective Oxidation of C-H Bond**

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## 1. Characterization

The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku B/Max-RB X-ray diffractometer with nickel-filtrated Cu K $\alpha$  radiation, and operating in a 2 $\theta$  range of 10-70° at scan step of 0.017°. A T.J.A. ICP-9000 type instrument was employed to detect the Zn contents of as-prepared catalysts by inductively coupled plasma optical emission spectrometer (ICP-OES). X-ray photoelectron spectroscopy (XPS) was conducted with a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an Al K $\alpha$  X-ray source. The XAFS spectra were obtained at 1W1B station in BSRF (Beijing Synchrotron Radiation Facility, P. R. China) operated at 2.5 GeV with a maximum current of 250 mA. XAS measurements at the Co K-edge were performed in fluorescence mode using a Lytle detector. All the single atom catalysts were characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Atomic resolution HAADF-STEM images were obtained by using a Titan 80-300 scanning/transmission electron microscope operated at 300 kV, equipped with a probe spherical aberration corrector. The surface area and porous properties of the samples were determined by nitrogen adsorption-desorption experiment using V-Sorb 2800P volumetric adsorption equipment (Jinaipu, China).

## 2. Calculation details

DFT calculations were carried out using the “Vienna ab initio simulation package” (VASP5.3)<sup>1</sup> The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used within the spin-polarized generalized gradient approximation (GGA).<sup>2</sup> A plane-wave basis set was employed within the framework of the projector augmented wave (PAW) method.<sup>3</sup> In order to get accurate results, the cutoff was set to 450 eV. A Gaussian smearing was used with a smearing width of 0.2 eV. Geometry relaxations were carried out until the residual forces on each ion were smaller than 0.02 eV/Å.

The Brillouin zone was sampled using a Monkhorst-pack 3 $\times$ 3 $\times$ 1 k-point grid for ZnN<sub>4</sub>. The two-dimensional system of nitrogen-doped carbon was modeled with a 6 $\times$ 6 supercell consisted of 66 carbon sites. Two neighboring carbon atoms were removed to anchor a Zn atom, and four of carbon atoms were replaced by N atom, forming the Zn-N<sub>4</sub> configuration, Fig. S1 (a). A Zn<sub>26</sub> nanocluster structure was built to simulate Zn nanoparticles Fig. S1 (b). The stability of adsorbed species can be described by the differential adsorption energy  $\Delta E$ , which is defined as

$$\Delta E_{\text{ad}} = E(\text{surface} + \text{A}^*) - E(\text{surface}) - E_{\text{A}}$$

where  $E(\text{surface}+\text{A}^*)$  is the total energy for the adsorbed species adsorbed on the catalysts surfaces,  $E(\text{surface})$  refers to the catalysts surfaces, and  $E_{\text{A}}$  is the energy for adsorbed species. The  $\Delta E_{\text{ad}}$  was obtained from the ground state calculations. With this definition, a negative value indicates an exothermic adsorption.

### 3. Calculation of the EB conversion, acetophenone selectivity and TOF

The conversion of hydrocarbons was calculated by the following equations:

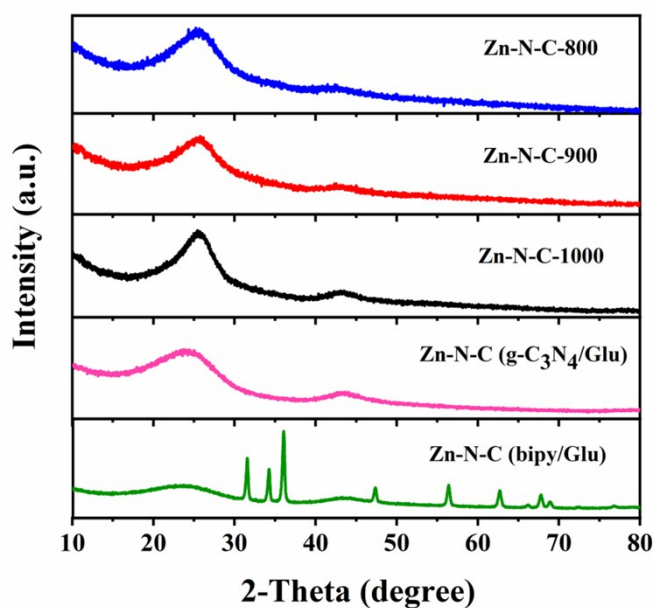
$$\text{Conversion} = \left( 1 - \frac{\text{mole of substrate after reaction}}{\text{mole of substrate before reaction}} \right) \times 100\%$$

