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# Mesoporous nitrogen-doped carbon for copper-mediated Ullmann-type C–O/–N/–S cross-coupling reactions†

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Copper-driven Ullmann-type cross-coupling reactions are regarded as one of the most important methods for the C–O, C–N, C–S and some other bonds formation. Herein, we report that mesoporous nitrogen-doped carbon materials with high nitrogen content function as novel, active and recyclable N-type heterogeneous promoters for copper-catalyzed cross-couplings. By using CuI as the catalyst and a mesoporous nitrogen-doped carbon material as the promoter, the Ullmann-type coupling reactions of various aryl halides with phenols, amines, imidazol, and thiophenols at 100 °C gave the corresponding products in good yields. Inspired by the efficiency of mesoporous nitrogen-doped carbon material as a promoter, nitrogen-doped carbon supported CuO nanoparticles are prepared and successfully employed as efficient heterogeneous catalysts in the C–O cross-coupling reactions. Furthermore, the nitrogen-doped carbon material supported CuO can be simply recycled by centrifugation and reused at least four times with trace copper leaching. The mesoporous nitrogen-doped carbon materials as heterogeneous promoters or copper-based catalyst supports may represent a promising catalyst system in modern Ullmann chemistry, which indeed could lead to improved processing steps.

## Introduction

The formation of C–heteroatom (O, N, S) bonds by cross-coupling reactions represents a powerful tool for the preparation of numerous compounds in biological, pharmaceutical, and material science on both laboratory and industrial scales.[1] Among the various strategies developed to date, the copper-catalyzed Ullmann-type reaction has proven to be a convenient synthetic route due to its cost-effectiveness and environmentally friendly nature. Nevertheless for a long time the unfavourable reaction conditions, such as high reaction temperature, low tolerance towards functional groups and the stoichiometric demand for copper reagents, prevented further development of these methods.[2] In the early 21st century, the discovery of versatile and very efficient copper/ligand systems for the Ullmann-type reactions, which employed only catalytic amounts of metal under much milder conditions (90–110 °C), has stimulated a renewed interest in the copper-assisted cross-coupling reactions.[3] Many electron-rich ligands with N–, O–, or a mixture of both types of binding sites, such as 1,2-diamines,[4a] 1,10-phenanthroline,[4b] ethylene glycol,[4c] amino acids,[4d] β-diketones,[4e] imino-pyridines,[4f,g] 8-hydroxyquinoline,[4h] oximes or Schiff bases,[4i] have been successfully introduced as promoters for the Ullmann-type cross-coupling reactions. While the introduction of these chelators has led to significant breakthrough, little progress has been made in the heterogeneous ligand.[5] Of the several reports, most focused on the C–N cross-coupling reactions, and very few have been assembled for the C–O cross-coupling processes.[6] The development of heterogeneous catalytic systems[7] is expected to reduce the time consumed for the purification processes and avoid metal residue contamination in the desired product, which is highly desirable in pharmaceutical chemistry.

Meanwhile, nitrogen-containing carbon materials have attracted more and more interest due to their improved performance in many fields such as $CO_2$ sequestration,[8] environmental protection,[9] or in electrochemistry[10] as oxygen reduction reactions.[11] It is believed that doping nitrogen into carbon nanostructures adds another dimension to these structures' properties. The strong electron donor behavior of nitrogen leads to enhanced π bonding ability and basic property.[12] The incorporated nitrogen atoms (Fig. S1, ESI†) can be distinguished as chemical nitrogen (such as amine or nitrosyl group) and structural nitrogen (such as pyridinic,

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pyrollic or quarternary-graphitic nitrogen).[13] The similar chemical environment of the nitrogen in the N-type ligands and the N-doped carbon materials offers an interesting hypothesis: Can N-doped carbon materials function as electron-rich promoters for the copper-mediated cross-couplings? To the best of our knowledge, this question has been so far not yet answered. Here, we wish to report our efforts in the search for N-doped carbon materials with both high nitrogen content and large specific surface areas for copper-catalytic Ullmann-type C–O, C–N, and C–S cross-couplings. Moreover, to reuse the copper species and eliminate wasted copper in the product, we also present N-doped carbon supported CuO nanoparticles as active and recyclable heterogeneous catalysts for this process.

