Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

One-pot Synthesis of Cobalt-coordinated N-doped Carbon Catalysts via Co-synthesis of Ionic Liquid and Cobalt Porphyrin

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Experimental Section

Characterization

High-resolution TEM (HRTEM) studies were performed on Tecnai F20. SEM images and elemental mapping studies were obtained on a FEI QUANTA 200 microscope. BET surface area and pore volume were obtained from 77 K N_2 adsorption-desorption isotherms using a NOVA 1000. Samples were outgassed at 200 ^oC for 3 h. The X-ray photoelectron spectra (XPS) were obtained with a PHI 5000C ESCA system (Perkin Elmer) using an aluminum anode (Al 1486.6 eV) X-ray source.

Materials

Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), benzaldehyde, pyrrole, propionic acid, dimethyl formamide, ethanol, dichloromethane, ethylbenzene, bromobenzene, 1, 4-dichlorobenzene and 1-butyl-3-methyl-imidazole bromine salt (BmimBr) were commercial available and used without further purification.

Catalytic performance measurement:

Catalytic tests and analytical procedures: The oxidation of ethylbenzene over CoNC-x samples was carried out in a Teflon-lined stainless steel batch reactor (25 mL total volume). Ethylbenzene (10 mL) and catalyst (20 mg) were introduced into the reactor. Then the reactor was sealed and the pressure increased to 8.0 atm using pure O_2. The reactor was heated to 120 °C over 5 h with stirring. The products were analyzed on a GC instrument (Shimadzu, GC-2014).

Methods

The cobalt(II) 5,10,15,20-tetraphenyl porphyrin (CoTPP) was synthesized as described preciously.[1] In a 500mL three necked flask, benzaldehyde (7.3 g, 0.069 mol) was dissolved in propionic acid (200 mL). Pyrrole was then added dropwise (4.7 g, 0.07 mol) and the solution was refluxed for 1 h. After the resultant product was cooled down to room temperature, precipitates were collected by suction-filtration and washed with ethanol and water, and then purified by column chromatography. After dried in the oven, purple solid was obtained as pure product (3.1 g, 5.1 mmol, 26 % yield). Following that, the prepared sample (615 mg, 1.0 mmol) and $CoCl_2 \cdot 6H_2O$ (2.5 g, 10.5 mmol) were added into 100 mL of N, N-dimethylformamide (DMF) and the mixture was refluxed for 1 h, After cooling down to room temperature, 100 mLof H_2O was introduced. The resultant precipitate was filtered, washed, and dried. The dark brown solid was obtained as pure product.

Synthesis of CoNC-10: In a typical synthetic procedure, BmimBr (1.0 g) was dissolved in ethanol (5 mL) and sonicated for 5 min. Then CoTPP (0.1 g) was added into the solution and the mixture was heated until the ethanol had completely evaporated, and the prepared sample was then transferred into a crucible. Under N_2 carrier gas flow (100 mL min^{-1}), temperature was controllably ramped at a rate of 5 °C min^{-1} to a final temperature of 500 °C. After heat treatment for 1 h, the furnace was cooled down to room temperature.

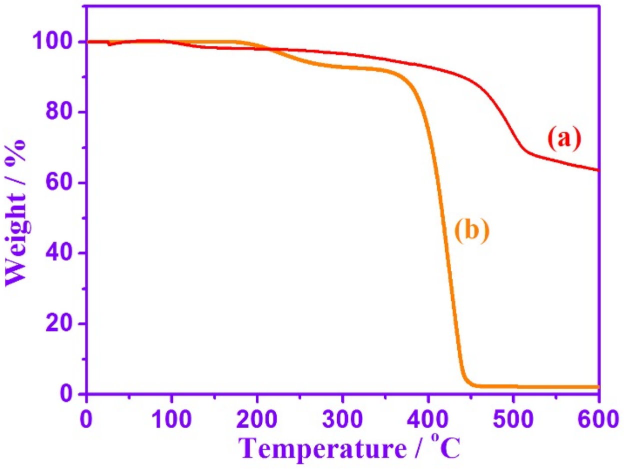

Figure S1. Scanning TGA profiles of (a) CoTPP and (b) BmimBr.