The selectivity of hydrocarbons were calculated by the following equations:

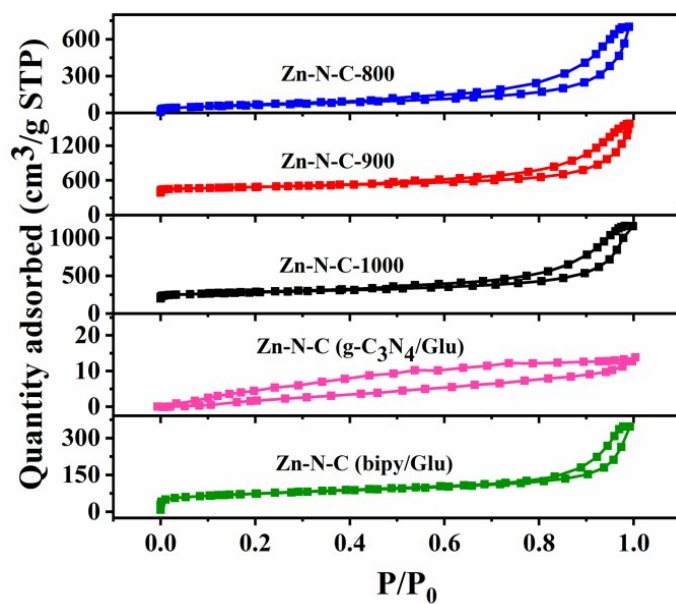
$$\text{Selectivity} = \frac{\text{mole of desired product}}{\text{mole of substrate before reaction} - \text{mole of substrate after reaction}}$$

The turnover frequency (TOF) based on total Zn was calculated by the following equations:

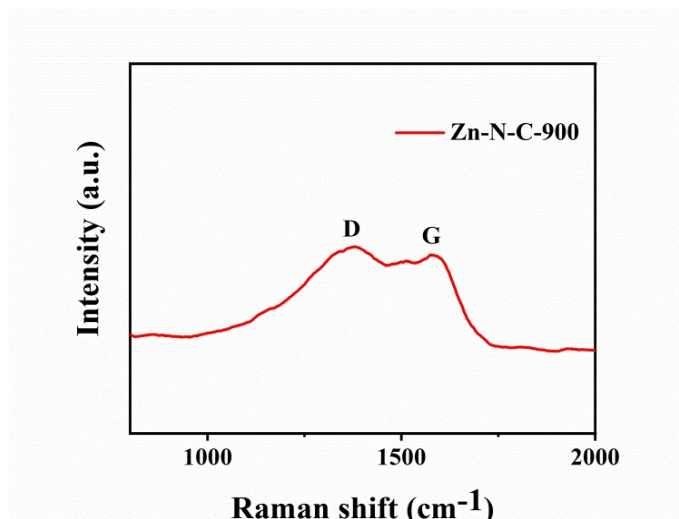
$$\text{TOF} = \frac{\text{the moles of converted substrate}}{\text{the moles of active metal atoms} \times \text{times}}$$