## Results and discussion

### Synthesis and characterization of mesoporous nitrogen-doped carbon

Here, we prepared mesoporous N-doped carbon materials by carbonizing nonvolatile ionic liquids (ILs) or ILs with nitrogen-rich additives (Fig. 1).[14,15] Mesoporous N-doped carbon materials with different nitrogen contents were obtained from three precursors: the IL 1-ethyl-3-methylimidazolium dicyanamide (Emim-dca) with 2-guanidinobenzimidazol (10 mol%), Emim-dca, and 3-cyanomethyl-1-vinylimidazolium bromide (Cmvim-Br), by using silica nanoparticles (Ludox HS40) as a hard template for the mesostructure. The transmission electron microscopy (TEM) image of Meso-N-C-1 (Fig. 2a) clearly visualized its pore morphology. The porosity was investigated by $N_2$ sorption measurements. Evaluating the data according to Brunauer–Emmett–Teller (BET) method, specific surface areas up to 1062, 831, and 427 $m^2\ g^{-1}$ for Meso-N-C-1, Meso-N-C-2, and Meso-N-C-3, respectively, are reached (Fig. 2b, Table S1, ESI†). X-Ray diffraction (XRD) patterns of the prepared materials afforded two broad diffraction peaks for all samples, in accordance to the inter-plane (002) ($2\theta$ = 24.7°) and inter-plane (110) ($2\theta$ = 43.7°) reflections of graphite-like carbon (Fig. 2c). The chemical composition of the prepared materials was analyzed by elemental analysis. As expected, Meso-N-C-1 contains a large amount of N (12.9 wt%) (Table S1, ESI†). The nature of the nitrogen species on the surface of Meso-N-C-1 was further investigated by XPS. The N 1(s) envelope analysis indicated a high pyridinic surface character (401.5 eV; 46.5%), contributions from pyrrolic motifs (400.3 eV; 29.2%) and amines (399.5 eV; 24.3%) (Fig. 2d).[16] These incorporated nitrogens with lone pairs (pyridinic character and amine type: 70.8%) are expected to anchor to copper for the cross-coupling reactions.[10b]

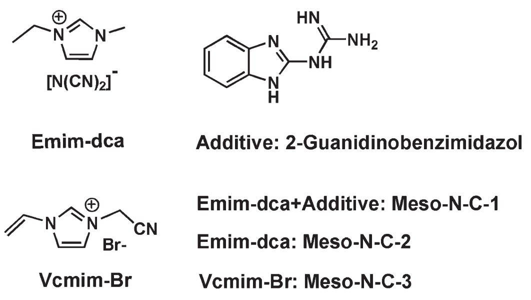


**Fig. 1** Chemical structures of the ionic liquids and the additive used as N-doped carbon precursors.

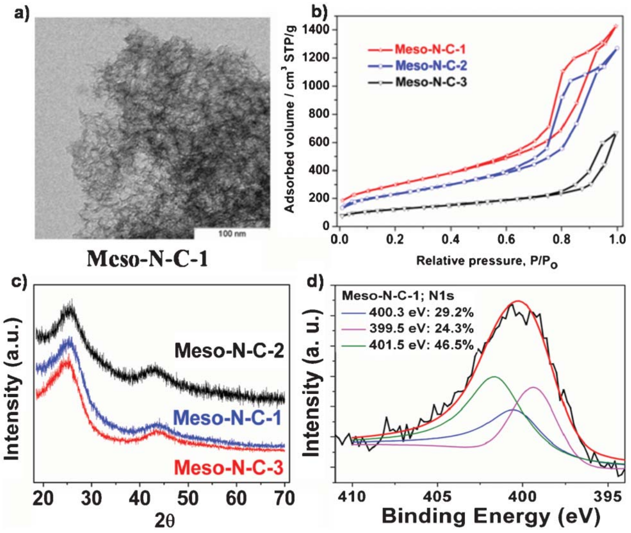
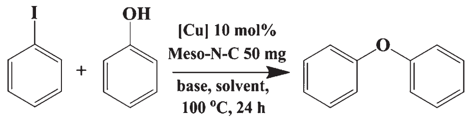


**Fig. 2** a) TEM image, b) $N_2$ adsorption–desorption isotherms and c) XRD patterns of the as-synthesized mesoporous N-doped carbon materials. d) XPS analysis of N 1s in Meso-N-C-1.