Figure S1 provides thermal gravimetric analysis (TGA) curves measured for CoTPP and BmimBr. Evident from the TGA profiles is the fact that negligible carbon residue was achieved for the attempted carbonization of BmimBr. As could be expected, significant yields were observed for the CoTPP. In order to make the BmimBr react with fully condensed CoTPP, the final condensation step was set at 500 °C, at which temperature the IL has already decomposed. What's more, Liu and Ji et al. described the synthesis of CoNC/SiO_2 by pyrolysis of CoTPP supported SiO_2 at different temperatures (300 °C~700 °C).[2] The results showed that CoNC/SiO_2 catalyst heated at 500 °C exhibited much higher activity than its counterparts heated at other temperatures.

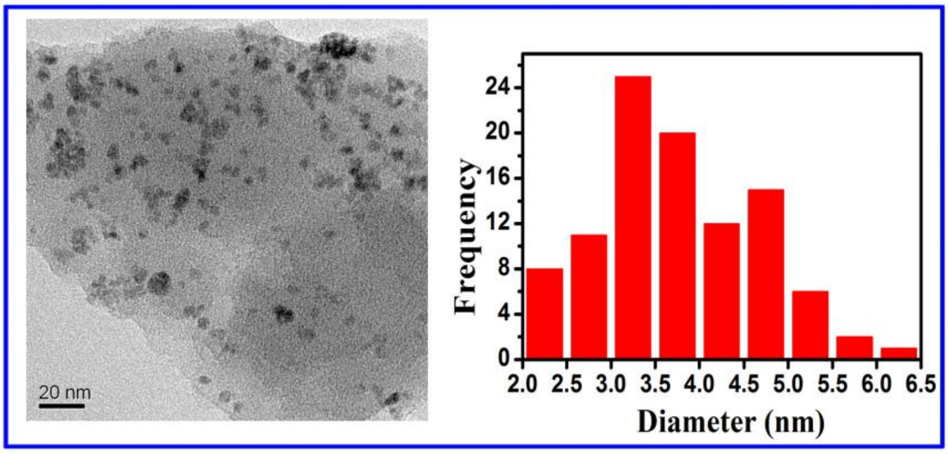

Figure S2. TEM images of CoNC (without addition of IL) with the corresponding particle-size distribution histogram.

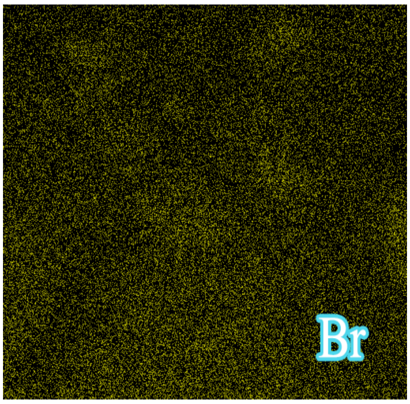

Figure S3. Elemental maps of CoNC-10, Br (yellow).

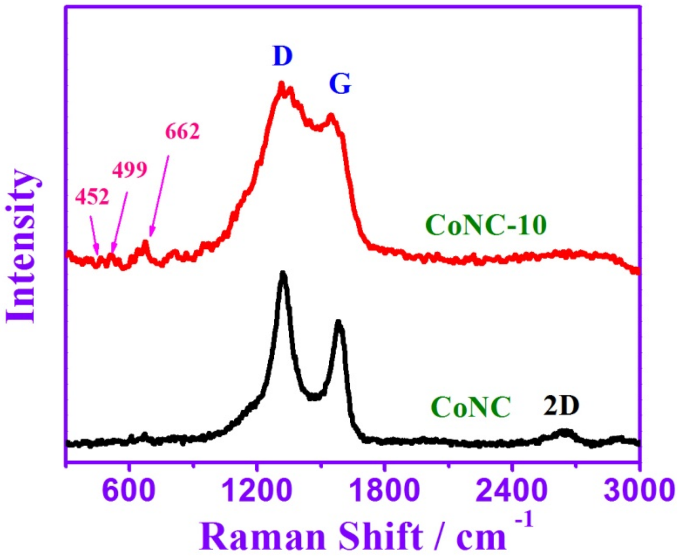

Figure S4. Raman spectrum of the CoNC and CoNC-10.

