Cu$^0$ Nanoparticles Deposited on Nanoporous Polymers: A Recyclable Heterogeneous Nanocatalyst for Ullmann Coupling of Aryl Halides with Amines in Water

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Cu$^0$ nanoparticles were deposited on a nanoporous polymer to develop a novel nanocatalyst (Cu-B) for carrying out Ullmann coupling of aryl halides with amines in water. Non-aqueous polymerization of a mixture of divinylbenzene and acrylic acid under hydrothermal conditions followed by the deposition of Cu$^0$ nanoparticles were adopted to afford the Cu-B nanocatalyst. In order to compare the catalytic activity of the Cu-B nanocatalyst in the Ullmann coupling reactions, another nanocatalyst, Cu$^0$ nanoparticle-loaded porous carbon (Cu-A), was also prepared. All the newly developed Cu$^0$ nanoparticle-based nanocatalysts were thoroughly characterized using several characterization techniques. The Ullmann coupling reactions were carried out in water only with 1.35 mol% loading of Cu as catalytically active sites in Cu-B. The Cu-B nanocatalyst exhibited higher catalytic activity as compared with Cu-A, and also showed a good catalytic recyclability with a high consistence in the catalytic activity. No Cu leaching from the nanocatalyst surface and the smooth nanocatalyst recovery confirm the true heterogeneity in these catalytic reactions.

Constructing a new C-N bond (amination) by Cu-catalyzed Ullmann coupling of aryl halides with amines has received a considerable interest as the products (aryl amines) could be utilized potentially in pharmaceutical and material-based applications. Most of the examples in the Ullmann amination, however, need the assistance of expensive N- or P-ligands to maintain the catalytic turnover (typically 5–20 mol%) in homogeneous reaction systems. Thus, the development of heterogeneous catalysts has shown promising potential in sustainable applications, in which the catalysts can be recovered by simple filtration and reused for the next catalytic cycles with the minimization of undesired wastes. Homogeneous metal catalysts could be heterogenized by anchoring them onto the surface of inorganic solids including silica, alumina, zeolite, etc. Among various heterogeneous matrix, nanoporous polymers have received much attention in catalysis on account of their large surface area, high thermal and mechanical stability, and well-defined pore size distribution. The tunable nanoporous polymers serve as the platforms to immobilize catalytically active sites (metal or metal oxide nanoparticles (NPs)) on their external surface as well as into the nanopores with the preservation of porous structures. The use of transition metal NPs as the catalysts in organic synthesis has emerged with a considerable interest due to their inherently large surface-to-volume ratio and tunable morphologies as compared with the bulk metals. Among them, Cu$^0$ NPs have been widely employed in various organic reactions. The stability and activity of metal NPs can be increased by avoiding the aggregation and leaching from the polymer networks due to a certain degree of chemical engagement (such as coordination and electron transfer) between the polymers and metal NPs.

In this work, we developed two new heterogeneous Cu$^0$ nanocatalysts Cu-A and Cu-B, where Cu$^0$ NPs were deposited on carbonaceous matrix and nanoporous polymer DVAC-1, respectively (Figure 1). Both of the catalysts were thoroughly characterized by wide-angle powder X-ray diffraction (XRD), transmission electron microscope (TEM), field emission scanning electron microscope (FE-SEM), Raman spectroscopy, X-ray photo-
electron spectroscopy (XPS), and N₂ adsorption/desorption analysis. The Cu-B showed good catalytic performance for the Ullmann coupling reactions of aryl iodides or bromides with primary and secondary amines in aqueous solution, delivering a series of N-aryl amines in good yields with high catalyst turnover. To the best of our knowledge, this is the first example of utilizing nanoporous polymer-supported Cu⁰ heterogeneous nanocatalyst for the Ullmann amination²⁰,²¹. This heterogeneous catalyst could be successfully recycled and reused for five consecutive catalytic cycles without Cu leaching from the reaction mixture.