### Catalytic tests of mesoporous N-doped carbon in Ullmann-type cross-couplings

We started the initial investigation on copper-mediated Ullmann-type reactions with the cross-coupling of phenyl iodide (PhI) and phenol as a model system. The experimental results showed that the catalyst system containing 10 mol% of $CuCl_2$ or CuCl and 50 mg of Meso-N-C-1 could drive the reaction, furnishing diphenyl ether (DPE) in 47% and 44% yield, respectively (Table 1, entries 1–2). In the absence of Meso-N-C-1 (Table 1, entries 3–4), relatively low yields of DPE were obtained, illustrating that Meso-N-C-1 largely promoted the *O*-arylation reaction. When Meso-N-C-1 alone was applied in this reaction (Table 1, entry 5), the product DPE was not formed at all. It seems that Meso-N-C-1 alone cannot induce this cross-coupling and it plays the role of a promoter, together with copper salts for the described reaction. Arylations conducted in DMSO were found faster than those conducted in DMF or 1,4-dioxane (Table 1, entries 6–7). Among various copper sources at the same concentration (10 mol%), CuI was the most effective, with a moderate yield (64%) (Table 1, entries 8–12). At an elevated concentration of CuI (15 mol%), a relatively satisfactory yield (85%) was reached (Table 1, entry 13). Therefore, CuI was chosen in the subsequent experiments aiming at investigating the effect of bases. Among the four different bases (KOH, $K_2CO_3$, $K_3PO_4$ and $Cs_2CO_3$), KOH apparently rendered the maximum yield for the *O*-arylation (Table 1, entries 9, 14–16). In addition, compared with Meso-N-C-1, the mesoporous N-doped carbon materials Meso-N-C-2

**Table 1** Effect of catalyst, base, and solvent on the cross-coupling of phenol with iodobenzene[a]



| Entry | Cu source | Carbon | Base | Solvent | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $CuCl_2$ | Meso-N-C-1 | KOH | DMSO | 47 |
| 2 | CuCl | Meso-N-C-1 | KOH | DMSO | 44 |
| 3 | $CuCl_2$ | — | KOH | DMSO | 4 |
| 4 | CuCl | — | KOH | DMSO | 9 |
| 5 | — | Meso-N-C-1 | KOH | DMSO | 0 |
| 6 | CuCl | Meso-N-C-1 | KOH | DMF | 14 |
| 7[c] | CuCl | Meso-N-C-1 | KOH | Dioxane | 30 |
| 8 | CuBr | Meso-N-C-1 | KOH | DMSO | 43 |
| 9 | CuI | Meso-N-C-1 | KOH | DMSO | 64 |
| 10 | $CuSO_4$ | Meso-N-C-1 | KOH | DMSO | 42 |
| 11 | $Cu(OAc)_2$ | Meso-N-C-1 | KOH | DMSO | 25 |
| 12 | $Cu(acac)_2$ | Meso-N-C-1 | KOH | DMSO | 55 |
| 13[d] | CuI | Meso-N-C-1 | KOH | DMSO | 85 (77) |
| 14 | CuI | Meso-N-C-1 | $K_2CO_3$ | DMSO | 16 |
| 15 | CuI | Meso-N-C-1 | $K_3PO_4$ | DMSO | 15 |
| 16 | CuI | Meso-N-C-1 | $Cs_2CO_3$ | DMSO | 27 |
| 17[d] | CuI | Meso-N-C-2 | KOH | DMSO | 36 |
| 18[d] | CuI | Meso-N-C-3 | KOH | DMSO | 59 |

[a] Reaction conditions: PhI (1 mmol), phenol (1.5 mmol), copper salts (0.1 mmol), Carbon 50 mg, base (3 mmol), solvent (4 mL), 100 °C, 24 h. [b] GC yields with biphenyl as internal standard (isolated yield in parenthesis). [c] Solvent: 1,4-dioxane. [d] CuI 0.15 mmol was used for the test.

and Meso-N-C-3 with less N content afforded lower yields, which hints that this coupling is really supported by the structural nitrogen on the carbon materials (Table 1, entries 17–18). That result agrees with observation in the oxidation of benzyl alcohol by Pd supported on polymeric carbon–nitrogen materials, in which the catalytic activity correlates with the concentration of nitrogen on the carbon supports.[17] It is therefore assumed that the doped nitrogen atoms, in particular those with lone pairs, can anchor the copper species, and then promote cross-coupling reactions to a larger degree.

