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FULL PAPER

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Copper nanoparticles incorporated on a mesoporous carbon nitride, an excellent catalyst in the Huisgen 1,3-dipolar cycloaddition and *N*-arylation of *N*-heterocycles

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Cu nanoparticles with average particles size around 10 nm were incorporated on the surface of a mesoporous carbon nitride support. The XRD and N_2 adsorption isotherms show that it maintains a hexagonal mesoporous structure with a high surface area (600.03 $m^2\ g^{-1}$). The embedded Cu nanoparticles exhibit extremely high catalytic performance in two different kinds of organic reactions. The Huisgen 1,3-dipolar cycloaddition and *N*-arylation of *N*-heterocycles were all accomplished.

KEYWORDS
arylation, cycloaddition, heterogeneous catalysis, mesoporous materials, nanoparticles

1 | INTRODUCTION

Recently, metal NPs have been widely explored to understand their physicochemical properties. Their favorable properties are impressed by quantum effects, high surface energy and large surface area to volume.[1] Among the metal nanoparticles, Cu NPs have received considerable public interest, which may be due to their excellent optical, electrical and thermal properties. Cu NPs were assumed cost-effective as compared to noble metals like Ag, Au, Pd and Pt. Recently, Cu NPs have attracted considerable attention in different catalytic reactions such as the azide – alkyne cycloaddition *via* click chemistry, coupling reactions, reduction reactions, oxidation reactions, 'one-pot' multicomponent reactions, miscellaneous reactions, etc.[2]

Recently, mesoporous carbon nitride (MCN) materials have been investigated as heterogeneous catalysts for various chemical transformations.[3] For instance, they have been examined for dye photocatalytic degradation,[4a] hydrogenation of aromatic carboxylic acids,[4b] photocatalytic hydrogen evolution,[4c] Friedel–Crafts reaction,[4d] oxygen reduction reaction[4e] and photocatalytic CO_2 reduction.[4f] The success of MCN materials is mainly attributed to their unique combination of multiple physicochemical properties such as large specific surface area, (~200 $m^2\ g^{-1}$), large pore volumes (≥0.5 $cm^3\ g^{-1}$), surface active sites, high stability, tunable porosity and a high nitrogen content.[5,6] The abundant nitrogen functionalities on the surface sites can modify the electronic structure of the carbon matrix and strength the interaction between carbon and guest molecules. Additionally, these functionalities be usually regarded as favorable anchor sites for enhancing particle nucleation and reducing the particle size which allow its direct use as heterogeneous catalysts.[3,7]

As shown in Scheme 1, MCN has been successfully prepared by using the SBA-15 material as a hard template through a simple polymerization reaction between ethane-1,2-diamine (EDA) and perchloromethane (PCM). Subsequently, the resulting composite is heat-treated in a nitrogen

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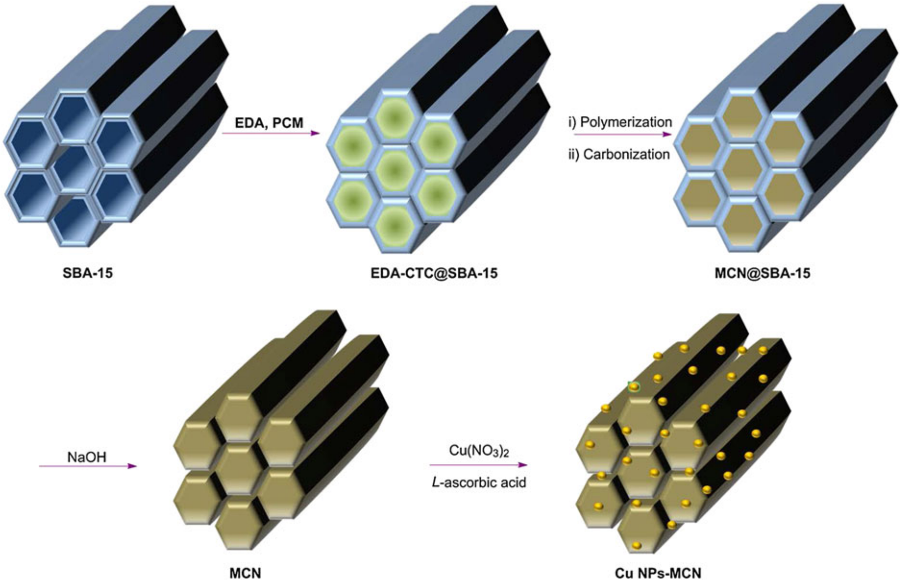


SCHEME 1 Schematic illustration of Cu NPs-MCN nanocomposite preparation

flow to carbonize the polymer. The MCN is recovered after digestion of the silica mold in sodium hydroxide. Finally, the incorporation of small and well dispersed Cu NPs onto the MCN framework is conducted by reduction of copper nitrate with *L*-ascorbic acid as a reducing agent to yield the CuNPs-MCN nanocomposite.