**Results**

**Synthesis and Characterization of Cu⁰ Nanocatalysts.** The catalyst Cu-A (Figure 1) was prepared by chelate-assisted co-assembly strategy using Cu(acac)₂ (acac = acetylacetone), soluble phenol formaldehyde resin and poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer Pluronic F127 (Mₚ ≈ 12600, PEO₁₀₆PPO₇₀PEO₁₀₆; PEO = polyethylene oxide and PPO = poly propylene oxide). After thermocuring treatment, copper-complex/resol/F127 hybrid thin film was obtained. The hybrid thin film was carbonized at 600 °C under an N₂ atmosphere. During the carbonization, F127 template was decomposed, resol polymer was carbonized to generate rigid carbon matrix, and in situ growth of Cu⁰ NPs took place by slow decomposition of Cu(acac)₂ complex. For the synthesis of the catalyst Cu-B, we used nanoporous polymer DVAC-1 developed by non-aqueous polymerization of acrylic acid. By following the synthesis route outlined in Figure 1, nanoporous organic polymer DVAC-1 was derived by non-aqueous polymerization of acrylic acid with cross linker divinyl benzene under hydrothermal condition. Azobisisobutyronitrile (AIBN) was used as the radical initiator for this reaction. The white color DVAC-1 was insoluble in water and common organic solvents. CuCl₂·2H₂O was utilized as the copper source. The Cu⁺⁺ ions were attached to the carboxylate moieties on the surface of nanoporous polymer via ligand exchange, leading to a color change from light green to dark grey. After the addition of EDA (ethylene diamine) in the reaction mixture, the color changed from dark grey to deep violet owing to the formation of Cu(EDA)₂⁺⁺ complex. N₂H₄·H₂O was then added to reduce Cu⁺⁺ ions to Cu⁰ NPs on the nanoporous polymeric network. The color of the resulted reaction mixture was deep brown, and subsequently blackish-brown Cu-B was obtained through precipitation.

Wide angle powder XRD patterns of Cu-A and Cu-B nanocatalysts display (Figure 2A-a and 2A-b) three well resolved peaks at 2θ = 43.1°, 50.3° and 74.0°, which can be readily indexed to the (111), (200) and (220) crystalline planes, respectively, corresponding to the face centered cubic (fcc) arrangement of Cu NPs (JCPDS no. 04-0836)²²,²³. The diffused peaks at 2θ = 22.7° and 18.3° for the Cu-A

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**Figure 1** | Preparation of the Cu-A and Cu-B nanocatalysts.
and Cu-B, respectively, are attributed to the amorphous frameworks of nanoporous polymer, suggesting that Cu-A and Cu-B are copper-polymer hybrids. These characteristic diffraction patterns indicate that Cu NPs are well crystallized inside the nanoporous carbon and polymer frameworks. Porous properties of these Cu nanocatalysts were established from the N₂ sorption analysis at 77 K. N₂ adsorption/desorption isotherms of the Cu-A and Cu-B nanocatalysts are displayed in Figure 2B. The Cu-A nanocatalyst exhibits a typical type

Figure 2 | (A) Wide angle powder XRD patterns, (B) N₂ adsorption/desorption isotherms, (C) Raman spectra, and (D) high resolution XPS spectra of (a) Cu-A and (b) Cu-B nanocatalysts. Inset of (B) shows the pore size distributions. (E) N₂ adsorption/desorption isotherms and (F) temperature programmed desorption (TPD) of ammonia for nanoporous polymer DVAC-1.
I isotherm (Figure 2B-a) corresponding to the presence of micro-
Pores. The BET (Brunauer-Emmett-Teller) surface area of the Cu-A
nanocatalyst is 90 m²g⁻¹. Its pore size distribution (inset of
Figure 2B) calculated by employing non-local density functional
theory (NLDFT) reveals the presence of micropores having the dia-
meter of 1.08 nm (Figure 2B-a'). On the other hand, the Cu-B cata-
lyst shows a typical type II isotherm with a small hysteresis loop and a
sharp N₂ uptake in the high P/P₀ pressure region (Figure 2B-b)
corresponding to the existence of interparticle void cavity²⁴,²⁵. The
BET surface area of this catalyst is 260 m²g⁻¹. The small hysteresis
loop in the isotherm may be generated by the swelling of the poly-
meric network upon the gas adsorption. Its pore size distribution
curve was derived by the BJH (Barrett-Joyner-Halenda) model, indi-
cating the presence of interparticle cavity with the diameter of 18 nm
(Figure 2B-b').

