

RESEARCH ARTICLE

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# Applied Organometallic Chemistry

# CuSO<sub>4</sub> nanoparticles loaded on carboxymethylcelulose/ polyaniline composites: A highly efficient catalyst with enhanced catalytic activity in the synthesis of propargylamines, benzofurans, and 1,2,3-triazoles

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#### Abstract

A novel and efficient heterogeneous CuSO<sub>4</sub> nanoparticles (CuSO<sub>4</sub> NPs) immobilized on carboxymethylcellulose/polyaniline (CuSO4NPs@CMC/PANI) composites were prepared via one-pot and one-step interfacial oxidative polymerization of aniline with sodium carboxymethylcellulose (CMC) as soft template and CuSO<sub>4</sub> as catalyst. The in situ formed CuSO<sub>4</sub> NPs were dispersed uniformly and firmly on the resultant composites and stabilized by complexation with hydroxyl groups (-OH), carboxylate groups (-COO<sup>-</sup>), nitrogen atoms, and delocalized  $\pi$ - $\pi$  conjugate benzenoid and quinoid moieties of CMC/PANI composites. The morphology, composition, and structure of the as-fabricated composites were systematically characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and derivative thermogravimetry (DTG) techniques. The CuSO<sub>4</sub>NPs@CMC/PANI composites were successfully applied catalysts in aldehyde-alkyne-amine  $(A^3)$  coupling reactions,  $A^3$ as cycloisomerization tandem reactions, and Cu-catalyzed azide-alkyne cycloaddition (CuAAC) reactions. All reactions proceeded smoothly and afforded the desired products in excellent yields. Moreover, no significant decrease in catalytic ability was observed in A<sup>3</sup> model reaction after 15 recycles, indicating CuSO<sub>4</sub>NPs@CMC/PANI composites exhibited easy separability and high reusability. Tolerance of wide scope of substrate, excellent catalytic activity, easy operation, recycling of catalyst, and environmental benign are the salient features of these catalytic process.

#### KEYWORDS

 $A^3$  reactions, carboxymethylcellulose, CuAAC reactions, CuSO<sub>4</sub> nanoparticles, polyaniline

# **1** | INTRODUCTION

With the development of modern nanoscience, nanoscale transition metal catalysts have attracted great attention in scientific research and extensively used in organic catalysis.<sup>[1-3]</sup> However, bare metal nanoparticles are easily aggregated during the catalysis process, thereby lowertheir catalytic performance and ing practical application.<sup>[4,5]</sup> Thus, heterogenization of metal nanoparticles on a desired supportive material has been regarded as an efficient approach to increase the stability of metal nanoparticles, which is conducive to the advantageous of maintenance of catalytic activity, simple operation, convenient recovery and recycling of catalyst, easy separation of product, and cost reduction.<sup>[6-10]</sup> However. the performance of heterogenized catalysts greatly depends on the physical and chemical properties of the supportive materials. Among the reported supportive materials, the composite materials, composed of two or more inorganic and/or organic constituents, have received great concerns owing to their intriguing properties superior to the individual component in regard of high loading capacity, excellent catalytic activity, good stability, and recycling performance.<sup>[11]</sup> Therefore, it is worthwhile to further develop novel and efficient composite catalysts, and some pioneering works on the design and fabrication of various composite catalysts have been reported in the past decade.<sup>[12,13]</sup> Among the documented works, the template-guided method is one of the commonly and efficient method to synthesis of composite materials.<sup>[14]</sup> However, most of the synthetic templates containing specific structure and functional groups are usually requirement of tedious multistep synthesis and thus made them inconveniently available and costly. Alternatively, inexpensive and naturally available multifunctional templates such as cellulose, starch, chitosan, alginate, and carboxymethylcellulose are now being captured considerable attention.