2 | EXPERIMENTAL

2.1 | Synthesis of MCN

The mesoporous SBA-15 silica was prepared by the method as described elsewhere.[8,9] The calcined SBA-15 (0.5 g) was added to a mixture of EDA (1.35 g) and PCM (3 g). The resultant mixture was stirred at 90 °C for 6 h. Then, the obtained dark solid mixture was put in an oven for 12 h. The resulting composite (a template-carbon nitride polymer) was heat-treated in a nitrogen flow at 600 °C with a heating rate of 3.0 °C min^{-1} and kept at 600 °C for 5 h to carbonize the polymer.[10] The MCN was recovered after digestion of the SBA-15 mold in 1 N NaOH solution (EtOH:H_2O 50:50 (v:v)) at 80 °C, by centrifugation, washed several times with EtOH and H_2O, and dried at 100 °C.

2.2 | Preparation of cu NPs-MCN nanocomposite

The MCN (100 mg) was dispersed in 20 ml of H_2O. $Cu(NO_3)_2.3H_2O$ (0.5 mmol) was added to the solution, the mixture was treated under ultrasonic condition for 30 min. *L*-ascorbic acid (5 mmol) was gradually added to the solution and stirred for 24 h. The resulted precipitation was collected by centrifugation, washed with H_2O (5 × 10 ml) and EtOH (3 × 10), and dried at 100 °C. The ICP-AES analysis gave the actual Cu contents as 3.6 wt.% for Cu NPs-MCN nanocomposite.

2.3 | Preparation of cu NPs-SBA-15 nanocomposite

The SBA-15 (100 mg) was dispersed in 20 ml of H_2O. $Cu(NO_3)_2.3H_2O$ $_2O$ (0.5 mmol) was added to the solution, the mixture was treated under the ultrasonic condition for 30 min. *L*-ascorbic acid (5 mmol) was gradually added to the solution and stirred for 24 h. The resulted precipitation was collected by centrifugation, washed with H_2O (5 × 10 ml) and EtOH (3 × 10), and dried at 100 °C. The ICP-AES analysis gave the actual Cu contents as 5.3 wt.% for Cu NPs-SBA-15 nanocomposite.

2.4 | Preparation of CMK-3 nanocomposite

The CMK-3 was prepared *via* a hard temple method.[11] First, 1.25 g of sucrose and 2.7 ml of H_2SO_4 were dissolved in 5 mL ol H_2O. Then, 1 g of SBA-15 was impregnated with the above solution and the mixture was transferred to an oven and maintained at 100 °C for 6 h and then at 160 °C for another 6 h. The obtained powder was then impregnated again with a solution obtained by dissolving sucrose (0.8 g) and H_2SO_4 (0.05 ml) in H_2O (5 ml). The mixture was then treated again at 100 and 160 °C. Finally, the carbonization was completed at 900 °C in a nitrogen flow. The SBA-15 mold was digested with 1 N NaOH solution (EtOH:H_2O 50:50 (v:v)) at 80 °C. After centrifugation and washing with EtOH, the carbon product was dried at 120 °C.

2.5 | Preparation of cu NPs-CMK-3 nanocomposite

The CMK-3 (100 mg) was dispersed in 20 ml of H_2O. Cu $(NO_3)_2.3H_2O$ (0.5 mmol) was added to the solution, the mixture was treated under the ultrasonic condition for 30 min. *L*-ascorbic acid (5 mmol) was gradually added to the solution and stirred for 24 h. The resulted precipitation was collected by centrifugation, washed with H_2O (5 × 10 ml) and EtOH (3 × 10) and dried at 100 °C. The ICP-AES analysis gave the actual Cu contents as 3.8 wt.% for Cu NPs-CMK-3 nanocomposite.

2.6 | General procedure for the multicomponent 1,3-dipolar cycloaddition

A mixture of Cu NPs-MCN nanocomposite (0.5 mol % of Cu), an organic halide (1.0 mmol), phenylacetylene (1.0 mmol) and sodium azide (1.2 mmol) in EtOH:H_2O (1:1; 3 mL) were heated at 60 °C for 10 h. The reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the heterogeneous mixture was cooled to r.t. and ethyl acetate was added to the flask and the catalyst was separated by centrifugation. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. The obtained triazole was purified by recrystallization from EtOH.

2.7 | General procedure for *N*-Arylation of *N*-heterocycles

A mixture of Cu NPs-MCN nanocomposite (2.5 mol % of Cu), K_3PO_4 (1.5 mmol), *N*-heterocycle (1.0 mmol), an aryl halide (1.0 mmol), and DMF (3 mL) under air was stirred for 4 h at 120 °C. The reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the heterogeneous mixture was cooled to r.t., diluted with Ethyl acetate (3 × 10 ml), and the catalyst was separated by centrifugation. The organic layer was concentrated under reduced pressure to give the corresponding coupled product. The Obtained *N*-arylated of heterocycle was purified by recrystallization from EtOH.