The pore volumes of the Cu-A and Cu-B nanocatalysts are 0.0426
and 0.703 ccg⁻¹, respectively. The pore volume of Cu-B is quite
larger than that of Cu-A. The large pore volume of Cu-B allows for
easy diffusion of reaction substrates throughout the nanoporous
channels and enables them to interact with each other as well as with
Cu sites for performing catalytic reaction in short reaction time²⁶,²⁷.
Raman spectra of the two nanocatalysts are shown in Figure 2C.
Raman spectrum of Cu-A (Figure 2C-a) displays two broad bands
centered at 1337 cm⁻¹ and 1597 cm⁻¹ corresponding to the D band
and G band, respectively, signifying the presence of amorphous car-
bon framework²⁸. In the Raman spectrum of Cu-B (Figure 2C-b), the
band at 1610 cm⁻¹ is indicative of the existence of G band, but the
peak concerning to the D band cannot be resolved properly. Two
peaks appeared at 2929 cm⁻¹ and 3062 cm⁻¹ (inset in Figure 2C-b)
for Cu-B could be assigned to the C-H stretching vibrations from the
CH₂ and CH₃ groups of the polymeric framework²⁹. XPS is an indis-
ispensable tool to evaluate the oxidation state of copper embedded into
the porous channels. In the XPS spectra (Figure 2D-a and 2D-b), the binding
energy 2p₃/₂ centered at 932.9 eV and 933.1 eV along with other
strong binding energy peaks of 2p₁/₂ at 952.7 eV and 952.8 eV for
Cu-A and Cu-B were observed respectively, indicating that Cu NPs
possess the oxidation state (0) inside the porous channels. The
absence of satellite peaks for the 2p region also refers to the oxidation
state (0) of copper³⁰,³¹. No signals from Cu²⁺ were observed from the
XPS spectra³². Nanoporous polymer DVAC-1 shows a typical type II
isotherm with corresponding BET surface area of 420 m²g⁻¹
(Figure 2E), presenting strong evidence of nanopores generated dur-
ing cross-linking polymerization under hydrothermal condition.
Moreover, the isotherms show that DVAC-1 adsorbs a large amount
of nitrogen at high P/P₀ values, indicating interparticle porosity. The
calculated pore volume of DVAC-1 is 1.27 ccg⁻¹. Appreciable
decreases in the BET surface area and pore volume of Cu-B as com-
pared with nanoporous polymer DVAC-1 suggest that Cu NPs were
successfully incorporated into the polymer framework. We also car-
rried out temperature programmed desorption (TPD) of ammonia
(Figure 2F) over nanoporous polymer DVAC-1 in order to calculate
the loading of –COOH group in DVAC-1. DVAC-1 polymer shows a
strong signal at higher desorption temperature of 434 °C, corres-
ponding to the total –COOH group loading of 1.01 mmol g⁻¹.

TEM analysis was performed to investigate the deposition of Cu
NPs on the nanoporous polymer DVAC-1 (Figure 3). It is quite
evident from Figure 3A that Cu NPs with black color were homog-
eneously dispersed on the surface of the conjugated polymeric net-
work DVAC-1³³,³⁴. Individual Cu NPs marked with white circle
could be clearly identified from Figure 3B, with the particle size
varying from 9.8 nm to 14.3 nm. It should be mentioned that Cu
NPs might undergo slight aggregation to generate copper nanoclus-
ters (black dots in Figure 3C and 3D) owing to the strong interactions
of Cu NPs with the surface –COOH groups of the nanoporous poly-
mer. TEM images of Cu-A are given in Figure 4A–4C, indicating that
Figure 4 | (A–C) TEM images of the Cu-A nanocatalyst and (D–F) FE-SEM images of the Cu-B nanocatalyst.
spherical Cu NPs with black color were uniformly distributed throughout the surface of the material and also incorporated inside the carbonaceous matrix. Its particle size range is from 4.7 nm to 5.3 nm. The morphology of Cu-B was further confirmed by FE-SEM images (Figure 4D–4F), showing uniform formation of sea-urchin-like copper-polymer nanoclusters at the surface, which undergo the self-assembly to develop three-dimensional (3D) urchin-like spheres through oriented attachment. Magnified FE-SEM image (Figure 4E) exhibits that these nanoclusters are composed of very thin needles. Thus, the formation mechanism can be explained on the basis of needle-to-urchin spheres, and polymer DVAC-1 has a definite role for the development of this special sea-urchin-like morphology.

EDX (energy dispersive X-ray) pattern and elemental mapping (Figure S1) of FE-SEM images prove the presence of C, O and Cu elements in the Cu-B nanocatalyst. EDX pattern and elemental mapping of each particular sea urchin nanostructures undoubtedly indicate that these nanostructures are composed of not only copper element but also C and O elements from the DVAC-1 polymer. It is expected that the unique nanostructures of Cu-B with high surface area could provide high catalytic performance for carrying out catalytic reactions.