Sodium carboxymethylcellulose (CMC–Na), a watersoluble anionic polymer derived from naturally abundant cellulose bearing a great number of free hydroxyl (–OH) and negatively charged carboxymethyl (–CH<sub>2</sub>COO<sup>-</sup>Na<sup>+</sup>) groups along its repeat glucose-unit chain, which make it capable of coordination with various multivalent metal cations.<sup>[15]</sup> Polyaniline (PANI), composed of benzoid and quinoid moieties, is a useful supportive material due to the unique coordination with metal ions via lone-pair electrons present in the nitrogen atoms and delocalized  $\pi$ - $\pi$  conjugate system of PANI.<sup>[16]</sup> Based on these unique properties, a number of CMC-based<sup>[17–20]</sup> and PANIbased<sup>[16,21,22]</sup> composite catalysts recently have been reported. Although these reported catalysts have excellent catalytic activity, the shortcomings such as poor mechanical strength, multistep synthetic approaches, and tedious operation in some cases are the main disadvantage that needs to be optimized. To mitigate these disadvantages, it is reasonable to develop one composite material merging the preponderances of both CMC—Na and PANI may be of potential interest for immobilization of metal nanoparticle to enhance the catalytic efficiency.

Recently, great efforts have been made to the Cucatalyzed one-pot multicomponent reaction of A<sup>3</sup> reactions,<sup>[23,24]</sup> CuAAC reactions,<sup>[25,26]</sup> and many other reactions<sup>[27,28]</sup> because they have become one of the most powerful tools in diverse fields such as drug discovery, polymer chemistry, and material science. Therefore, the development of a novel Cu-composite catalyst with superior catalytic activity for these reactions is of great importance and highly desirable.

In light of the above facts, for the first time, we have attempted to synthesize  $CuSO_4NPs@CMC/PANI$  composites by a one-pot and single-step method via in situ interfacial oxidative polymerization of aniline using CMC as soft template and  $CuSO_4$  as catalyst and further explored it as a catalyst for  $A^3$  reactions,  $A^3$ -cycloisomerization tandem reactions, and CuAAC reactions (Scheme 1).

#### 2 | EXPERIMENTAL

#### 2.1 | Materials and instrumentations

Sodium carboxymethylcellulose (CMC—Na) and all other chemicals were obtained from commercial sources and used as received without further purification.

Gas chromatography (GC) was performed on a Shimadzu GCMS-OP2020. The elemental copper content of the catalyst was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using X Series 2 instrument. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher Scientific K-Alpha instrument. Transmission electron microscopy (TEM) was obtained with a Philips Tecnai instrument. Scanning electron microscopy (SEM) and energydispersive spectroscopy (EDS) were conducted with a Zeiss Sigma 500 instrument. Flourier transform infrared spectra (FTIR) were collected on a Nicolet 6,700 spectrophotometer in KBr pellet within the spectral range of  $4.000-400 \text{ cm}^{-1}$ at 2 cm<sup>-1</sup> resolution and 32 scans. X-ray powder diffraction (XRD) data were collected on an MSALXRD2 diffractometer using Cu Ka radiation in a range of Bragg's angles (5-80°). Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were performed on a Netzsch STA449 under a nitrogen atmosphere from 30°C to 800°C in a



SCHEME 1 CuSO<sub>4</sub>NPs@CMC/PANI-mediation of A<sup>3</sup>, A<sup>3</sup>-cycloisomerization tandem reactions, and CuAAC reactions

50 ml·min<sup>-1</sup> N<sub>2</sub> flow and a ramp rate of  $10^{\circ}$ C·min<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were obtained with a Bruker Avance instrument with CDCl<sub>3</sub> as solvent and TMS as internal standard. HRMS was determined by using Agilent 6545 Q-TOF MS.