3 | RESULTS AND DISCUSSION

3.1 | Characterization

The SEM images of MCN and Cu NPs-MCN are shown in Figure 1a-b. The MCN exhibits a tubular structure with uniform particles, which the diameters are about 300 nm, being highly similar to those of the parent SBA-15 template that shows the successful replication process of MCN from

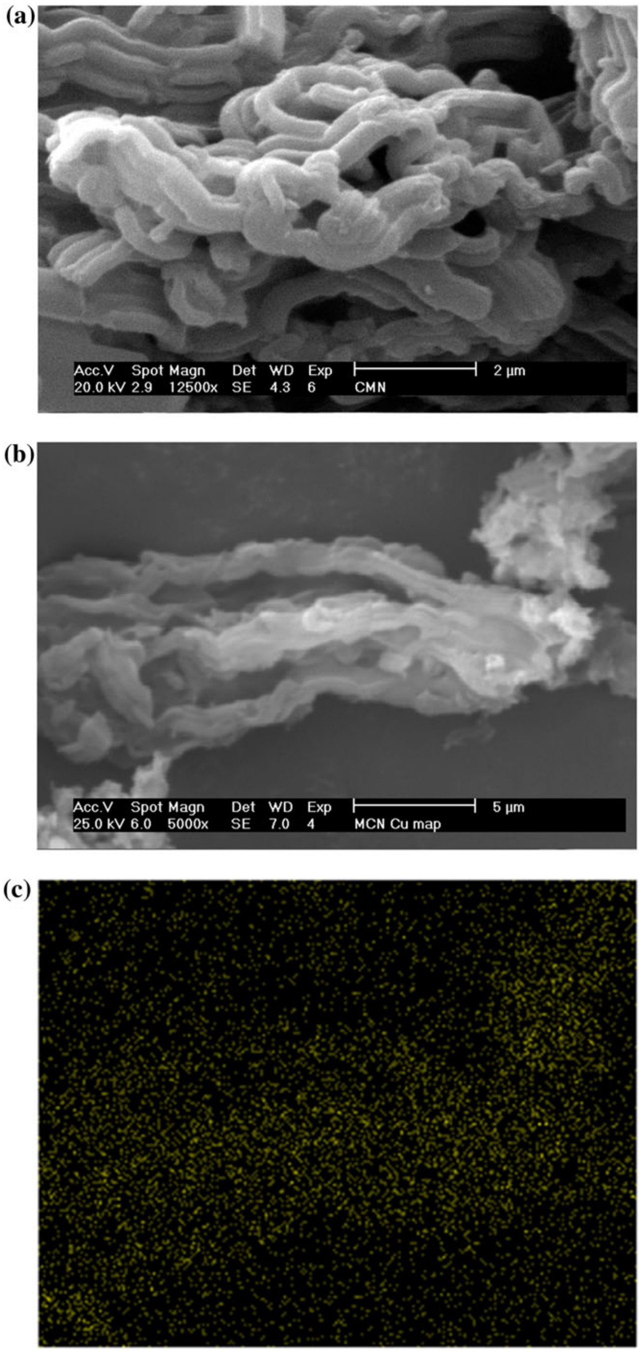


FIGURE 1 SEM images of a) MCN and b) cu NPs-MCN nanocomposite; c) corresponding quantitative EDS element mapping of cu