Catalytic Performance of Cu⁰ NP Based Nanocatalysts. We then employed the newly prepared Cu⁰ NP based nanocatalysts Cu-A and Cu-B for the Ullmann coupling of aryl halides with amines. The reaction is shown in Figure 5. Our study began with the reaction of 4-iodoanisole (1a, 1.0 mmol) with methylamine (2a, 40% aqueous solution, 2.5 mL, 28.9 mmol) in the presence of Cs₂CO₃ (2 equiv) and Cu-B nanocatalyst (20 mg, 1.38 mol% for Cu) in a sealed tube at 110°C (oil bath). The Cu content in the Cu-A catalyst is 0.690 mmol g⁻¹, measured by inductive coupled plasma-mass spectroscopy (ICP-MS). The catalytic conversion could be observed and 4-methoxy-Ν-methylaniline (3aa) was isolated in 64% yield after 24 h (Table 1, entry 1). On the other hand, by employing the Cu-B catalyst (20 mg, 1.35 mol% for Cu) in the coupling reaction under otherwise identical reaction conditions, the yield of 3aa could be improved to 76% and the reaction finished within only 3h (Table 1, entry 2). The Cu content in the Cu-B catalyst is 0.675 mmol g⁻¹, determined by ICP-MS. The catalytic Ullmann coupling using Cu-B was also effective in large-scale reaction (10 mmol) with a consistent yield of 80% (Table 1, entry 3). The reaction with K₂CO₃ as the base instead of Cs₂CO₃ lowered the yield of 3aa to 53% (Table 1, entry 4), while no reaction was observed when K₂PO₄ or Et₃N was employed (Table 1, entries 5 and 6). In addition, the reaction did not take place in the presence of N,N-dimethylmethanamide or dimethyl sulfoxide as the solvent (Table 1, entries 7 and 8). We also checked the catalytic activity of Cu-B at room temperature (25°C) in the presence of Cs₂CO₃, and no conversion of the product was observed (Table 1, entry 9). We then conducted the Ullmann amination using bare Cu⁰ NPs as the catalyst (Table 1, entry 10). In this case, it took 24 h to complete the reaction and only 50% yield of 3aa was obtained, suggesting that nanoporous polymer and unique sea-urchin nanostructure of Cu-B play a crucial role in the reaction efficiency. An additional control experiment for

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**Table 1** Optimization of the reaction conditions for the Ullmann coupling of 4-iodoanisole (1a) and methylamine (2a)⁴

| Entry | Catalyst | Base       | Temperature (°C) | Time (h) | Yield (%) | TON     |
|-------|----------|------------|-----------------|----------|-----------|---------|
| 1     | Cu-A     | Cs₂CO₃    | 110             | 24       | 64        | 46.3    |
| 2     | Cu-B     | Cs₂CO₃    | 110             | 3        | 76        | 56.2    |
| 3     | Cu-B     | Cs₂CO₃    | 110             | 3        | 80        | 59.2    |
| 4     | Cu-B     | K₂CO₃     | 110             | 24       | 53        | 39.2    |
| 5     | Cu-B     | K₂PO₄     | 110             | 24       | NR        | 0       |
| 6     | Cu-B     | NEt₃      | 110             | 24       | NR        | 0       |
| 7     | Cu-B     | Cs₂CO₃    | 110             | 24       | NR        | 0       |
| 8     | Cu-B     | Cs₂CO₃    | 110             | 24       | NR        | 0       |
| 9     | Cu-B     | Cs₂CO₃    | 25              | 24       | 50        | 36.2    |
| 10    | Cu⁰ NPs  | Cs₂CO₃    | 110             | 24       | 50⁵       | 35.9    |
| 11    | Cu⁰ Carbon Black | Cs₂CO₃   | 110             | 24       | 50        | 36.2    |
| 12    | DVAC-1   | Cs₂CO₃    | 110             | 24       | NR        | 0       |

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⁴Reaction conditions: 4-iodoanisole (1a, 1 mmol, 234 mg), methylamine (2a, 40 wt% aqueous solution, 2.5 mL, 28.9 mmol) and inorganic base (2 mmol);
⁵Isolated yields;
⁶The reaction was conducted using 1a (10 mmol), 2a (40 wt% aqueous solution, 25 mL), and Cs₂CO₃ (20 mmol);
⁷Methyl amine (40 wt% aqueous solution, 1 mL) and N,N-dimethylformamide (2 mL);
⁸Methyl amine (40 wt% aqueous solution, 1 mL) and dimethyl sulfoxide (2 mL);
⁹The reaction was performed at room temperature;
⁵⁵Determined by ¹H NMR spectra. NR = no reaction; TON = turn over number [mole of substrate converted per mole of active site].
Ullmann coupling was carried out using Cu\textsuperscript{0} NP-loaded carbon black catalyst (Cu\textsuperscript{0}-carbon black, synthesized by following a same procedure), showing the reaction yield of 50% after 24 h (Table 1, entry 11). The Cu loading in Cu\textsuperscript{0}-carbon black catalyst is 0.695 mmol (1 mmol), showing the reaction yield of 50% after 24 h (Table 1, entry 12), suggesting that the copper component is the major catalytically active site responsible to the catalytic reaction.