### 2.2 | Preparation of CuSO<sub>4</sub>NPs@CMC/ PANI composites

CMC-Na (7.26 g, 30 mmol) was dissolved in 400 ml deionized water at ambient temperature with continuous stirring for overnight. Then aniline monomer (2.79 g, 30 mmol) was dissolved in 250 ml methanol and then mixed with as-prepared CMC-Na solution with stirring until the mixture was homogeneous. The mixture was then sonicated for 30 min to facilitate self-assemble of aniline on CMC-Na molecular chain. After that, preprepared  $CuSO_4 \cdot 5H_2O$  solution (7.50 g, 30 mmol, in 100 ml deionized water) was added dropwise into the mixture at room temperature with constant stirring. The green precipitation appeared and further allowed to oxidative polymerize at room temperature for 8 h. The precipitates were separated from the solution by suction filtration and washed five to six times successively with deionized water and methanol and then dried in vacuum

at  $60^{\circ}$ C for 12 h. The CuSO<sub>4</sub>NPs@CMC/PANI composites was obtained as dark green powders.

# 2.3 | General procedure for CuSO<sub>4</sub>NPs@CMC/PANI-catalyzed A<sup>3</sup> threecomponent coupling reactions

A mixture of aldehyde/ketone (1.0 mmol), amine (1.2 mmol), terminal alkyne (1.5 mmol), and catalytic amount of CuSO<sub>4</sub>NPs@CMC/PANI (30 mg, 6.0 mol% of Cu) was stirred in neat at 120°C in a sealed vessel for the specific time indicated by TLC. After the completion of reaction, ethyl acetate was added to the vessel to extract the product, and the left catalyst was separated by filtration. The catalyst was washed with ethyl acetate adequately and dried at 60°C for the next run. The crude product was obtained after removal of the organic solvent using a rotary evaporator under reduced pressure. The crude products were further purified by silica gel column chromatography to afford pure compounds. All the products except 1h and 1i are known, and their <sup>1</sup>H NMR and <sup>13</sup>C NMR data were found to be identical to those reported in the literature. The new compounds 1h and 1i were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FTIR, and HRMS.

### 2.4 | General procedure for CuSO<sub>4</sub>NPs@CMC/PANI-catalyzed A<sup>3</sup>cycloisomerization tandem processes for synthesis of benzofurans

A mixture of aldehyde (1.0 mmol), amine (1.2 mmol), terminal alkyne (1.5 mmol), DMAP (0.5 mmol), toluene (1.0 ml), and CuSO<sub>4</sub>NPs@CMC/PANI (30 mg, 6.0 mol% of Cu) was stirred at 120°C in a sealed vessel. The progress of the reaction was tracked by TLC. Upon the completion of reaction, ethyl acetate was added to the vessel to extract the product, and the catalyst was recovered by suction filtration. The crude product was obtained after removal of the combined organic solvent and further purified with column chromatography to afford pure compound. All the products are known, and their <sup>1</sup>H NMR and <sup>13</sup>C NMR data were found to be in accordance with those reported in the literature.

#### 2.5 | General procedure for CuSO<sub>4</sub>NPs@CMC/PANI-catalyzed CuAAC reaction

Benzyl halides (1.0 mmol), NaN<sub>3</sub> (1.2 mmol), terminal alkyne (1.0 mmol), and catalytic amount of CuSO<sub>4</sub>NPs@CMC/PANI (20 mg, 4.0 mol% of Cu) were added in 3.0 ml solvent (H<sub>2</sub>O/MeOH = 1:1, v/v), and the mixture was rigorously stirred at 70°C for the specific time indicated by TLC. After the completion of reaction, ethyl acetate was added to the vessel to extract the product and separate the catalyst. The filtrate was washed with saturated brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The desired pure products were obtained by column chromatography after removal of organic solvent using a rotary evaporator. All the products except 3r and 3s are known, and their <sup>1</sup>H NMR and <sup>13</sup>C NMR data were found to be consistent with those reported in the literature. The new compounds were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FTIR, and HRMS.