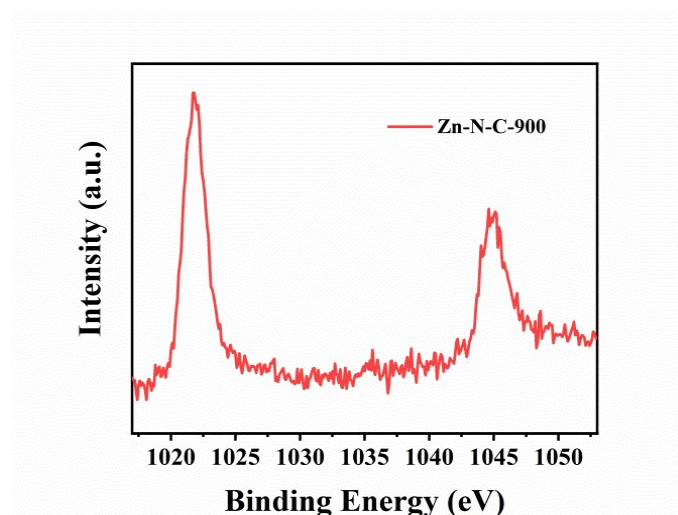
**Fig. S1.** XRD patterns of Zn-N-C-800, Zn-N-C-900, Zn-N-C-1000, Zn-N-C (g-C<sub>3</sub>N<sub>4</sub>/Glu), Zn-N-C (bipy/Glu).



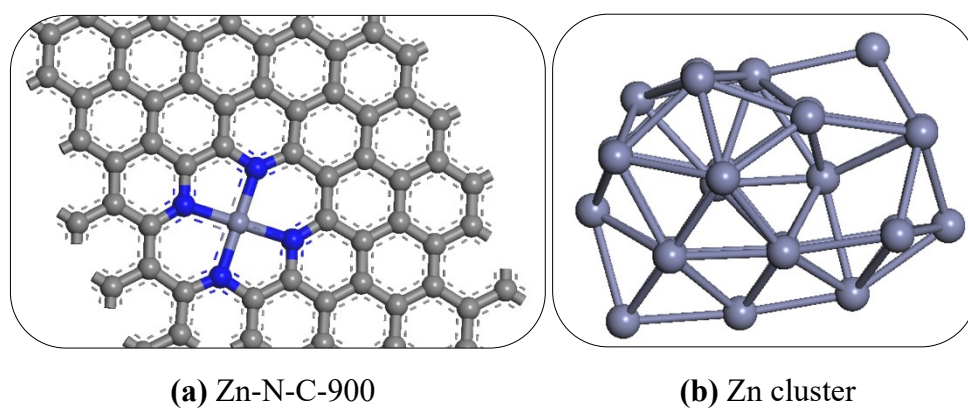
**Fig. S2.** N<sub>2</sub> adsorption–desorption isotherms of Zn-N-C-800, Zn-N-C-900, Zn-N-C-1000, Zn-N-C (g-C<sub>3</sub>N<sub>4</sub>/Glu), Zn-N-C (bipy/Glu).