By using Cu-B as the catalyst, we next examined the substrate scope of this catalytic Ullmann coupling by employing various aryl halides 1 with methylamine 2a (Table 2 and Figure 5). With meta- and ortho-iodoanisoles 1b and 1c, the corresponding anilines 3ba and 3ca could be prepared in 86% and 71% yields, respectively (Table 2, entries 1 and 2). Similarly, 4-iodotoluene (1d) and 1-chloro-4-iodobenzene (1e) could be transformed into the corresponding anilines 3da and 3ea in good yields (Table 2, entries 3 and 4). We tested several aryl bromides such as 1f and 1g as the coupling partners with methylamine (2a), delivering the corresponding anilines 3fa (=3ba) and 3ga in moderate yields (Table 2, entries 5 and 6).

The scope of amines 2 for the Ullmann amination with iodoanisoles 1a and 1b (Table 3 and Figure 5) was also examined. The reactions were smoothly performed with ethylamine (2b), allylamine (2c), and pyrrolidine (2d) in 12–18 h, affording the corresponding anilines in good yields (Table 3, entries 1–6), while the reaction with morpholine (2e) resulted in a moderate yield of the coupling product (Table 3, entry 7).

Recyclability and Reusability of Cu-B Nanocatalyst. In order to investigate heterogeneous nature of the Cu-B nanocatalyst, hot filtration test and leaching test were carried out. These experimental results undoubtedly demonstrated that there was no leaching of copper from the nanocatalyst during the course of reaction and the nanocatalyst was indeed heterogeneous in nature. To evaluate the recyclability and reusability of the Cu-B nanocatalyst, we performed the Ullmann N-arylation of 4-iodoanisole (1a) with methylamine (2a) under the optimized reaction conditions. After the completion of the reaction, the reaction mixture was centrifuged and filtered. The recovered Cu-B nanocatalyst was washed by sufficient amount of water, ethyl acetate, and acetone. Finally, the nanocatalyst was dried in an oven at 80 °C before the use for next catalytic cycle. The nanocatalyst could be reactivated in a very easy way. No addition of acid, base, and special reagent, and no special treatment (such as calculations at high temperature) were needed during the reactivation. In every cycle, the nanocatalyst recovery was almost quantitative.

Figure 6 shows that the Cu-B nanocatalyst could be effectively recycled and reused up to five consecutive catalytic cycles, but an obvious decrease in the product yield was observed at the 5th cycle. The drop of product yield at the 5th catalytic cycle may be due to the clogging of nanocatalyst by reagents. To identify the possible reagents responsible for the clogging of nanocatalyst, EDX analysis and elemental mapping (Figure S2) of reused Cu-B nanocatalyst after the 5th catalytic cycle followed by thorough washing with water, ethyl acetate and acetone were carried out. Surprisingly, The results reveal that a significant amount of Cs(I) ion from Cs\textsubscript{2}CO\textsubscript{3} was adsorbed and trapped into the nanopores, limiting the diffusion of the organic substrates into the nanocatalyst, and thus reducing the catalytic activity\textsuperscript{38}. Unfortunately, thorough washing did not improve the catalytic yield at the 5th catalytic cycle. Washing with organic solvents could remove unreacted organic substrates, but that with water cannot completely remove adsorbed Cs(I) ion from nanocatalyst owing to hydrophobic nature of the nanoporous polymer. We also analyzed the filtrate after the recovery of the nanocatalyst by utilizing AAS (atomic absorption spectroscopy) technique in order to check if any Cu leaching took place from the nanocatalyst into the filtrate. The results indicate that the Cu content in the filtrate was below the detection limit of the instrument, and the filtrate was completely colorless.

Characterization of Reused Cu-B Nanocatalyst. After the fifth catalytic cycle, we characterized the reused Cu-B nanocatalyst to confirm its mechanical stability. Figure S3 indicates that the nanocatalyst was stable during the course of catalytic reaction. Wide angle powder XRD pattern (Figure S3A) of the reused Cu-B

![Table 2: Scope on the Ullmann coupling with methylamine (2a)\textsuperscript{10}]

| Entry | Aryl Iodides | Amines | Yield (%)\textsuperscript{b) TN |  
|-------|-------------|--------|-----------------|
| 1     | 1b          | 2b     | 3ba 86% (16 h) 63.7 |
| 2     | 1c          | 2c     | 3ca 71% (4 h) 52.6 |
| 3     | 1d          | 2c     | 3da 70% (3 h) 51.8 |
| 4     | 1e          | 2c     | 3ea 73% (4 h) 54.0 |
| 5     | 1f          | 2c     | 3fa 51% (67%)\textsuperscript{a} (12 h) 49.6 |
| 6     | 1g          | 2c     | 3ga 51% (64%)\textsuperscript{a} (16 h) 49.4 |

\textsuperscript{a)Reaction conditions: aryl iodides 1 (1 mmol), methylamine (2a, 40 wt % aqueous solution, 2.5 ml, 28.9 mmol), Cs\textsubscript{2}CO\textsubscript{3} (2 mmol, 651 mg), Cu-B (20 mg, 1.35 mol% for Cu), and temperature 110°C.