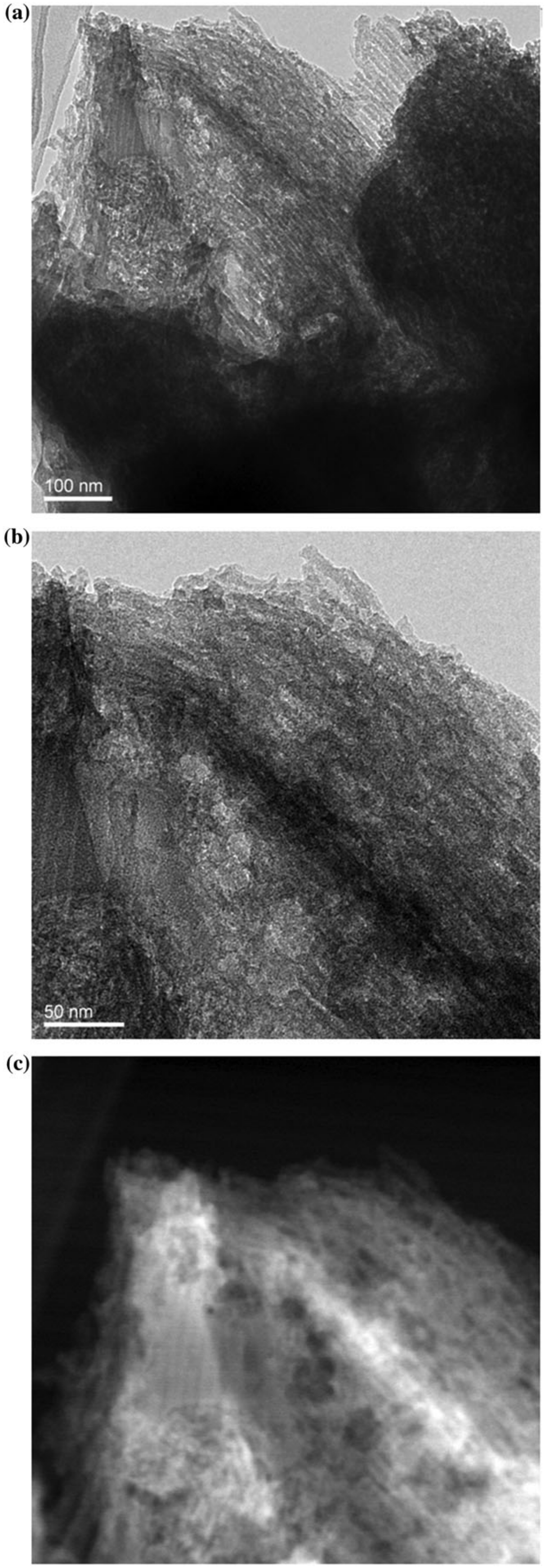


FIGURE 2 a-b) TEM images and c) HAADF image of cu NPs-MCN nanocomposite

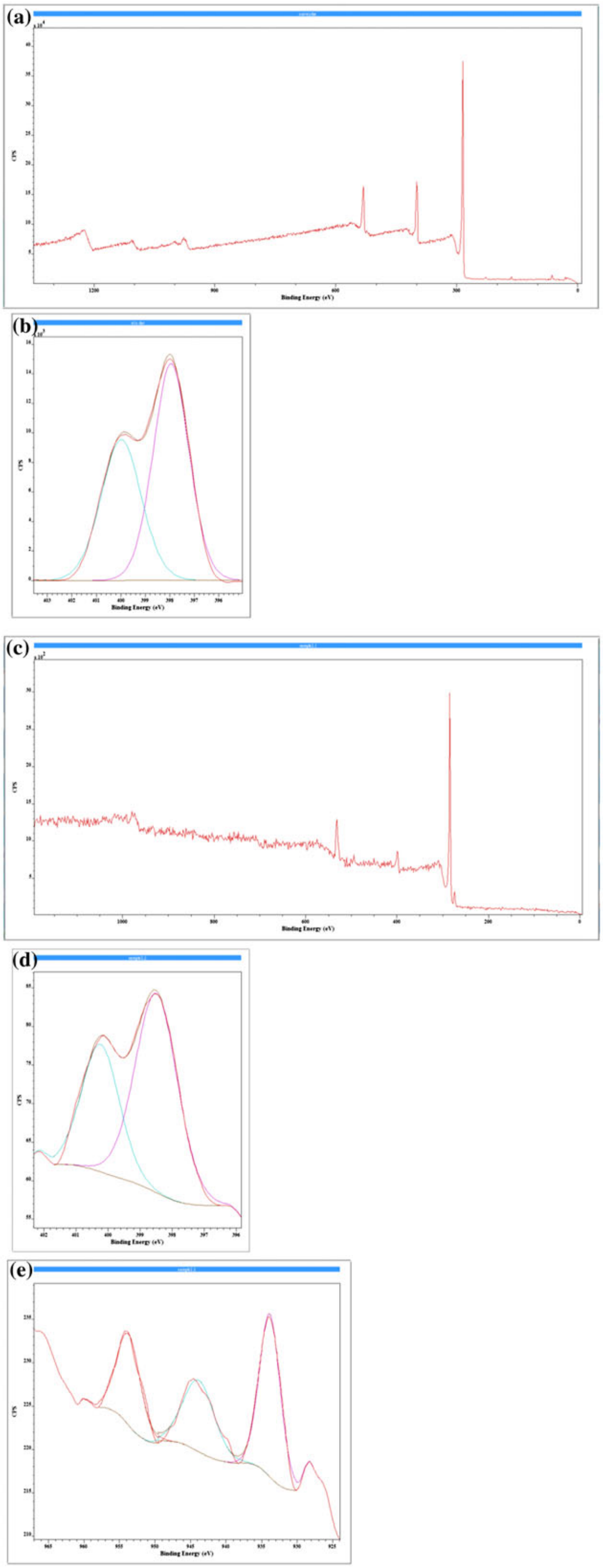


FIGURE 3 a) Full range XPS spectrum of MCN, b) N 1 s core level region XPS spectra of MCN, c) Full range XPS spectrum of cu NPs-MCN nanocomposite, d) N 1 s and e) cu 2p, core level regions XPS spectra of cu NPs-MCN nanocomposite, respectively

SBA-15.[12] The morphology of MCN do not change after the incorporation Cu NPs onto the MCN framework (Figure 1b). Additionally, the density and distribution of copper on the Cu NPs-MCN nanocomposite is evaluated by energy dispersive X-ray spectroscopy (EDS) mapping. The Cu NPs are uniformly distributed and anchored along the heterogeneous mesoporous surface of the MCN (Figure 1c).

The TEM images of Cu NPs encapsulated MCN is shown in Figure 2a-b. The HAADF image of Cu NPs-MCN composite shows that the copper nanoparticles are on the surface of MCN (Figure 2c).

The electronic properties of MCN and Cu NPs-MCN composites are probed by XPS analysis (Figure 3). The binding energies are calibrated based on the C1s peak at 284.5 eV as a reference. The high-resolution XPS spectrum of N 1 s core level for MCN composite displays main peaks at 397.9 and 399.9 eV (Figure 3b). The peak at 397.9 eV corresponds to nitrogen atoms bonded with the graphitic carbon atoms,[10] while the peak at 399.9 eV corresponds to *N* atoms trigonally bonded to two sp^2 carbon atoms and one sp^3 carbon atom in an amorphous C-N network or to all sp^2 carbons.[13] After the conjugation of the copper nanoparticles on MCN, these binding energies shift to higher value 398.5 and 400.2 eV. These result show that the copper nanoparticles bonded the nitrogen atoms in MCN.[14] The high-resolution XPS spectrum of Cu 2p is shown in Figure 3e, the two peaks at 933.9 and 953.8 eV, are assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. This indicates that supported copper species are kept in a zero-valent chemical state.[15]

