## ChemComm

COMMUNICATION



**View Article Online** 

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Cite this: DOI: 10.1039/c5cc06456b

Received 2nd August 2015, Accepted 16th September 2015

## One-pot synthesis of cobalt-coordinated N-doped carbon catalysts *via* co-synthesis of ionic liquids and cobalt porphyrins<sup>†</sup>

Yuan Chen, Lingling Fu and Zhigang Liu\*

DOI: 10.1039/c5cc06456b

www.rsc.org/chemcomm

Cobalt-coordinated N-doped carbon (CoNC) was fabricated by heating cobalt porphyrins and ionic liquids. The prepared catalysts displayed superior catalytic capacity for the direct oxidation of ethylbenzene, and unprecedented stability was obtained even after six runs with a similar catalytic performance.

Recently, diverse types of carbon-based materials, such as carbonaceous nanospheres, carbon nanotubes, carbon nitrite, or metal-coordinating N-doped carbon materials (MNCs), have been actively pursued because of their unique properties in electrochemistry and catalytic applications.<sup>1</sup> For example, metal coordinated transition (Fe, Co, and Mn) N-doped carbon materials extend the property profile of a carbon nanostructure and have extensive potential areas of applications ranging from electrocatalysis to chemical catalysis.<sup>1e,g</sup>

Normally, nitrogen-doped carbon materials can be synthesized according to the following strategies: (i) direct carbonization of N-containing carbon precursors, such as polyacrylonitrile (PAN), polypyrrole and furfuryl alcohol filled in N-rich porous organic frameworks (POF);  $2^{a-e}$  (ii) post-treatment of the as-prepared carbon materials with polymers in an N-containing atmosphere (e.g. polyaniline, NH<sub>3</sub>).<sup>3</sup> Particularly, MNC composites synthesized via pyrolysis of precursors containing metal salts, macrocyclic compounds and nitrogen have been intensively researched.<sup>4</sup> However carbonization of these precursors usually breaks down the polymer chain and generates low molecular weight organic compounds and considerable volatile species, which induces severe loss of carbon mass and shorten the lifespan of these catalysts.5 To circumvent these drawbacks, researchers embarked on a concerted effort to explore defined non-volatile organometallic complexes as precursors for the production of stable heterogeneous catalysts.<sup>6</sup> It is worth mentioning that these organometallic complexes are often supported on commercially available

carbon before carbonization, carbon yields are normally very poor because of the vaporization of the carbon support during high temperature pyrolysis. These deficiencies prompted us to recently develop a new strategy for the synthesis of MNC materials in the presence of ionic liquids.

Ionic liquids (ILs) are generally defined as semi-organic salts with a low melting point, negligible low vapour pressure and high thermal stability.<sup>7</sup> Their unique physical and chemical properties make ILs potential precursors or templates to produce functional N-doped carbon materials with the following trends.<sup>8</sup> On one hand, direct atmospheric-pressure carbonization of cyano/nitrilecontaining ILs is capable of producing carbon materials in high yields.9 On the other hand, ILs may assist inorganic or organic materials in the successful fabrication of carbon materials, such as hollow porous carbon, heteroatom-doped (e.g. N, B, F and P) nanoporous carbon and metal-doped carbon materials.<sup>10</sup> Recently, synthesis of metal-doped carbon from ionic liquids has been performed through carbonization of the mixture of ILs and metal salts, or direct thermolysis of IL-based metal-containing precursors.<sup>10e-g</sup> Although all the IL-based precursors can give a homogeneous distribution of metal nanoparticles (NPs) in the carbon-based materials, the above mentioned methods are not cost effective, because they require large amounts of ILs or metal salts for anion exchange.