# 3 | RESULTS AND DISCUSSION

# 3.1 | Synthesis and characterization of catalyst

The CuSO<sub>4</sub>-catalyzed polymerization of aniline onto a CMC molecular chain led to the formation of CuSO<sub>4</sub>NPs@CMC/PANI nanocomposites. Notably, in this process, Cu(I) ions resulted from Cu (II)-initiated the oxidative polymerization of aniline could be re-oxidized by oxygen in the air to form Cu (II) ions in solution.<sup>[29]</sup>

Briefly, aqueous  $CuSO_4$  were added into the mixture of CMC—Na and aniline monomer solution, which was selforganized together by H-bond interactions, to initiate the oxidative polymerization of aniline monomers on the molecular chain of CMC—Na. Simultaneously,  $CuSO_4$ NPs grew in situ on the resultant CMC/PANI composites and stabilized by complexation with hydroxyl groups (—OH), carboxylate groups (—COO<sup>—</sup>), nitrogen atoms (—NH— and —N=) of CMC/PANI composites. The Cu content in fresh CuSO<sub>4</sub>NPs@CMC/PANI composites was determined by ICP-AES to be 2.006 mmol/g. The synthetic route to prepare CuSO<sub>4</sub>NPs@CMC/PANI composite catalyst was outlined in Scheme 2.

Then, various analytical techniques including XPS, TEM, SEM, EDS, FTIR, XRD, TGA, and DGT were performed to identify the components and structures of  $CuSO_4NPs@CMC/PANI$  composites.

The XPS is used to confirm the oxidation state of elements present in the CuSO<sub>4</sub>NPs@CMC/PANI composites. Figure 1 showed the survey scan XPS spectra of the typical elements in the binding energy rang of 0-1,400 eV and high-resolution spectra of  $Cu_{2p}$ ,  $S_{2p}$ ,  $C_{1s}$ ,  $N_{1s}$ , and  $O_{1s}$ of fresh catalyst. It was found that Cu, S, C, N, and O elements were the predominate species in Figure 1a. As shown in Figure 1b, the binding energies of  $Cu_{2n3/2}$  and Cu<sub>2p1/2</sub> are found at 933.71 and 953.24 eV correspondingly, which confirmed that the oxidation state of Cu in fresh catalyst is divalent.<sup>[30,31]</sup> Besides, the shake-up satellites (940.23, 943.18, and 962.18 eV) in  $Cu_{2p}$  spectra are also the indication of the presence of Cu (II) species.<sup>[30]</sup> In Figure 1c, the S<sub>2p</sub> peak at 168.5 eV matched the reported values of the binding energy of S from  $CuSO_4$ .<sup>[32,33]</sup> The C<sub>1s</sub> XPS spectra in Figure 1d exhibited the peak with binding energies of 284.7 eV, which were attributed to the presence of carbon-containing groups. Figure 1e depicted two distinct peaks centered at 401.3 and 399.2 eV corresponding  $N_{1s}$ , which can be ascribed to benzenoid amine and protonated amine in the PANI components,<sup>[34]</sup> respectively. In Figure 1f, the binding energies of O<sub>1s</sub> at 531.8 eV was satisfactorily correspond to the presence of the oxygen in CMC and  $SO_4^{2-}$ , respectively.

In order to have an insight into the morphology of the composites, the SEM and TEM images of freshly  $CuSO_4NPs@CMC/PANI$  composites were examined and depicted in Figure 2. As can be seen from SEM images, the composites were composed of micron-scale grains with very rough surface (Figure 2a). For easy clarity and comparison, the images with more high magnification showed these grains were built by the accretion of smaller flakes composed of nanoscale spherical particles (Figure 2b). It also can be clearly observed in TEM images that quasi-spherical nanoparticles deposited well



**SCHEME 2** Schematic illustration of the preparation process of CuSO<sub>4</sub>NPs@CMC/PANI composites

onto the CMC/PANI nanofibers with dendritic structure (Figure 2c-e). The histogram of nanoparticle sizes showed that the average diameter of nanoparticles was 5.78 nm (Figure 2f).