\textsuperscript{b)Isolated yields;

\textsuperscript{c)Conversion yield.

![Table 3: Scope on the Ullmann amination with aryl iodides 1a and 1b\textsuperscript{d}]

| Entry | Aryl Iodides | Amines | Yield (%)\textsuperscript{a) | TON |
|-------|-------------|--------|-----------------|-----|
| 1     | 1a          | 2b     | 3ab 63% (12 h) 46.6 |
| 2     | 1b          | 2b     | 3bb 68% (12 h) 50.3 |
| 3     | 1a          | 2c     | 3ac 64% (18 h) 47.4 |
| 4     | 1b          | 2c     | 3bc 64% (12 h) 47.4 |
| 5     | 1a          | 2d     | 3ad 74% (16 h) 54.8 |
| 6     | 1b          | 2d     | 3bd 68% (12 h) 50.3 |
| 7     | 1a          | 2e     | 3ae 41%, 60%\textsuperscript{a} (24 h) 30.7 |
nanocatalyst after the fifth catalytic cycle proves that the crystalline phase of the CuNPs on the framework remains unchanged after the catalytic reaction. The XPS data (Figure S3B) of the reused Cu-B nanocatalyst suggest that the oxidation state of Cu remains unaltered after the Ullmann coupling. N2 adsorption/desorption isotherm analysis (Figure S3C) was also carried out for the reused Cu-B nanocatalyst after the 5th catalytic cycle. The BET surface area and pore volume of the reused Cu-B nanocatalyst are 180 m²/g and 0.432 cm³/g, respectively. Substantial decreases in the BET surface area and pore volume of the reused Cu-B nanocatalyst after the 5th catalytic cycle as compared with the fresh Cu-B nanocatalyst indicate that the clogging of nanopores took place, hindering the adsorption of nitrogen into the nanoporous channels.

In order to check mechanical stability of reused Cu-B nanocatalyst after five catalytic cycles, 13C solid state CP MAS (cross-polarization magic angle spinning) NMR analysis was carried out (Figure S3D), demonstrating that the structural integrity of organic functional groups in the nanoporous polymer backbone was retained. The TEM analysis (Figure S4) of the Cu-B nanocatalyst after each catalytic cycle shows no obvious aggregation of NPs, further indicating its high stability during the catalytic reactions. The Cu leaching test was also carried out. The Cu content of the nanocatalyst after the 5th catalytic cycle was found to be 0.669 mmol g⁻¹, which is still comparable to that of the fresh catalyst (0.675 mmol g⁻¹). This observation proves that no Cu leaching occurred during the course of reactions.

Discussion

In this work, a novel nanoporous polymer DVAC-1 was designed and synthesized using acrylic acid through a facile one-pot hydrothermal technique, which was employed as a platform for the encapsulation and deposition of CuNPs to achieve nanoporous polymer supported Cu heterogeneous nanocatalyst (Cu-B). Using the easy and efficient approach, the developed carboxylic acid functionalized polymer network could act as a strong anchoring agent for the coordination with metallic copper. The white color nanoporous polymer DVAC-1 contains 1.01 mmol/g carboxylic acid sites, determined by employing NH₃-TPD profile (Figure 2F). Deposited CuNPs with 1D needle-like structures self-assembled to deliver 3D sea-urchin-like morphology, which was confirmed by FE-SEM images. The deposition of CuNPs on the external surface as well as in the nanoporous channel of the polymer was proven by the TEM images and N2 adsorption/desorption isotherms (Figures 2 and 3). Higher catalytic activity of the Cu-B nanocatalyst as compared with the CuA nanocatalyst is due to the synergetic effect of high surface area and unique hierarchical sea-urchin-like morphology. The most exposed crystallographic facets play a crucial role to tune catalytic property of the nanocatalyst. The adsorption followed by the activation of the most reactive alkenes as well as the desorption of the products are significantly assisted by the surface atomic arrangement of the most exposed crystalline planes. In other words, the most exposed crystal planes of the nanocatalyst noticeably alter the catalytic property. From a catalysis point of view, high density of atomic steps, ledges, kinks and dangling bonds on high-index crystallographic facets facilitates the improvement of catalytic activity. This phenomenon could be referred as morphology-dependent nanocatalysis. The special sea-urchin-like nanostructures of Cu-B could allow multiple reflections, so that catalytically active Cu sites interact preferably with the organic aryl halides by exposing their more reactive (111) crystalline facet. Thus, it is clear that the morphology and surface area play an important role in the enhancement of catalytic activity of the Cu-B nanocatalyst (Table 1, entry 2)³⁰⁻⁴⁰. In addition, higher catalytic activity of Cu-B nanocatalyst as compared with bare CuNPs and Cu-carbon black catalyst may be due to the synergetic effects of nanocarbonization and electron donation of nanoporous polymer DVAC-1. The organic functional groups could donate electrons to the surface of CuNPs, making the surface more active for Ullmann amination reaction. After the reuse of the Cu-B nanocatalyst for five catalytic cycles, it was proven that the nanocatalyst was mechanically stable and no Cu leaching took place. The Cu-B nanocatalyst becomes more economic as compared with commercially available black copper powder, which requires 5 mol% Cu loading⁴¹.