**Fig. S3.** Raman patterns of Zn-N-C-900.

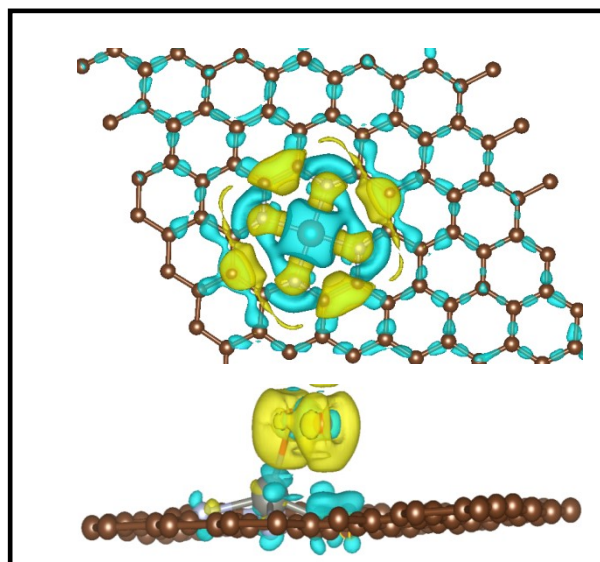


**Fig. S4.** Zn 2p spectra of Zn-N-C-900.

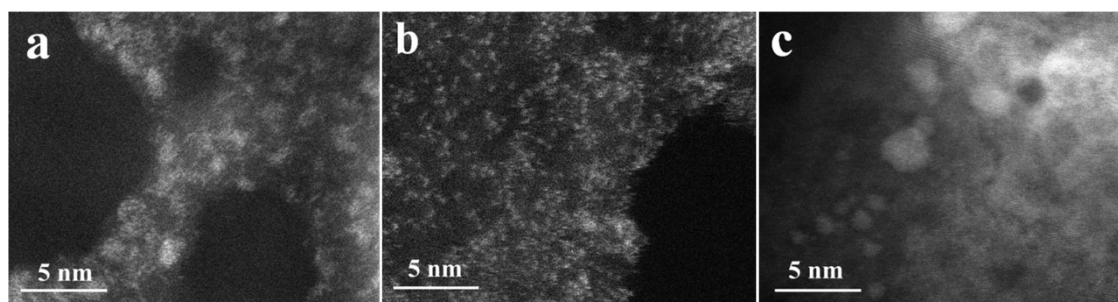


**Fig. S5.** Optimized configuration of (a) ZnN<sub>4</sub> sites in Zn-N-C-900 and (b) Zn cluster.

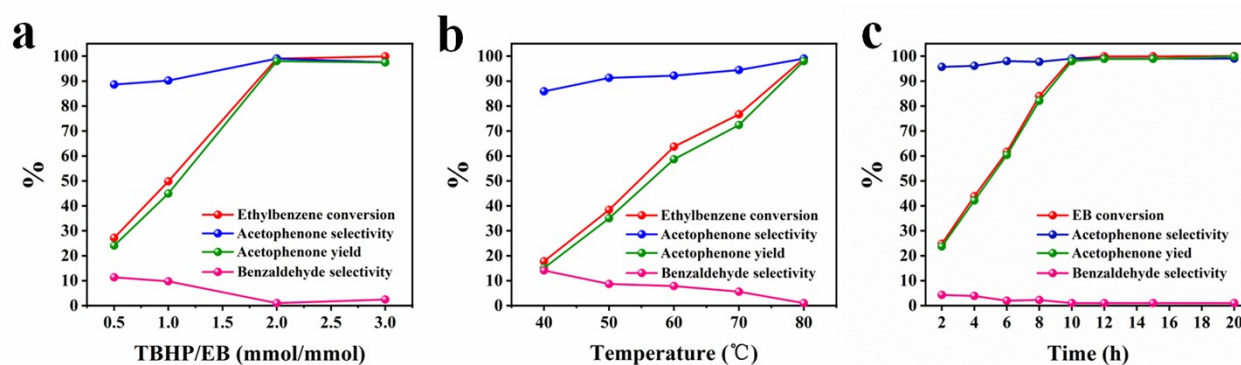




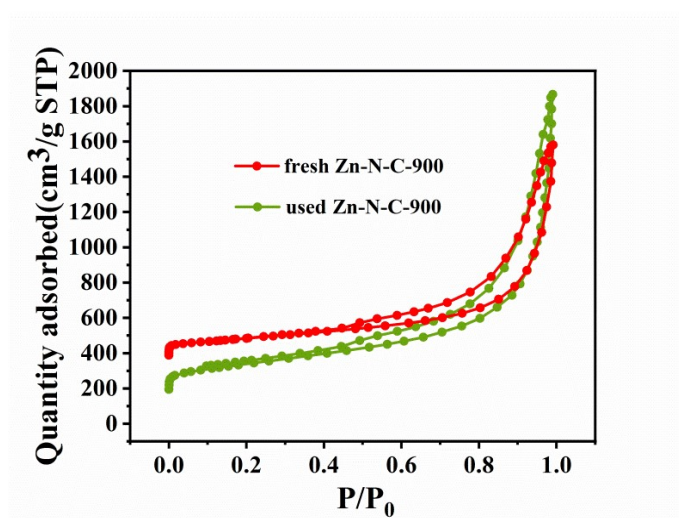
**Fig. S6.** Plots of charge density difference of Zn-N<sub>4</sub> sites at isosurfaces value  $3.0 \times 10^{-3} e/\text{Bohr}^3$ . (yellow is charge accumulation and blue is charge depletion)



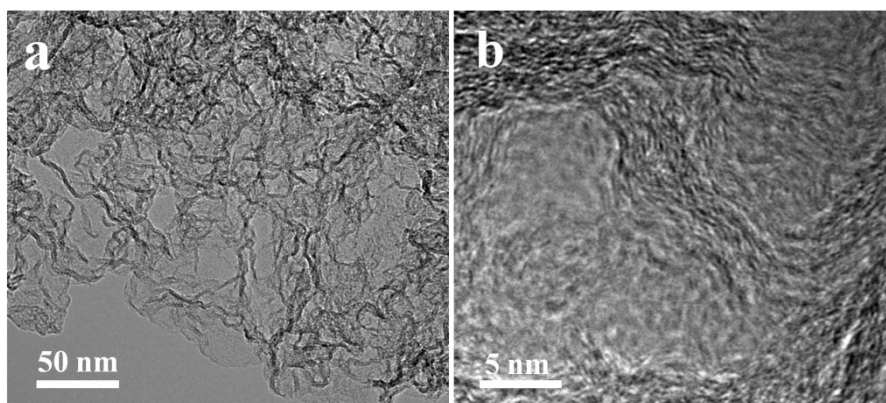