The EDS analysis shown in Figure 3 revealed local elemental information for the CuSO<sub>4</sub>NPs@CMC/PANI composites. The non-metallic elements C, N, O, and S as well as metallic element Cu are clearly visible, which indicated that the Cu, S, and O elements were successfully incorporated into the prepared composites, while the CMC-Na and aniline components were free any Cu and S elements. These findings imply the successful introduction of CuSO<sub>4</sub> in the composites.

The distribution of Cu has impact on the catalytic activity. To adequately analyze the elemental distribution of CuSO<sub>4</sub>NPs@CMC/PANI composites, SEM element mapping images are presented in Figure 4. The elemental mappings conclusively evidence the C, N, O, S, and Cu elements are homogeneously dispersed throughout the composites.

The FTIR of CMC-Na (curve a), PANI (curve b), and CuSO<sub>4</sub>NPs@CMC/PANI composites (curve c) in the range of  $4,000-500 \text{ cm}^{-1}$  are presented in Figure 5. According to the spectrum of CMC-Na (curve a), the characteristic absorption peaks at 1,607 and 1,424  $\text{cm}^{-1}$ are, respectively, assigned to the asymmetric and symmetric stretching vibration of carboxylate (-COO<sup>-</sup>) groups.<sup>[17-20]</sup> In the spectrum of PANI (curve b), the peaks at 1,558 and 1,126  $\text{cm}^{-1}$  are attributed to

the moiety of N=O=N (where O represents a quinoid ring), while the peak at 1,482 and  $802 \text{ cm}^{-1}$  are correlated to the structure of N-B-N (where B represents a ring).<sup>[31]</sup> benzenoid From the spectrum of CuSO4NPs@CMC/PANI composites (curve c), a new absorption band at around  $1,159 \text{ cm}^{-1}$  is indicative for the  $SO_4^{2-}$  presence,<sup>[35]</sup> which may be due to the presence of CuSO<sub>4</sub>. Meanwhile, the peaks at 1,624 (group -COO<sup>-</sup>), 1,495 (group N-B-N), 1,421 (group -COO<sup>-</sup>), and 1,111 cm<sup>-1</sup> (group N=O=N) in the curve c confirm that CMC and PANI were successfully merged into the composites. Moreover, the shift of the peaks (group -COO<sup>-</sup>: 1,607 shift to 1,624 cm<sup>-1</sup>; group N-B-N: 1,482 shift to  $1,495 \text{ cm}^{-1}$ ; group N=Q=N: 1,126 shift to 1,111 cm<sup>-1</sup>) indicate that both CMC and PANI are coordinated with Cu (II) ions.

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The X-ray diffraction (XRD) patterns of the CMC-Na (curve a), PANI (curve b), and CuSO<sub>4</sub>NPs@CMC/PANI composites (curve c) were shown in Figure 6. The amorphous aboard diffraction peaks at  $2\theta = 20.7^{\circ}$  in curve (a) and  $2\theta = 25.4^{\circ}$  in curve (b) were assigned to native Na-CMC<sup>[20]</sup> and PANI,<sup>[31]</sup> showing a very low degree of crystallinity in the pure form. These peaks of CMC-Na and PANI can be also observed in curve (c) of CuSO<sub>4</sub>NPs@CMC/PANI, which proved the successful combination of CMC and PANI. But no CuSO<sub>4</sub> crystalline related peaks was detected in curve c; it is probably attributed that CuSO<sub>4</sub> NPs was dispersed in the CMC/PANI matrix as an amorphous form.