In conclusion, we have successfully developed the CuNPs embedded nanoporous polymer (Cu-B) as a heterogeneous catalyst, which exhibits excellent catalytic activity for the Ullmann coupling of aryl halides with primary and secondary amines to produce N-aryl amines in aqueous solution. All the catalytic reactions have been conducted in a low loading of Cu (1.35 mol%). The high BET surface area and unique sea-urchin-like nanostructure of the Cu-B nanocatalyst make it more catalytically efficient as compared with its analogue CuA nanocatalyst. Cu-B nanocatalyst also exhibits better catalytic performance as compared with Cu-carbon black catalyst and bare CuNPs. The Cu-B nanocatalyst could be recycled and reused for five consecutive reaction cycles without obvious Cu leaching during the reactions. Thus, the developed heterogeneous Cu catalyst may find its way towards more practical catalytic applications.

Methods

Characterization techniques. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D-8 Advance SWAX diffractometer operated at 40 kV voltage and 40 mA current. The instrument was calibrated with a standard silicon sample using Ni-filtered Cu Ka (λ = 0.15406 nm) radiation. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb IC at 77 K. Prior to gas adsorption, the sample was degassed at 373 K for 4 h. A JEOL JEM 6700F field emission scanning electron microscope (FE-SEM) was used for determining the morphology of the samples. Transmittance electron microscope (TEM) images were recorded on a JEOL JEM 2010 transmission electron microscope. Cu loading in the sample was estimated by using the Perkin Elmer Optima 2100 DV Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Raman spectra on cleaned silicon substrate were measured using a Raman microscope (LabRAM HR, Horiba Yvon). The excitation wavelength of the irradiating light was 632.8 nm (He-Ne Laser, Melles Griot, laser excitation 0.1 mW) and signals were collected by using ×50 objective lens. X-ray photoelectron spectroscopy (XPS) analysis was carried out by using a PHI Quantera SAM spectrometer equipped with Mg X-ray source.³¹ NMR (400 MHz) spectra were recorded on a Bruker Advance 400 spectrometers in CDCl₃ by using CDCl₃ (for 1H, δ = 7.26) as the internal standard unless otherwise stated.³² ¹³C NMR spectra were
performed on a Bruker Avance 400 spectrometer in CDCl₃, using CDCl₃ (for ¹³C, δ = 77.0) as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet. Temperature programmed desorption (TPD) of ammonia from the sample was carried out using a thermal conductivity detector (TCD) in a Micromeritics Chemisorb 2720 instrument. For the experiment, the sample was first degassed at a flow rate of 30°C at 100°C for 2 h. Then, the sample was saturated with 10% NH₃ in He at room temperature for 30 min. The excess NH₃ was removed by flow of He (flow rate of 30°C) for 45 min. TPD of ammonia was studied by heating from room temperature to 700°C at a temperature ramp of 10°C/min.

**Synthesis of Cu-A nanocatalyst.** The Cu-A catalyst was synthesized by chelate-assisted assembly strategy using Cu(acac)₂ as a source of copper. Soluble phenol formaldehyde resin precursor was developed according to previously reported procedure. Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer Pluronic F127 (Mₚ = 12600, PE₉₀PO₇₀PE₉₀) (500 mg) was dissolved in ethanol (15 mL) with the addition of aqueous HCl (12 M, 0.825 g). After getting a clear solution at room temperature, phenolic resin (0.645 g) in ethanol (5 mL) was added dropwise, which was stirred at room temperature for 15 min. Then, Cu(acac)₂ (108 mg, 0.412 mmol) in ethanol (10 mL) was added dropwise into the above dispersion and resulted reaction mixture was stirred at room temperature for another 6 h. The mixture was poured into a petridish and evaporated under nitrogen atmosphere for about 6 h. The mixture was poured into a petridish and evaporated under nitrogen atmosphere for about 6 h. The mixture was cooled down to room temperature under nitrogen atmosphere for 10 h. Then, the resultant mixture was hydrothermally treated in an autoclave at 120°C under static condition for 24 h. The final white color solid material DVAC-1 was isolated and dried in air.