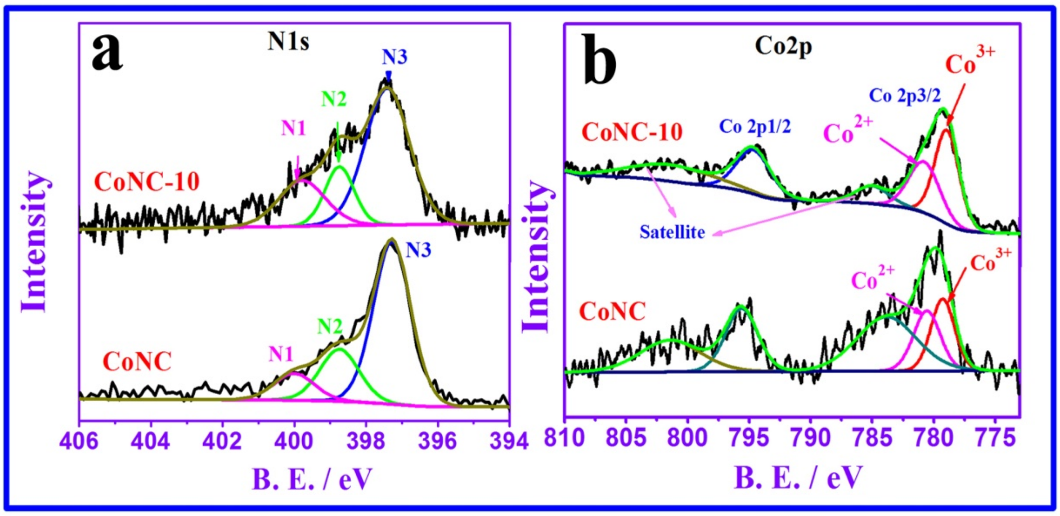

Figure S5. N 1s and Co 2p XPS spectra of CoNC and CoNC-10.

Table S1. Ratio analysis of the elements and BET surface area in the catalysts

Sample	C at%	N at%	O at%	Co at%	Br at%	BET Surface Area (m^2 g^{-1})	Pore volume (cc g^{-1})
CoNC	82.5	5.1	10.3	2.1	-	<10	0.025
CoNC-5	87.2	3.9	7.2	1.6	0.2	12.6	0.055
CoNC-10	86.1	4.0	8.3	1.3	0.5	17.5	0.086
CoNC-15	87.0	2.5	9.0	1.0	0.6	23.9	0.092
CoNC-20	87.9	1.1	9.6	0.6	0.9	28.1	0.101
CoNC-10[a]	84.0	3.8	11.2	0.8	0.4	-	-

[a] CoNC-10 catalyst after reused six times.

As shown in Table S1, as increasing amount of IL, the content of some elements (Co and N) are reduced. The reason may be is to add more IL, the system is boiling more intense, resulting in the volatilization of IL with some necessary element at elevated temperatures.

Table S2. Characteristics of prepared samples

Sample[a]	Mass[b]	Mass[c]	Carbonization Yeild[d] (%)	Theoretical Value[e] (%)
BmimBr	1.2g	-	-	93.2
BmimBr	2.2g	trace	trace	93.2
CoNC	150.3 mg	40.5 mg	26.9	95.8
CoNC-10[f]	160.5 mg	115.6 mg	72.0	95.8

[a] Conditions: 500 °C under N_2 (g); heating rate=5 °C min^{-1}; dwell time=1 h. [b] The mass of before calcinations. [c] The mass of after calcinations. [d] Theoretical values of C, N or/and Co % for each precursor. [e] Theoretical values of C, N or/and Co % for each precursor. [f] Conditions: CoTPP (160.5 mg), BmimBr (1.6 g).

Table S3. Measurement of the reusability of CoNC-x catalysts for selective oxidation of ethylbenzene[a]

Catalysts	Run times	Conversion (%)	Selectivity (%)		
			AP	PE	BA
CoNC-5	1	20.7	73.9	22.4	3.7
	2	18.3	75.2	18.6	6.2
	3	17.9	73.1	22.7	4.2
CoNC-10	1	22.1	75.1	20.5	3.4
	2	20.2	76.6	19.9	3.5
	3	19.2	75.3	21.3	3.4
	4	18.9	75.2	21.2	3.5
	5	19.4	75.3	20.4	4.2
	6	19.5	76.1	19.5	4.3
CoNC-15	1	20.6	75.7	19.4	4.9
	2	19.3	75.6	19.4	5.0
	3	18.2	75.7	19.4	4.9
CoNC-20	1	20.4	75.2	20	4.8
	2	19.8	74.9	20.4	4.7
	3	18.0	74.9	20.2	4.9

[a] Reaction conditions: catalyst 20 mg, ethylbenzene 10 mL, O_2 pressure 8.0 atm, temperature 120 °C and reaction time 5 h.