FIGURE 1 The XPS and spectra scan of element survey (a),  $Cu_{2p}$  (b),  $S_{2p}$  (c),  $C_{1s}$  (d),  $N_{1s}$  (e), and  $O_{1s}$  (f)

In order to explain thermal behaviors of catalyst, TGA and corresponding DTG analyses of CMC-Na, PANI, and CuSO<sub>4</sub>NPs@CMC/PANI composites were performed and depicted in Figure 7. All the samples revealed the first stage mass loss below 160°C, originated from the

Binding Energy (eV)

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removal of physical adsorptive moisture. The sample of CMC-Na (curve a) exhibited sharp loss in mass between 255°C and 312°C, related to the polymeric chain decomposition, including the disintegration of side groups and glycoside bonds. PANI (curve b) showed the second

Binding Energy (eV)



**FIGURE 2** SEM images of fresh CuSO<sub>4</sub>NPs@CMC/PANI composites (a in 10 μm, b in 300 nm), TEM images of fresh CuSO<sub>4</sub>NPs@CMC/PANI composites (c in 100 nm, d in 50 nm, and e in 20 nm) and nanoparticles diameter histogram of fresh catalyst (f)

step extending from 220°C to 800°C was mainly caused by the chemical decomposition of PANI. The CuSO<sub>4</sub>NPs@CMC/PANI composites (curve c) showed the second one at the temperature range of 195–255°C may account for the PANI decomposition, and the last one ranged from 255°C to 420°C was assigned the degradation of CMC—Na. In addition, the curve (c) produced higher ash content, which is associated with copper. In the DTG analysis, as can be seen from curve d, the maximal mass loss rate of CMC—Na was obtained for the temperature at 291°C. The plot of PANI (curve e) seemed to consist of three broad peaks around 88°C,



FIGURE 3 The EDS element analysis of CuSO<sub>4</sub>NPs@CMC/PANI composites

267°C, and 518°C. The obvious uneven loss of CuSO<sub>4</sub>NPs@CMC/PANI (curve f) from 188°C to 438°C was attributed to the decomposition of the catalyst; two stages of mass losses like as shoulders are observed at the temperature ranges of 188-233°C. The first and second shoulders are related to the degradation of CMC-Na and PANI, respectively. The DTG intension peak in CuSO<sub>4</sub>NPs@CMC/PANI was shifted to lower temperatures, illustrating the interaction between PANI and CMC-Na. These results indicated that CuSO<sub>4</sub>NPs@CMC/PANI composite has a good thermal stability from room temperature to 188°C and suitable for the following reactions.

Furthermore, XPS, TEM, and SEM of recovered catalyst were also performed to explore the change in valence of copper and morphology of catalyst. As shown in Figure 8a, the peaks at 932.30(Cu  $2p_{3/2}$  BE) and 952.05 eV (Cu  $2p_{1/2}$  BE) prove that parts of Cu (II) in the recovered catalyst from CuAAC reaction were converted into Cu(I)<sup>[30]</sup> and the shoulder peaks (934.33 and 954.28 eV) and satellites peaks (943.13 and 961.91 eV) illustrate the remain of Cu (II). It also can be observed that after A<sup>3</sup> coupling reaction, nearly all the Cu (II) was turned into Cu(I) by evidence of the presence of peaks at 932.97 (Cu  $2p_{3/2}$  BE), 952.77 (Cu  $2p_{1/2}$  BE) (Figure 8b), and 569.88 eV (Cu LMM BE) (Figure 8c)<sup>[36]</sup> as well as the

disappearance of satellites. Similarly, the appearance of peaks at 932.82 (Cu  $2p_{3/2}$  BE), 952.61 (Cu  $2p_{1/2}$  BE) (Figure 8d), and 569.62 eV (Cu LMM BE) (Figure 8e) indicated the generation of Cu(I) in  $A^3$ cycloisomerization tandem processes. In conclusion, the Cu (II) species in fresh catalyst were converted into  $A^3$ all of couplings,  $A^3$ -Cu(I)species in cycloisomerization tandem reactions, and CuAAC reactions. Notably, after CuAAC reaction, the SEM images showed the grains turned to rigid with rough surface (Figure 8f), and the TEM images showed the resultant Cu(I) nanoparticles have a slight agglomeration with the average diameter of 12.83 nm by comparison with fresh catalyst (Figure 8g).