The XRD patterns of the MCN and Cu NPs-MCN composites are shown in Figure 4. The diffraction peaks for the Cu NPs are scarcely detected, resulting from the small size of Cu NPs.[16] The small angle XRD patterns of MCN and Cu NPs-MCN composites show the three characteristic peaks, the highly-ordered two-dimensional hexagonal mesostructure with the space group of *p6mm* at $2\theta = 1.6°$, 2.6° and 3.8° corresponding to (11¯0), (110) and (200) crystallographic planes, respectively.[10] The diffraction peaks at

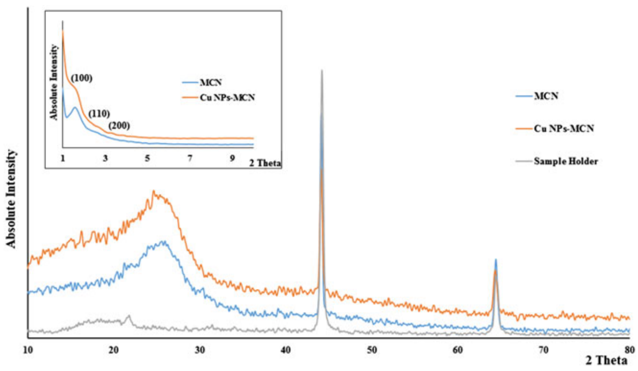


FIGURE 4 The high angle XRD patterns of MCN and cu NPs-MCN (inset: Low angle)

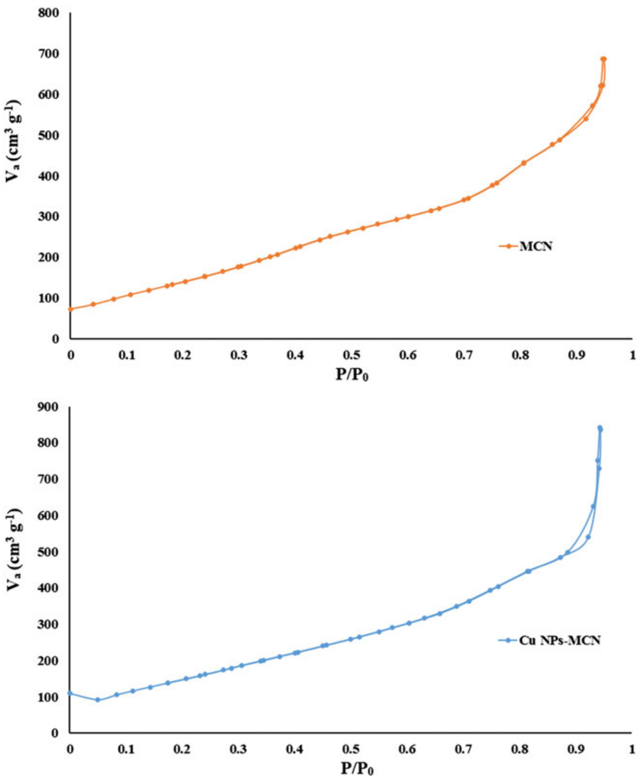
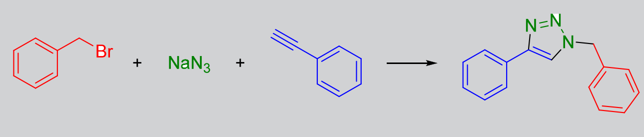


FIGURE 5 Nitrogen adsorption/desorption isotherms of MCN and cu NPs-MCN

TABLE 1 Screening of the reaction conditions[a]



Entry	Solvent	Catalyst (mol% of cu)	Temp. (°C)	Yield[b] (%)
1	CH_2Cl_2	Cu NPs-MCN (0.5)	60	59
2	CH_3CN	Cu NPs-MCN (0.5)	60	72
3	EtOH	Cu NPs-MCN (0.5)	60	90
4	H_2O	Cu NPs-MCN (0.5)	60	84
5	EtOH/ H_2O	Cu NPs-MCN (0.5)	60	98
6	EtOH/ H_2O	Cu NPs-MCN (0.5)	50	75
7	EtOH/ H_2O	Cu NPs-MCN (0.25)	60	56
8	EtOH/ H_2O	Cu NPs-SBA-15 (0.5)	60	73
9	EtOH/ H_2O	Cu NPs-CMK-3 (0.5)	60	88
10	EtOH/ H_2O	MCN[c]	60	28[c]

[a] benzyl bromide, (1.0 mmol), phenylacetylene (1.0 mmol), sodium azide (1.2 mmol), solvent (3 mL), 10 h.

[b] Isolated yield. MCN (0.05 g)

[c] two 1,4- and 1,5- regioisomers (1:1).

2θ = 44 and 64° correspond to the stainless steel sample holder of powder diffractometer.