In the next step, our efforts were directed to identify the scope of this method. The cross-couplings between several aryl halides and phenol were tested under the optimized conditions. It was found that the CuI/Meso-N-C-1 system can also work with iodobenzene having an electron rich group, for example: 1-methyl-4-iodobenzene, but with a moderate yield (Table 2, entry 1). In the presence of iodobenzene substituted by an electron-withdrawing group (–F), our catalytic system gave an excellent yield for the corresponding biphenyl ether in 10 h (Table 2, entry 2). Phenyl bromide proved to be less efficient than PhI, giving 79% yield in 48 h (Table 2, entry 3). The coupling of phenol and chlorobenzene containing an electron-withdrawing group ($–NO_2$) proceeded smoothly (Table 2, entry 4).

In an endeavour to expand the scope of the above methodology, various substituted phenols, amines, imidazol, and thiophenols were examined with PhI for the respective O–, N–, and S-arylated products. Phenols containing electron-donating groups at the *para* site provided moderate to good yields (Table 2, entries 5, 10, 11). Relative good reactivity was observed with sterically hindred *o*-cresol (Table 2, entry 12). As a heterogeneous promoter, the Meso-N-C-1 can be easily separated by centrifugation and washed with water and ethanol. The recovered Meso-N-C-1 can be reused at least four times without losing activity and showed no difference in FT-IR spectra (Table 2, entries 6–9; Fig. S2, ESI†). The reaction conditions were also suitable for the cross-coupling of phenylamine with PhI (Table 2, entry 13). *N*-arylation of imidazole with PhI gave the coupled product in 88% yield (Table 2, entry 14). Furthermore, thiophenol and 4-methylthiophenol were coupled with PhI under the generalized reaction conditions to afford the corresponding products in good yields (Table 2, entries 15–16).

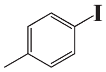
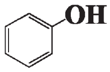
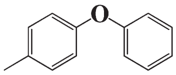
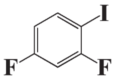
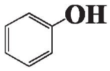
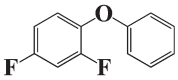
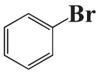
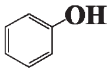
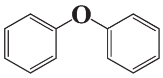
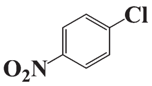
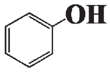
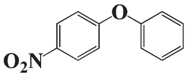
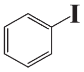
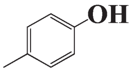
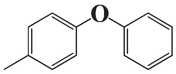
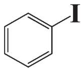
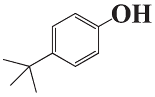
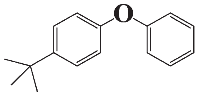
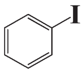
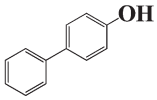
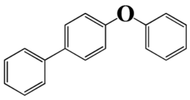
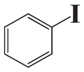
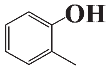
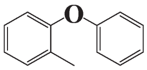
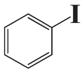
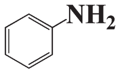
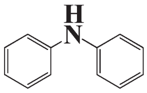
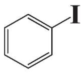
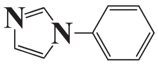
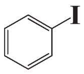
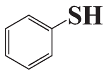
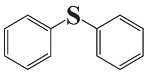
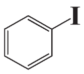
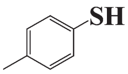
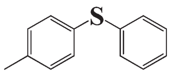
### Synthesis and characterization of (CuO)*x*@Meso-N-C