**Fig. S7.** HAADF-STEM images of (a) Zn-N-C-800, (b) Zn-N-C-900 and (c) Zn-N-C-1000.



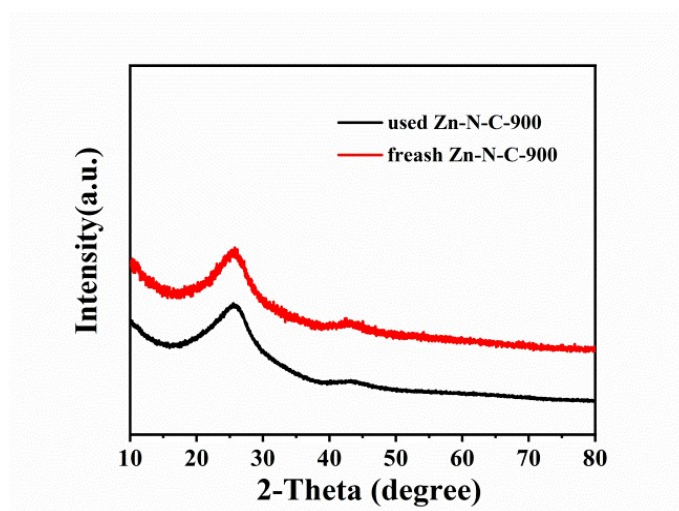
**Fig. S8.** Optimization of the reaction conditions for the selective oxidation of ethylbenzene reaction over Zn-N-C-900. (a) Effect of the TBHP amount: 30 mg of Zn-N-C-900, 3 mmol of EB, 10 h, 80 °C, air atmosphere. (b) Effect of the reaction time: 30 mg of Zn-N-C-900, 3 mmol of EB, 70 wt % TBHP aqueous solution (2 equiv), 80 °C, air atmosphere. (c) Effect of the reaction temperature: 30 mg of Zn-N-C-900, 3 mmol of EB, 70 wt % TBHP aqueous solution (2 equiv), 10 h, air atmosphere.