**Synthesis of Cu-B nanocatalyst.** The Cu-B nanocatalyst was developed from nanoporous polymer DVAC-1. DVAC-1 nanoporous polymer was prepared via polymerisation of divinylbenzene containing acetone (15 mL). To the mixture, AIBN (0.152 mmol, 25 mg) was added and the resulted mixture was allowed to stir at room temperature under nitrogen atmosphere for 2 h. Then, CuCl₂·2H₂O (98 mg, 0.574 mmol) was added dropwise into the above dispersion and the resulted mixture was allowed to stir at room temperature for another 6 h. Light yellow color solution was obtained. Then, CuCl₂·2H₂O (98 mg, 0.574 mmol) was added dropwise into the above dispersion and the resulted mixture was allowed to stir at room temperature for another 6 h. Light yellow color solution was obtained. Then, CuCl₂·2H₂O (98 mg, 0.574 mmol) was added dropwise into the above dispersion and the resulted mixture was allowed to stir at room temperature for another 6 h. Light yellow color solution was obtained. Then, CuCl₂·2H₂O (98 mg, 0.574 mmol) was added dropwise into the above dispersion and the resulted mixture was allowed to stir at room temperature for another 6 h. Light yellow color solution was obtained. Then, CuCl₂·2H₂O (98 mg, 0.574 mmol) was added dropwise into the above dispersion and the resulted mixture was allowed to stir at room temperature for another 6 h.

**Synthesis of nanoporous polymer DVAC-1.** DVAC-1 nanoporous polymer was synthesized by 1,3-divinylbenzene and 2-propanol. In a typical synthesis procedure, divinylbenzene (5.99 mmol, 781 mg) and 2-propanol (7.47 mL) were mixed together in a round-bottomed flask containing acetone (15 mL). To the mixture, AIBN (0.152 mmol, 25 mg) was added and the resulted mixture was allowed to stir at room temperature under nitrogen atmosphere for 10 h. Then, the resultant mixture was hydrothermally treated in an autoclave at 120°C under static condition for 24 h. The final white color solid material DVAC-1 was isolated and dried in air.

General procedure for Ullmann N-arylation of aryl iodides 1 with methyl amine (2a) in water catalyzed by the Cu-B nanocatalyst. Aryl iodide 1 (1.0 mmol), Cu-B (20 mg, 1.35 mol% for Cu) and Cu₂O (2.0 mmol, 650 mg) dissolved in aqueous solution of MeNH₂·H₂O (28.9 mmol, 2.5 mL, 40 wt%) were placed in a 25 mL sealed tube. The tube was capped tightly and subjected to heat at 110°C in an oil bath for the time referred. When the reaction was completed (monitored by TLC), the sealed tube was taken out from the oil bath and cooled down to room temperature. The reaction mixture was filtered with EtOAc (5 mL) and then centrifuged. The nanocatalyst was settled down and the biphasic mixture was taken into a separating funnel. The organic layer was collected in a conical flask and the aqueous layer was washed twice with EtOAc (2 × 30 mL). Combined organic layer was dried over anhydrous MgSO₄ and then evaporated to give the crude mixture, which was purified by column chromatography using a mixture of hexane and EtOAc.

**Hot filtration test.** Hot filtration test was conducted to confirm that the nanocatalysis was indeed heterogeneous. In this test, a mixture of Cu-B (20 mg), 4-iodoanisole (1 mmol) and aqueous methylamine (2.5 mL) was subjected to heat at 110°C for 1 h. The Cu-B nanocatalyst was then filtered off from the hot reaction mixture, and the N-arylation reaction in the filtrate was still monitored. No increase in conversion was observed in the filtrate.

**Leaching test.** ICP-MS technique was applied in order to determine the content of Cu in fresh nanocatalyst before and after the reaction. AAS analysis was employed to make sure that no leaching of Cu occurs in the reaction mixture during the course of Ullmann amination reaction. After the catalytic reaction was over, the Cu-B nanocatalyst was separated from the reaction mixture and the Cu content decreased a little bit to 0.690 mmol g⁻¹ after five catalytic cycles. This decrease is within the experimental error of chemical analysis. The experimental data clearly demonstrate that the Cu-B nanocatalyst is truly heterogeneous in nature, and there was no leaching of Cu from the Cu-B nanocatalyst during the course of reactions.
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Author contributions

Y.L.Z. and J.M. have designed the research. A.B. and S.C. have designed methodology the catalytic reactions, isolated the Cu-nanocatalysts. A.B. and J.M. have carried out all the catalytic reactions, isolated the products and characterized the all products. All the authors discussed the results and commented on the manuscript.

Additional information

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