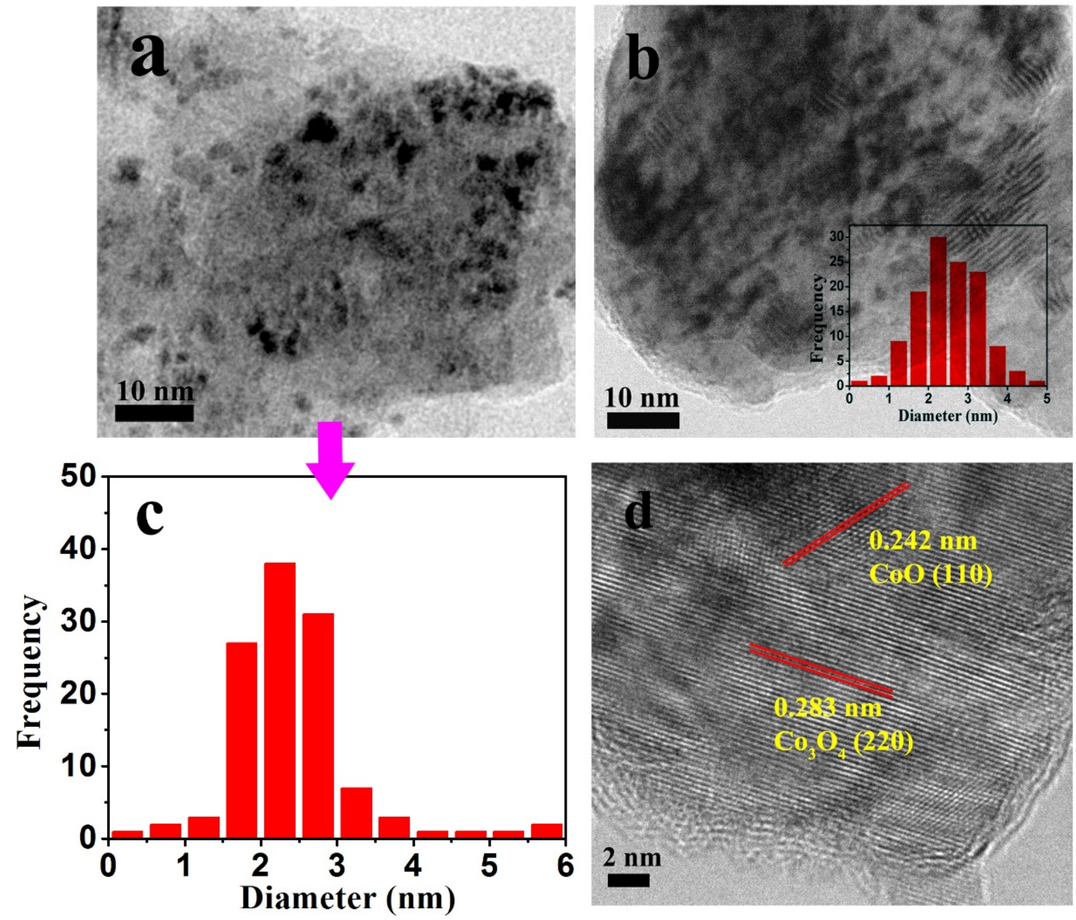

Figure S6. a, b) TEM images of CoNC-10 after reused six times at different regions; Inset (b) and (c) are metal particle size distribution histograms; d) HRTEM images of CoNC-10 after six runs.

The morphology of CoNC-10 after six runs was unambiguously characterized by high-resolution transmission electron microscopy. As shown in Figure S6a-c, we can see most NPs dispersed effectively with a mean size of 2.6 nm and 2.9 nm (the overall average size is 2.8 nm) by counting >120 NPs at different regions, respectively. Particularly worth mentioning is that the particle size is larger than the fresh sample (the average size is 2.3 nm), implying that some particles are aggregated during reaction. Whereas, most of the particle size is maintained at about 2.3 nm on the whole (see inset Figure S6b and S6c).

References

1. Y. Chen, S. Zhao, Z. Liu, *Phys. Chem. Chem. Phys.* 2015, **17**, 14012.
2. Z. Liu, L. Ji, J. Liu, L. Fu, S. Zhao, *J. Mol. Catal. A: Chem.* 2014, **395**, 315.