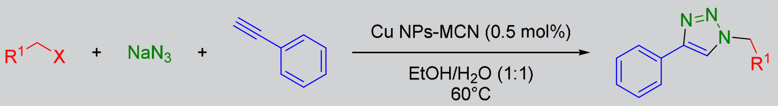
The porous nature of MCN and Cu NPs-MCN composites are evaluated by nitrogen physisorption measurements. The prepared composites showed type IV N_2 adsorption–desorption isotherms which are characteristic of mesoporous materials based on the IUPAC classification.[17] The BET total surface areas of MCN, and Cu NPs-MCN composites are found to be 567.09 and 600.03 $m^2\ g^{-1}$, respectively (Figure 5). From these results, it can be concluded that the Cu NPs act as spacers between MCN roads thereby preventing their aggregation.[18]

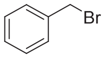
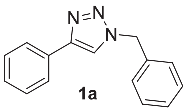
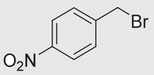
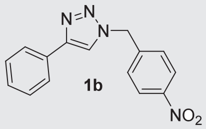
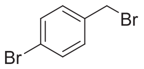
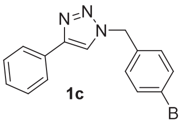
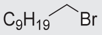
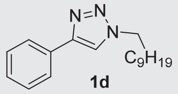
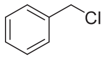
3.2 | The catalytic activity of cu NPs-MCN nanocomposite toward the multicomponent 1,3-dipolar cycloaddition

After the careful investigation of the prepared Cu NPs-MCN nanocomposite, it was employed in the multicomponent 1,3-dipolar cycloaddition of phenylacetylene, sodium azide and different organic halides. This reaction has found broad applications in various disciplines including materials science, chemical biology, and medicinal chemistry. Several members of the 1,2,3-triazole family have indeed shown interesting biological and biochemical activities, such as anti-allergic, anti-bacterial, anticancer, antiviral and anti-HIV. Additionally, 1,2,3-triazoles are found extensive use in herbicides, fungicides, corrosion inhibitions, photostabilizers, and lubricants and dyes.[19,20] Recently, the copper catalysis discovered for this transformation, which accelerates the reaction up to 10 million times, placed it in a category of its own and has enabled many novel applications.[20]

As the initiating point of our exploration, the reaction between phenylacetylene, sodium azide and benzyl bromide as a model reaction was chosen to show the feasibility of the strategy and optimize the reaction conditions (Table 1). By using Cu NPs-MCN (0.5 mol% of Cu) as the catalyst, the reaction was tested for employing various solvents such as CH_2Cl_2, CH_3CN, EtOH, H_2O and the mixture of EtOH/H_2O (Table 1, Entries 1–5). The best results were obtained by using the mixture of EtOH/H_2O as solvent in the model reaction (Table 1, entry 5). A lower reaction temperature decreased the yield of the reaction (Table 1, entry 6). As can be seen from the Table 1, the optimized amount of catalyst in the reaction was obtained to be 0.5 mol% of Cu (Table 1, entries 5 and 7). In order to study the effect of the

TABLE 2 Multicomponent 1,3-dipolar cycloaddition catalyzed by cu NPs-MCN nanocomposite[a]



Entry	Organic halide	Product	Yield[b] (%)
1		 **1a**	98
2		 **1b**	98
3		 **1c**	94
4[c]		 **1d**	78
5[c]		**1a**	86

[a]Organic halide, (1.0 mmol), phenylacetylene (1.0 mmol), sodium azide (1.2 mmol), 10 h

[b]Isolated yield.

[c]Reaction time = 16 h.

support and the role of nitrogen doping in the carbon framework, the array of copper catalysts were prepared (Table 1, entries 8–9). We used Cu NPs-SBA-15 and Cu NPs-CMK-3 in the model reaction. The observed yields of triazole in both cases were surprisingly inferior. The addition of the nitrogen in the support leads to an increase in the triazole yield. Probably, the nitrogen atoms in the carbon framework can act as a ligand for Cu NPs. For comparison, the model reaction was conducted in the presence of MCN as a catalyst for 10 h at 60 °C in EtOH/H_2O, which cycloaddition products were isolated without regioselectivity and in 28% yield (Table 1, entry 10).

With the optimized conditions in hand, the scope of the reaction was explored by reacting various halides in the mixture of EtOH/H_2O at 60 °C, using Cu NPs-MCN nanocomposite (0.5 mol% of Cu) (Table 2). Different substituents such as *p*-NO_2 and *p*-Br of benzyl bromide were equally effective toward the nucleophilic substitution of N_3^-, followed cycloaddition (Table2, entries 2 and 3). A non-activated alkyl halide (*n*-decyl bromide) and benzyl chloride also participated in the reaction and produced the corresponding triazoles in moderate yields, although the prolongation of reaction time was needed (Table 2, entries 4 and 5).

Reusability is an important characteristic of the heterogeneous catalysis which should be examined in catalytic reactions. Therefore, we performed a reusability test for the Cu NPs-MCN catalyst in the multicomponent 1,3-dipolar cycloaddition of benzyl bromide, phenylacetylene and sodium azide under the optimized conditions. After the completion of the reaction, the catalyst was easily separated by centrifugation from the reaction solution and washed with ethyl acetate (3 × 10 mL) and EtOH (2 × 10 mL), and used for the next run. This process was repeated for the eight cycles. After eight cycles, Cu NPs-MCN nanocomposite was still stable and active, and provide 96% yield (Table 3). Furthermore, no significant change was observed in the morphology of Cu NPs-MCN after the eight runs, which is concluded by the TEM image given in Figure 6.