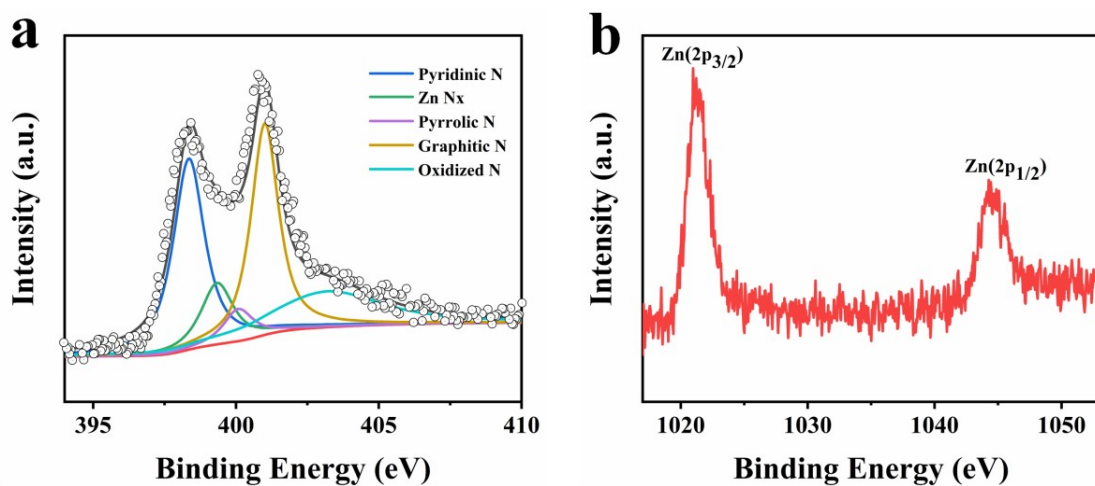
**Fig. S9.** Nitrogen adsorption-desorption isotherms of fresh Zn-N-C-900 and recycled Zn-N-C-900.



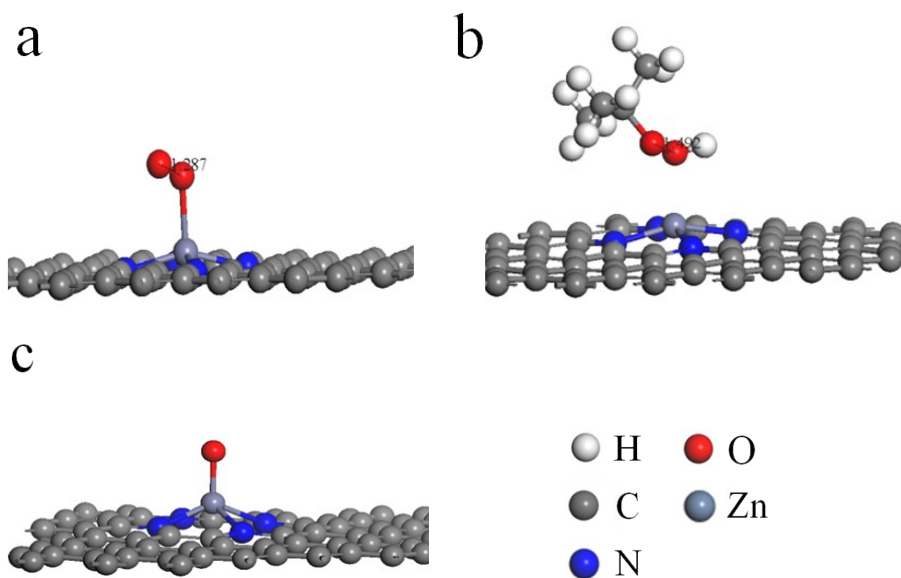
**Fig. S10.** TEM image (a) and HRTEM image (b) of recycled Zn-N-C-900.