Encouraged by the efficiency of N-doped carbon materials as promoters for the copper-catalyzed Ullmann-type cross-couplings, we tried to use N-doped carbon materials to support copper species as heterogeneous catalysts for the same transformation.[18] In the subsequent work, we prepared CuO nanoparticles supported on N-doped carbon (Meso-N-C-1) with a high surface area by deposition-precipitation method.[19] These samples were denoted as $(CuO)_x$@Meso-N-C: *x* corresponds to the used amount of $CuCl_2$ in mmol while the amount of Meso-N-C-1 remains the same (200 mg). The appearance of diffraction lines at $2\theta = 35.4°$, $2\theta = 38.6°$ indicates the presence of the crystalline phase of CuO in the $(CuO)_{1.0}$@Meso-N-C (Fig. 3a).[18c] The average size of the CuO crystallite was calculated to be ~14.5 nm using Scherrer's formula, a little larger than the average particle size (12.6 ± 3 nm) determined by TEM image (Fig. S3, ESI†). The pore structures were retained after the incorporation of CuO into Meso-N-C-1, resulting in high specific surface areas from 373 to 488 $m^2\ g^{-1}$, which in principle can be a benefit for heterogeneous catalysis, as the pore structure is believed to largely enhance the mass transfer properties and result in good CuO dispersity (Fig. 3b, Table S2, ESI†). Based on X-ray photoelectron spectroscopy (XPS) analysis, it is clear that copper is in the divalent state with $d^9$ character. XPS detected the $2p_{3/2}$ and $2p_{1/2}$ main peaks at 934.8 and 955.2 eV, respectively. Two shake-up satellite peaks, about ~8 eV higher than main peaks, were observed, which were diagnostic of an open $3d^9$ shell, corresponding to the $Cu^{2+}$ state (Fig. 3c).[20]

### Catalytic tests of (CuO)*x*@Meso-N-C in Ullmann-type cross-couplings

Indeed, the catalytic system $(CuO)_{1.0}$@Meso-N-C gave an excellent yield in the cross-coupling of PhI and 4-methylphenol (Table 3, entry 1). The final CuO content of the $(CuO)_{1.0}$@Meso-N-C was determined as ~30% by TGA thermograms under $O_2$ flow (Fig. 3d). Being a heterogeneous catalyst, $(CuO)_{1.0}$@Meso-N-C can be easily recovered by centrifugation and reused four times without any loss of efficiency (Table 3, entries 2–5; Fig. S3, ESI†). The liquid phase of the reaction mixture was collected by hot filtration after the reaction and analyzed by ICP-MS. A very low amount of dissolved copper (~0.5% of the total copper) was detected in the solution at the end of the reaction. Moreover, after we

**Table 2** The CuI/Meso-N-C-1 catalyzed Ullmann-type O–, N–, and S-arylation with aryl halides[a]

| Entry | Aryl halide | Phenol/amine/imidazol/thiophenol | Product | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 |  |  |  | 24 | 33 |
| 2 |  |  |  | 10 | 94 |
| 3[c] |  |  |  | 48 | 79 |
| 4 |  |  |  | 24 | 95 |
| 5 |  |  |  | 20 | 96 (87) |
| 6[d] | | | | 20 | 96 |
| 7[e] | | | | 20 | 94 |
| 8[f] | | | | 20 | 94 |
| 9[g] | | | | 20 | 95 |
| 10 |  |  |  | 24 | 84 |
| 11 |  |  |  | 24 | 57 |
| 12 |  |  |  | 24 | 86 |
| 13[h] |  |  |  | 24 | 73 (65) |
| 14[c] |  |  |  | 24 | 88 |
| 15[h] |  |  |  | 15 | 98 (90) |
| 16[h] |  |  |  | 15 | 96 |

[a] Reaction conditions: Aryl halide (1 mmol), phenol/amine/imidazol/thiophenol (1.5 mmol), CuI (0.15 mmol), Meso-N-C-1 (50 mg), KOH (3 mmol), DMSO (4 mL), 100 °C. [b] GC yield with biphenyl as internal standard (isolated yield in parenthesis). [c] Reaction temperature: 125 °C. [d] Second run to test the reusability of catalyst. [e] Third run to test the reusability of the catalyst. [f] Fourth run to test the reusability of the catalyst. [g] Fifth run to test the reusability of the catalyst. [h] In Ar atmosphere.

removed the $(CuO)_{1.0}$@Meso-N-C from the reaction solution after 7 h (Yield: 47%), the supernatant did not show any further reactivity in the next 10 h. These results indicated that the copper catalyst indeed functioned in a heterogeneous manner.