3.3 | The catalytic activity of cu NPs-MCN nanocomposite toward *N*-arylation of *N*-heterocycles

N-arylazoles are ubiquitous in bioactive compounds, natural products, pesticides, pharmaceuticals, dyes, polymers, ionic liquids and *N*-heterocyclic carbenes.[21] Thus, the development of a novel, efficient, simple and practical method for *N*-arylation of heterocycles is an important end in the modern organic synthesis.[22]

Inspired by the high activity and stability of Cu NPs-MCN nanocomposite, the Ullmann C-N cross-coupling was further used as another model reaction to test the further performance of Cu NPs-MCN nanocatalyst. In our initial experiment,

TABLE 3 Reusability of the cu NPs-MCN nanocomposite in multicomponent 1,3-dipolar cycloaddition

Reaction cycle	1st	2nd	3rd	4th	5th	6th	7th	8th
Yield[b] (%)	98	98	98	97	97	97	97	96

[a] benzyl bromide, (6.0 mmol), phenylacetylene (6.0 mmol), sodium azide (7.2 mmol), Cu NPs-MCN nanocomposite (0.5 mol% of Cu), EtOH/H_2O (18 mL), 10 h and Temp. = 60 °C

[b] Isolated yield.

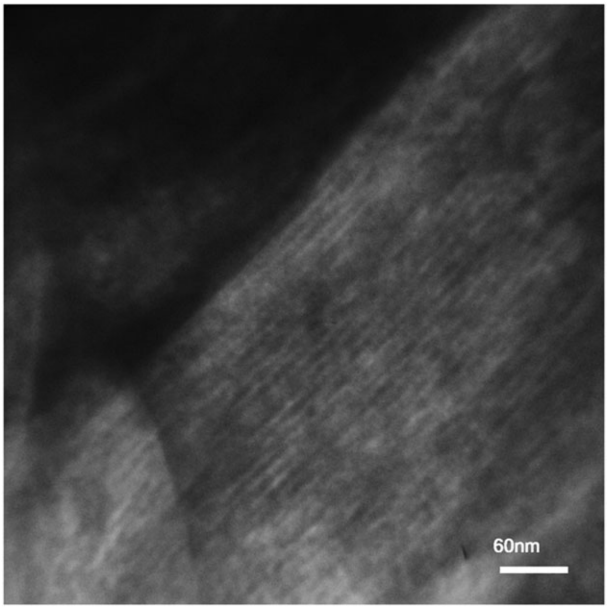
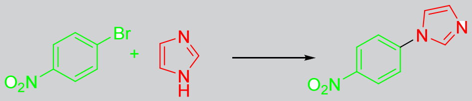


FIGURE 6 TEM image of cu NPs-MCN reused after eight cycles in multicomponent 1,3-dipolar cycloaddition between of benzyl bromide, phenylacetylene and sodium azide

TABLE 4 Screening of the reaction conditions[a]



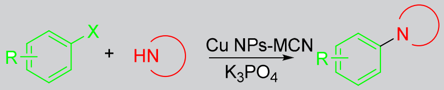
Entry	Base	Solvent	Temp.	Yield[b] (%)
1	K_3PO_4	EtOH	reflux	47
2	K_3PO_4	H_2O	reflux	trace
3	K_3PO_4	NMP	120	65
4	K_3PO_4	CH_2Cl_2	reflux	trace
5	K_3PO_4	DMSO	120	72
6	K_3PO_4	DMF	120	98
7	K_3PO_4	DMF	110	72
8	Cs_2CO_3	DMF	120	98
9	K_2CO_3	DMF	120	64
10[c]	K_3PO_4	DMF	120	Trace

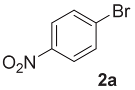
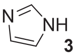
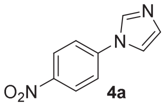
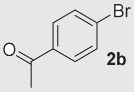
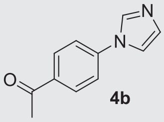
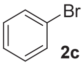
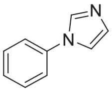
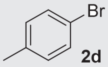
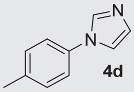
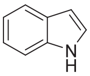
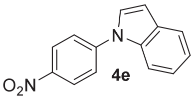
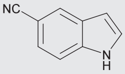
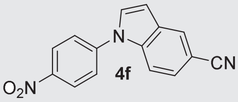
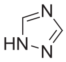
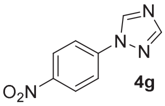
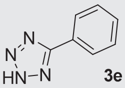
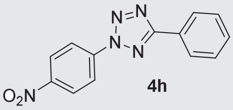
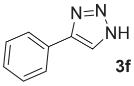
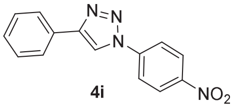
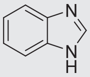
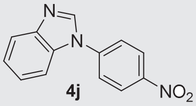
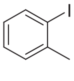
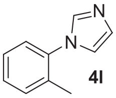
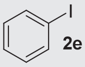
[a] Imidazole (1 mmol), 1-bromo-4-nitrobenzene (1 mmol), Cu NPs-MCN nanocomposite (2.5 mol% of Cu), base (1.5 mmol), solvent (3 mL), 4 h.

[b] Isolated yield.