**Fig. S11.** XRD patterns of fresh Zn-N-C-900 and recycled Zn-N-C-900.

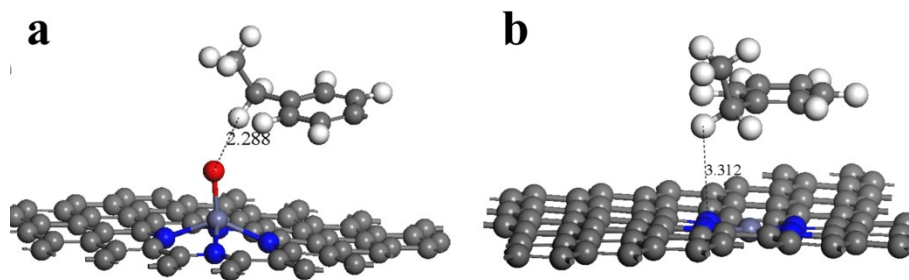


**Fig. S12.** N1s (a) and Zn 2p (b) spectra of the recycled Zn-N-C-900.



**Fig. S13.** Optimized configuration of O<sub>2</sub> (a) and TBHP (b) on Zn-N<sub>4</sub> sites, (c) optimized configuration of ZnN<sub>4</sub>O.





**Fig. S14.** Optimized configuration of ethylbenzene on  $\text{ZnN}_4\text{O}$  (a) and  $\text{Zn-N}_4$  (b) sites.

**Table S1.** The results of  $\text{N}_2$  adsorption–desorption measurements.

Entry	Sample	BET <sup>a</sup>	Pore volume <sup>b</sup>	Pore size <sup>c</sup>
		( $\text{m}^2/\text{g}$ )	( $\text{cm}^3/\text{g}$ )	(nm)
1	Zn-N-C-800	331	1.57	17.89
2	Zn-N-C-900	603	2.69	19.10
3	Zn-N-C-1000	376	1.96	18.15
4	NC-900	107	0.57	17.50
5	Zn-N-C (g- $\text{C}_3\text{N}_4/\text{Glu}$ )	115	0.33	11.75
6	Zn-N-C (bipy/Glu)	81	0.04	7.07

<sup>a</sup>BET Surface Area, <sup>b</sup>BJH Adsorption cumulative volume, <sup>c</sup>BJH Median pore width.

**Table S2.** The relative concentrations of different N species based on XPS of the all samples.

Catalyst	Total N (atom %)	Relative concentrations of different N species( area%)				
		Pyridinic N	Zn-N <sub>x</sub>	Pyrrolic N	Graphitic N	N-oxide
Zn-N-C-800	16.69	51.05	14.56	10.08	18.83	5.47
Zn-N-C-900	9.01	25.14	15.35	8.65	35.32	15.53
Zn-N-C-1000	7.49	24.42	13.09	7.25	36.95	18.28
NC-900	7.90	19.12	-	14.15	51.83	14.89
Zn-N-C (g- $\text{C}_3\text{N}_4/\text{Glu}$ )	6.94	27.35	11.20	17.88	25.90	17.66
Zn-N-C (bipy/Glu)	3.38	33.01	8.06	28.55	26.48	3.89

**Table S3.** Structural parameters extracted from the Zn *K*-edge EXAFS fitting. ( $S_0^2=0.84$ )

Scattering pair	Bond length (Å)	CN	$\sigma^2$ (Å)	$E_0$ shift (eV)
Zn-N(O)	$1.99 \pm 0.01$	$4.2 \pm 0.4$	$0.007 \pm 0.003$	3.6

CN is the coordination number;  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatter distances);  $E_0$  is edge energy shift.