We also studied the $(CuO)x$@Meso-N-C catalysts with different Cu amounts using the cross-coupling between PhI and phenol as a model reaction. The $(CuO)_{1.0}$@Meso-N-C exhibited the best activity for this cross-coupling reaction with a 94% yield for DPE, while $(CuO)x$@Meso-N-C ($x$ = 0.5; 0.2) with less Cu content gave lower yields (Table 3, entries 6–8). These results provide evidence that the activity is attributed to the copper species loaded on the carbon material.

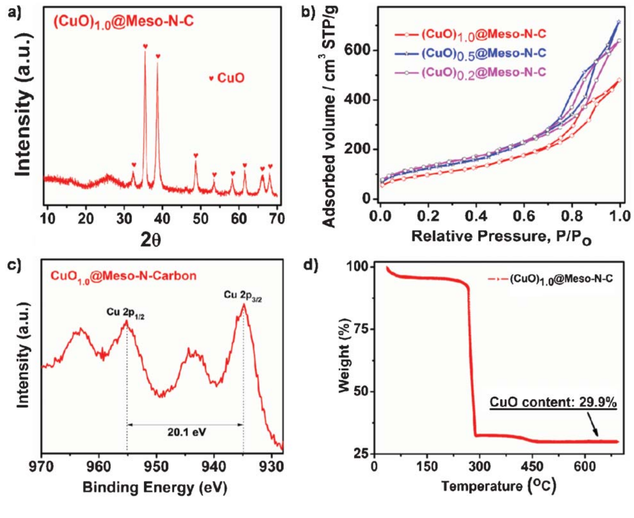


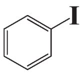
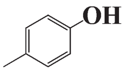
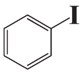
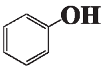
**Fig. 3** a) XRD pattern, b) $N_2$ adsorption–desorption isotherms and c) XPS spectrum of the copper-containing catalysts; d) TGA thermograms of $(CuO)_{1.0}$@Meso-N-C under flowing $O_2$.

## Conclusions

In summary, mesoporous nitrogen-doped carbon materials with high nitrogen contents were developed as simple, sustainable, and efficient heterogeneous N-type ligands for the copper-mediated Ullmann-type C–O, C–N, and C–S cross-couplings. Under the optimized conditions, the CuI/Meso-N-C-1 system successfully promoted the cross-couplings between various aryl halides and phenols, amines, imidazol, and thiophenols with moderate to high yields. This novel catalyst system offers an excellent complement to the Cu-catalyzed methodology, at the same time revealing an important application of nitrogen-doped carbon materials in the field of catalysis.

Furthermore, CuO supported on nitrogen-doped carbon was proven as an active and recyclable heterogeneous catalyst for the Ullmann-type cross-coupling of aryl halides with phenols. The high catalytic performance is to be contributed to the heterojunction between special nitrogen-containing structure in the carbon materials and copper species. Meanwhile, $(CuO)_{1.0}$@Meso-N-C, a copper-based fully heterogeneous catalyst, presented outstanding performance with high activity and stability in the Ullmann-type cross-coupling reaction.

**Table 3** The Ullmann-type cross-couplings between phenols and PhI catalyzed by copper supported on N-doped carbon materials[a]

| Entry | Aryl halide | Phenols | Catalyst | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 |  |  | $(CuO)_{1.0}$@Meso-N-C | 17 | 93 (84) |
| 2[c] | | | $(CuO)_{1.0}$@Meso-N-C | 17 | 91 |
| 3[d] | | | | 17 | 95 |
| 4[e] | | | | 17 | 96 |
| 5[f] | | | | 17 | 94 |
| 6 |  |  | $(CuO)_{1.0}$@Meso-N-C | 24 | 94 |
| 7 | | | $(CuO)_{0.5}$@Meso-N-C | 24 | 42 |
| 8 | | | $(CuO)_{0.2}$@Meso-N-C | 24 | 13 |

[a] Reaction conditions: PhI (1 mmol), phenols (1.5 mmol), (CuO)x@Meso-N-C (50 mg); 100 °C, DMSO 4 mL. [b] GC yield with biphenyl as internal standard (isolated yield in parenthesis). [c] Second run to test the reusability of catalyst. [d] Third run to test the reusability of the catalyst. [e] Fourth run to test the reusability of the catalyst. [f] Fifth run to test the reusability of the catalyst.