[c] MCN (0.05 g)

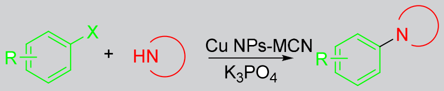
TABLE 5 Cu NPs-MCN nanocomposite catalyzed *N*-arylation of *N*-heterocycles

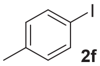
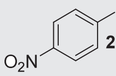
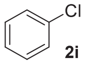


Entry	Aryl halide	*N*-heterocycle	Product	Yield (%)
1	 **2a**	 **3a**	 **4a**	98
2	 **2b**	3a	 **4b**	98
3	 **2c**	3a	 **4c**	91
4	 **2d**	3a	 **4d**	79
5	2a	 **3b**	 **4e**	75
6	2a	 **3c**	 **4f**	68
7	2a	 **3d**	 **4g**	94
8	2a	 **3e**	 **4h**	98
9	2a	 **3f**	 **4i**	73
10	2a	 3g	 **4j**	72
11	 **2d**	3a	 **4l**	86
12	 **2e**	3a	4c	98

(*Continues*)

TABLE 5 (Continued)



Entry	Aryl halide	*N*-heterocycle	Product	Yield (%)
13	 2f	3a	4d	94
14	 2g	3a	4a	98
15	 2i	3a	4c	65

[a] Aryl halide (1 mmol), *N*-heterocycle (1 mmol), Cu NPs-MCN nanocomposite (2.5 mol% of Cu) K_3PO_4 (1.5 mmol), DMF (3 ml), 4 h and Temp. = 120 °C.

[b] Isolated yield.

imidazole and 1-bromo-4-nitrobenzene were chosen as the model substrates to optimize reaction conditions including bases, solvents and reaction temperatures, and the results are presented in Table 4. The results indicate that the base, solvent and temperature significantly influence on the product yield. The reaction was not done when this reaction was carried out with MCN as the catalyst (Table 4, Entry 10).

With these results in hand, the *N*-arylation of various substituted aryl halides bearing electron-donating and electron-withdrawing groups with imidazole were chosen to explore the scope and the generality of the reaction (Table 5 , entries 1–4). These reactions were done effectively and gave good yields. Other *N*-heterocycles such as indole, 1,2,4-triazole, 5-phenyl-2*H*-tetrazole, benzotriazole, and benzimidazole reacted with 1-bromo-4-nitrobenzene under standard experimental conditions and provided products with 68–98% yields (Table 5, entries 5–10). The 1-iodo-2-methylbenzene as a hindered substrate converted to the corresponding product with a moderate yield (Table 5, entry 11). Furthermore, chlorobenzene had lower reactivity in comparison with bromobenzene and iodobenzene (Table 5, entry 15).

We performed a reusability test for the Cu NPs-MCN catalyst in the Ullmann cross-coupling of bromobenzene and imidazole under the optimized conditions. The Cu NPs-MCN catalyst was stable during the catalytic reaction and easily separated by centrifugation the reaction solution at the end of the reaction. A new batch of coupling reactions was started by using the separated Cu NPs-MCN catalyst and this process was continued up to the eight cycles. As seen in the Table 6, Cu NPs-MCN was still active and provide 77% yield in 4 h after eight runs.

The Table 7 provides a comparison of the present method with other reported copper heterogeneous catalytic systems in the Ullmann cross coupling reaction between bromobenzene and imidazole. Clearly, the present catalyst exhibited a simple, high effective, less time-consuming method for the C-N coupling reaction.

TABLE 6 Reusability of the cu NPs-MCN nanocomposite in Ullmann cross coupling of bromobenzene and imidazole[a]

Reaction cycle	1st	2nd	3rd	4th	5th	6th	7th	8th
Yield[b] (%)	91	91	90	87	85	82	80	77

[a] Imidazole (6 mmol), bromobenzene (6 mmol), Cu NPs-MCN nanocomposite (2.5 mol% of Cu) K_3PO_4 (9 mmol), DMF (18 ml), 4 h and Temp. = 120 °C

TABLE 7 Comparison of efficiency of various copper catalysts in Ullmann cross-coupling reaction of bromobenzene and imidazole

Catalyst	Condition	Yield (%)	Time (h)	Ref.
Cu NPs-MCN (2.5 mol%)	K_3PO_4, DMF, 120 °C	91	4	This work
CuFAP (12.5 mol%)	K_2CO_3, DMSO, 110 °C	90	10	[23]
CuNPs/MagSilica (10 mol%)	K_2CO_3, DMF, 152 °C	85	24	[24]
Cu(II)-NaY (10 mol %)	K_2CO_3, DMF, 120 °C	99	30	[25]
CuPc (10 mol%)	KOH, DMSO, 90 °C	31	24	[26]

4 | CONCLUSIONS

In conclusion, we have successfully demonstrated that Cu NPs-MCN nanocomposite is a novel, simple, effective and reusable heterogeneous catalyst for the Huisgen 1,3-dipolar cycloaddition and *N*-arylation of *N*-heterocycles taking a short reaction time leading to good yields under aerobic conditions without using any external ligands or additives as promoters. In order to study the effect of the support and the role of *N*-doping in the carbon framework, the array of copper catalysts were prepared. We used Cu NPs-SBA-15 and Cu NPs-CMK-3 in the model reaction. The results show that the addition of the nitrogen in the support leads to an increase in the triazole yield. Probably, the nitrogen atoms in the support can act as a ligand for Cu NPs. The reusability is high, and the catalyst can be recycled for several times without the considerable loss of activity.

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