Herein, we deliver a strategy to prepare a novel cobalt-based N-doped carbon catalyst in the presence of ILs. A cobalt( $\alpha$ ) 5,10,15,20-tetraphenyl porphyrin (CoTPP), a most widely available organometallic compound, was utilized as a non-volatile precursor containing metal, C and N sources. As a result, metalloporphyrins, as natural suppliers of metal active sites, can give well-dispersed and well-interacted metal-coordinated N-doped carbon catalysts, which may have a better catalytic performance than those synthesized in an artificial way, *i.e.*, the impregnation of metal ions on N-doped carbon supports. 1-Butyl-3-methyl-imidazole bromine (BmimBr), a common and cheap ionic liquid, was used as an artificial porogen or a soft template for the preparation of porous carbon materials. The complete satisfaction of our requirements lies in the high mobility of liquid carbon precursors at elevated

State Key Laboratory of Chemo/Biosensing and Chemometrics College of Chemistry and Chemical Engineering Hunan University, Changsha 410082, China. E-mail: liuzhigang@hnu.edu.cn

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cc06456b



**Scheme 1** Scheme for the fabrication of CoNC-*x* (*x* denotes the mass ratio of BmimBr to CoTPP).

temperatures, providing great opportunities in the development of advanced functional materials.<sup>11</sup> After pyrolysis of the mixture of CoTPP and ILs, the obtained catalysts possess high carbonization yield, uniform distribution of metal particles and small metal particle size. In addition, the catalysts exhibit a preferential catalytic performance for the oxidation of ethylbenzene, namely high conversion and remarkable stability.

As illustrated in Scheme 1, the synthesis of CoNC-*x* (*x* denotes the mass ratio of BmimBr to CoTPP) was achieved by heat treatment of the starting materials at 500 °C in N<sub>2</sub> atmosphere. Numerous protrusions formed on the surface of the resulting hybrids were observed in the scanning electron microscopy (SEM) images (Fig. 1a, 2a and b). The transmission electron microscopy (TEM) image of CoNC-10 in Fig. 1b indicated that the generated cobalt NPs were uniformly dispersed on a N-doped carbon system. The size distribution histogram in the inset of Fig. 1d demonstrated that these  $CoO_x$  NPs have an average size of 2.3 nm. Interestingly, the sample, CoNC, without the addition



**Fig. 1** (a) SEM images of CoNC-10; (b and d) typical TEM images of CoNC-10 (b) with the corresponding particle-size distribution histogram (d); (c) high-resolution TEM images of CoNC-10.



**Fig. 2** (a and b) SEM images of CoNC-10 at different regions; (c) EDX image; (d) STEM-EDS elemental maps of CoNC-10, C (red), Co (purple), N (green), O (blue), respectively.

of ILs, has a larger particle size (average size is 3.8 nm, as shown in Fig. S2, ESI<sup>†</sup>). The mobility and volatility of ILs which can cause the material to disperse more evenly during high temperature pyrolysis may be a reason for the smaller particle size. The high-resolution (HR) TEM image in Fig. 1c clearly revealed that lattice fringe spaces of 0.48 nm were consistent with the (111) plane of the cubic Co<sub>3</sub>O<sub>4</sub> spinel-phase, and also displayed lattice fringes of CoO(111) planes with a spacing of 0.24 nm. Scanning TEM energy dispersive X-ray spectroscopy (STEM-EDS) elemental mapping was employed to obtain elemental distribution of Co, C, N, O and Br in the hybrids (Fig. 2c and Fig. S3, ESI<sup>†</sup>), which verified the uniform dispersion of five elements. The textural properties of CoNC-x were measured by N2 adsorption-desorption analysis, and are listed in Table S1 (ESI<sup>†</sup>). CoNC-x has larger specific surface area than CoNC without addition of ILs, which implied that BmimBr can serve as a porogen.