We believe that mesoporous nitrogen-doped carbons, acting as nitrogen-rich promoters, can be combined with many more transition metals (Pd, Au, Ni, Zn, Co *etc.*) in two ways: (1) merging with metal salts in a physical manner; (2) acting as support structures for metal nanoparticles, thereby opening up new possibilities for discovering many attractive heterogeneous catalytic methodologies in both organic research and chemical industries.

## Experimental section

### Synthesis of mesoporous N-doped carbon

After adding 2.5 g of 12 nm $SiO_2$ nanoparticles (Ludox HS40) to 1 g ionic liquid (IL): 1-ethyl-3-methylimidazolium dicyanamide (Emim-dca), 3-cyanomethyl-1-vinylimidazolium bromide (Cmvim-Br), or a prepared mixture of Emim-dca (1 g) with 2-guanidinobenzimidazol (0.1 g), the resulting mixtures were heated to 80 °C overnight to remove the water. Then, the obtained mixtures were transferred into a crucible and heated to 1000 °C in 5 h under nitrogen flow. The final temperature was kept for 1 h. After cooling, the dark solid was treated with 4 M $NH_4HF_2$ (twice) for one day to remove the Si template. The dispersion was then filtered, and the precipitate was washed with deionized (DI) water. The obtained solid was dried in an air oven at 80 °C for 24 h.

### Synthesis of $(CuO)_x$@Meso-N-C

The deposition of CuO was achieved using the deposition-precipitation (DP) method. In the DP process, $CuCl_2 \cdot 2H_2O$ ($x$ = 1, 1 mmol; $x$ = 0.5, 0.5 mmol; $x$ = 0.2, 0.2 mmol) was added to the Meso-N-C-1 solution (200 mg in 40 mL $H_2O$) and the mixture was ultrasonicated for 20 min. Then, 0.1 M NaOH was added drop by drop to adjust the solution pH value to ∼9 under ultrasonication (∼20 min). The precipitate was centrifuged and washed with DI water until the solution pH value was around 7. The obtained solid was dried at 80 °C for 24 h and then calcined at 180 °C for 24 h to obtain the catalyst.

### Typical procedure for the Ullmann-type cross-coupling reaction

Aryl halide (1 mmol), phenol/amine/imidazol/thiophenol (1.5 mmol), base (3 mmol), catalysts (used as described in the manuscript) and 4 mL solvent were added into a 10 mL round bottom glass-reactor. The reaction was performed at 100 °C in an oil bath with magnetic stirring for the desired time. When the reaction was carried out in an Ar atmosphere, the atmosphere inside was replaced with Ar three times and then the reaction started with an Ar balloon. After completion of the reaction, biphenyl was added to the mixture as the internal standard. The obtained solution was stirred at room temperature for 10 min. Then, the solution was filtered and washed with acetone and the obtained liquid mixture was injected into the GC-MS for analysis.

For the isolated yield: After completion of the reaction, the solution was filtered and washed with ethyl acetate. Then, 50 mL DI water was added to the filtrate and the organic layer was separated. The water layer was exacted with ethyl acetate (3 × 15 mL). All the organic layers were combined and dried over anhydrous $MgSO_4$. After filtering $MgSO_4$, the filtrate was concentrated *in vacuo*. The crude product was purified by silica gel chromatography to provide the desired product.

For the recycling study, the Ullmann-type reaction was performed with phenyl iodide and 4-methylphenol maintaining the same reaction conditions as described above, except using the recovered catalyst. Each time, after the completion of reaction, the catalyst was recovered by centrifugation and then washed thoroughly with ethyl acetate followed by DI water to remove the base present in the used catalyst. The recovered catalyst was dried under vacuum at 80 °C overnight and reused in the next run.

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