**Table S4.** ICP-OES analysis result for the Zn contents in Zn-N-C-900 by before and after use.

catalyst	Zn contents (wt.%)
fresh Zn-N-C-900	2.27
used Zn-N-C-900	2.08

**Table S5.** The relative concentrations of different N species based on XPS of the fresh Zn-NC-900 and used Zn-NC-900.

Catalyst	Total N (atom %)	Relative concentrations of different N species (area %)				
		Pyridinic N	Zn-N <sub>x</sub>	Pyrrolic N	Graphitic N	N-oxide
fresh Zn-N C-900	9.01	25.14	15.35	8.65	35.32	15.53
used Zn-N C-900	8.84	28.76	14.52	5.28	32.21	21.85

**Table S6.** Comparison for catalytic performance of the Zn-N-C-900 with the reported catalysts in references

Entry	Ethylbenzene	Catalysts	Oxidant	Solvents	T (°C) / Time(h)	Con.(%) / Sel.(%)	Cycles	Refs.
1	3 mmol	Zn-N-C-900 (30 mg)	6 mmol TBHP	0.23 mL H <sub>2</sub> O	80 / 10	99 / 99	15	this work
2	1 mmol	Pd-(4wt%)/g-C <sub>3</sub> N <sub>4</sub> (10 mg)	4 mmol TBHP	5 mL C <sub>2</sub> H <sub>3</sub> N	80 / 24	67 / 97	5	4
3	0.1 mmol	CIPC-750	0.3 mmol TBHP	2 mL C <sub>2</sub> H <sub>3</sub> N	80 / 12	58.7 / >95	3	5
4	10 mmol	Co <sub>1</sub> Zn <sub>99</sub> -ZIF-800-H <sub>2</sub> (5 mg)	2.8 mmol TBHP	3 mL H <sub>2</sub> O	60 / 17	57 / 93.1	4	6
5	1 mmol	Co-MnO@CN-700/15 (15 mg)	0.5 mL TBHP	5 mL H <sub>2</sub> O	50 / 6	>99.9 / 99.9	7	7
6	1 mmol	Co-N-C-10 (15 mg)	3.5 mmol TBHP	3 mL H <sub>2</sub> O	80 / 6	93 / 100	5	8
7	120 μL	Co-N-C-900/PCMk (15 mg)	490 μL TBHP	3 mL H <sub>2</sub> O	80 / 12	96 / 99	5	9
8	0.5 mmol	CoTMPP-500 (5 mg)	500 μL TBHP	1 mL H <sub>2</sub> O	80 / 6	91.9 / 97.5	3	10
9	1 mmol	Co-N-C-9 (15 mg)	3.5 mmol TBHP	H <sub>2</sub> O	80 / 12	96.5 / 97.3	5	11
10	0.5 mmol	SNC-Ca-850 (10 mg)	2 mmol TBHP	2 mL H <sub>2</sub> O	80 / 4	92.4 / 97.4	4	12
11	1 mmol	GS1000 (10 mg)	1 mL TBHP	2 mL H <sub>2</sub> O	80 / 6	>99 / >99	5	13
12	0.5 mmol	Fe-ISAS/CN (20 mg)	1 mL TBHP	2 mL H <sub>2</sub> O	60 / 24	99 / 99	5	14
13	0.1 mmol	SACo@g-C <sub>3</sub> N <sub>4</sub> (5 mg)	0.5 mmol PMS	10 mL C <sub>2</sub> H <sub>3</sub> N / H <sub>2</sub> O 1 : 1	60 / 24	97.5 / 95.6	4	15
14	0.25 mmol	Fe <sub>1</sub> /NC (20 mg)	1 mL TBHP	2 mL H <sub>2</sub> O	35 / 48	97 / 99	5	16
15	5 mL	Co <sub>1.5</sub> Ni <sub>1.5</sub> Al <sub>1</sub> O <sub>x</sub> (200 mg)	15 mL TBHP	10 mL Acetic acid	120 / 8	73.7 / 85.1	4	17

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