Further insights into the structural and electronic properties of the nanohybrids were gained from Raman spectroscopy. Two well-defined peaks located at 1338 and 1567 cm<sup>-1</sup> in Fig. S4 (ESI<sup>†</sup>) could be assigned to typical D- and G-bands of carbon, respectively. Other peaks at about 452, 499 and 662 cm<sup>-1</sup> were recorded and can be assigned to the E<sub>g</sub>, F<sub>2g</sub> and A<sub>1g</sub> Raman-active modes of Co<sub>3</sub>O<sub>4</sub>.<sup>12</sup> It is noteworthy that a well-defined Co<sub>3</sub>O<sub>4</sub> peak gives information about more active sites exposed in CoNC-10. The carbon yields under pyrolytic conditions (500 °C in a nitrogen atmosphere) were evaluated by calculating the mass of samples before and after calcination. We found that carbonization of BminBr almost affords no carbon yield (Table S2, ESI<sup>†</sup>). This result is consistent with the thermal gravimetric analysis of BmimBr (Fig. S1, ESI<sup>†</sup>), which may be due to the lack of stable intermediate polymeric structures and the formation of volatile vapors during thermal decomposition of such conventional ionic liquids without any cross-linkable functional groups.<sup>11c</sup> Significant carbonization yields were achieved with CoNC-10, which implied that the introduction of the IL could improve the carbonization rate to a certain extent.

Moreover, in comparison to pristine carbon matrices, doping N atoms into carbon structure can also increase the catalytic activity due to the nitrogen-induced charge delocalization.<sup>1f</sup> The chemical status of N was validated by X-ray photoelectron spectroscopy (XPS). As shown in Fig. S5a (ESI<sup>+</sup>), the high-resolution N 1s spectra of CoNC-10 displayed three nitrogen species, corresponding to N1 (graphitic quaternary N), N2 (pyrrole N), and N3 (pyridine N). Pyridine N has been bound to a metal ion and considered as the possible active site in the reaction.<sup>4c</sup> Furthermore, the presence of cobalt oxide was also confirmed by XPS (Fig. S5b, ESI<sup>†</sup>). As illustrated in Fig. S5b (ESI<sup>†</sup>), the two corelevel signals of Co in a sample located at  $\sim$  780 and 796 eV were attributed to Co 2p3/2 and Co 2p1/2, respectively. After deconvolution, the peaks at around 780 and 795.6 eV were assigned to the  $Co_3O_4$  phase. Integral data showed the  $Co^{3+}/Co^{2+}$  ratio to be 1.7. It is noteworthy that a higher abundance of  $Co^{3+}$  species on the surface of CoNC-10 compared with CoNC (the Co<sup>3+</sup>/Co<sup>2+</sup> ratio is 1.2) implies that a strong interaction exists between Co<sub>3</sub>O<sub>4</sub> and nitrogen-doped carbon matrices through Co-O-C or Co-N-C bonds.13 All of these observations manifested that CoNC-10 hybrids have been prepared successfully through a one-pot annealing method.

To demonstrate the usefulness of these carbon based materials, selective oxidation of ethylbenzene was tested. The selective oxidation of ethylbenzene to acetophenone is a very important industrial process because acetophenone is the starting material for the synthesis of perfumes, pharmaceuticals, alcohols and aldehydes.<sup>14</sup> Commercially, acetophenone is produced from the liquid-phase oxidation of ethylbenzene with Co(OAc)2·4H2O as a catalyst and oxygen as the oxidant.15 These homogeneous catalysts deactivate easily and this process also produces several byproducts. But in recent years, a lot of other different catalytic systems (heterogeneous and homogeneous catalysts of different metallic species) have been proposed for this process.<sup>16</sup> Unfortunately, the majority of these catalysts requires acidic solvents and complex and environmentally unfriendly processes. These drawbacks of the existing catalytic systems reinforce the need for new catalytic systems, including heterogeneous catalysts and clean oxidants. Herein, we used the CoNC-x materials as catalysts and oxygen as the oxidant for the high stability to selective oxidation of ethylbenzene.

Cobalt salt and the addition of IL homogeneous catalysts worked in the oxidation of ethylbenzene but showed poor conversion (Table 1, entries 1–4). What is more, the CoNC catalyst without ILs did not show the desired activity (Table 1, entry 5).

The lower surface area and larger particle size may be a reason for the conspicuous loss in activity (Table S1 and Fig. S2, ESI†). We speculated that ILs are indispensable in the fabrication of active catalysts and directly related to the catalytic performance. To our delight, pyrolysis of the *in situ* generated

 Table 1
 Catalytic oxidation of ethylbenzene<sup>a</sup>

Entry	Catalysts	Conv. <sup>b</sup>	Selectivity <sup>b</sup> (%)		
			$\overline{\operatorname{AP}^d}$	$\mathrm{PE}^d$	$BA^d$
1	Со	9.1	64.4	29.2	6.4
2	Co-IL	10.5	69.1	24.5	6.3
3 <sup>c</sup>	CoC-IL	11.8	65.5	28.4	6.1
4	N-C-IL	13.7	75.0	19.3	5.7
5	CoNC	14.6	76.7	18.7	4.6
6	CoNC-5	20.7	73.9	22.4	3.7
7	CoNC-10	22.1	75.1	20.5	3.4
8	CoNC-15	20.6	75.7	19.4	4.9
9	CoNC-20	20.4	75.2	20.0	4.8

<sup>*a*</sup> Reaction conditions: 10 mL ethylbenzene, 20 mg catalyst, 120 °C, 0.8 MPa, 5 h. <sup>*b*</sup> Determined by GC (internal standard: 1,4-dichlorobenzene and bromobenzene). <sup>*c*</sup> CoC-IL is obtained from the calcination of 4-carboxybenzaldhyde, cobalt salt and ILs at 500 °C. <sup>*d*</sup> AP = acetophenone, PE = phenylethanol, BA = benzaldehyde.

complex of CoNC-*x* led to a highly active catalyst material for the direct oxidation of ethylbenzene and produced acetophenone in ~20% conversion (Table 1, entries 6–9). It must be noted that the nitrogen-free catalyst (CoC-IL) gives indeed low yield (Table 1, entry 3), which may manifest that the doped nitrogen atoms play a crucial role in our system. The versatile nitrogen can provide more surface nucleation sites and promote the formation of some individual sections around the N-rich sites, allowing efficient anchoring of metal NPs.<sup>17</sup> This result indicates that the series of CoNC-*x* materials are reasonable and environmentally friendly catalysts to selective oxidation of ethylbenzene under these conditions. Moreover, the catalysts can be easily separated from the reaction solution by simple filtration. The samples are highly stable and can be reused several times without losing the activity (Table S2, ESI†), which is a prerequisite for practical applications.

Furthermore, TEM images of CoNC-10 after six runs are given in Fig. S6 (ESI<sup>†</sup>). Particularly worth mentioning is that the particle size (the overall average size is 2.8 nm) is larger than the fresh sample (the average size is 2.3 nm), implying that some particles are aggregated during reaction. Overall, most NPs are maintained at about 2.3 nm (see the inset of Fig. S6b and c, ESI<sup>†</sup>). What's more, the Co content of the CoNC-10 catalyst after six runs is reduced, but its N content remains largely unchanged (see Table S1, ESI<sup>†</sup>), which further indicates that N plays a decisive role in the reaction. In addition, this catalyst is expected to give excellent results in other organic reactions.

To sum up, we have demonstrated a versatile strategy to synthesize CoNC-*x* by pyrolysis of CoTPP-IL. Notably, the results indicate that the IL can control the structure (increase surface area), particle size (decrease particle size) and composition. Surprisingly, these materials exhibit good catalytic performance for the selective oxidation of ethylbenzene. The catalysts afford a remarkably high stability, and could be recycled several times. Furthermore, we believe that this simple and efficient ionic-liquid-based strategy can not only control the structure, morphology and composition of a catalyst, but also be extended to incorporate other heteroatoms by changing the cation or the anion of the ILs into carbon materials. This approach may widen the application range of carbon materials. This work was supported by the National Natural Science Foundation of China (No. 21103045, 1210040, and 1103312), the State Key Laboratory of Heavy Oil in China (No. SKCHOP201504) and the Key Laboratory of Mineralogy and Metallogeny in Chinese Academy of Sciences (No. KLMM20150103).

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