# 3.2 | Application of CuSO<sub>4</sub>NPs@CMC/ PANI composites in A<sup>3</sup> three-component coupling reactions

To search the optimal reaction conditions for  $A^3$  reactions, *p*-chlorobenzaldehyde (1.0 mmol), morpholine (1.2 mmol), and phenylacetylene (1.5 mmol) were selected as model substrates, and different conditions were systematically explored (Table S1). The optimized reaction condition for the  $A^3$  model reaction was set



FIGURE 4 SEM corresponding elemental mapping images of CuSO<sub>4</sub>NPs@CMC/PANI composites



**FIGURE 5** The FTIR spectra of the CMC–Na (a), PANI (b), and  $CuSO_4NPs@CMC/PANI$  composites (c)



**FIGURE 6** The XRD patterns of the CMC–Na (a), PANI (b), and  $CuSO_4NPs@CMC/PANI$  composites (c)



FIGURE 7 The TGA and DTG curves of the CMC-Na (a, d), PANI (b, e), and CuSO<sub>4</sub>NPs@CMC/PANI (c, f)

at the usage of *p*-chlorobenzaldehyde (1.0 mmol), morpholine (1.2 mmol), phenylacetylene (1.5 mmol), and 30 mg CuSO<sub>4</sub>NPs@CMC/PANI (6 mol % of Cu) under neat conditions at 120°C.

On obtaining the optimal reaction conditions, we further examined the generality and limitation of this methodology; various aldehydes, amines, and alkynes were investigated under optimized condition. The results were summarized in Table 1. It can be seen that aryl aldehydes with either electron-donating or electronwithdrawing group afforded satisfactory vields. Phenylacetylenes with electron-donating groups on its aromatic ring afforded higher yields compared to electron-withdrawing groups due to the electronwithdrawing group reduces the nucleophilic activity. Notably, trace amount of product was found when aliphatic alkyne was applied owing to the activity of aliphatic alkyne is too low to form a Cu-alkyne intermediate. Among the different amines studied, morpholine and piperidine proceeded smoothly to furnish the superior yields compared with dialkylamine and arylamine. Unfortunately, aliphatic primary amines afforded no desired products.

# 3.3 | Application of CuSO<sub>4</sub>NPs@CMC/ PANI composites in A<sup>3</sup>-cycloisomerization tandem processes for synthesis of benzofurans

In keeping with our former research, the  $CuSO_4NPs@CMC/PANI$  composite catalyst was furtherly extended to the synthesis of benzofuran via  $A^3$ -cycloisomerization tandem processes in the presence of

N,N-dimethylaminopyridine (DMAP) as Brønsted base which facilitated the deprotonation of the –OH group and in favor of the 5-exo-dig-cyclization process.<sup>[37]</sup> The model reaction of salicylaldehyde (1.0 mmol), morpholine (1.2 mmol), and phenylacetylene (1.5 mmol) was selected to optimize reaction condition; several important parameters including solvent, the loading of catalyst, base, and temperature were systematically investigated (Table S2). It could be concluded that the optimal condition for  $A^3$ -cycloisomerization tandem reactions involves the usage of salicylaldehyde (1.0 mmol), morpholine (1.2 mmol), phenylacetylene (1.5 mmol), DMAP (0.5 equiv.), and 30 mg CuSO<sub>4</sub>NPs@CMC/PANI (6.0 mol% of Cu) in toluene at 120°C.

Having the optimal condition, diverse aldehydes, amines, and alkynes were chosen to investigate the scope and limitation of this methodology. The results were summarized in Table 2. When phenylacetylene reacted with morpholine and piperidine, the phenylacetylene bearing with the electron-withdrawing group afforded lower product yields comparing to electron-donating groups due to the electron-withdrawing group decreases the nucleophilic activity. Besides, 1-octyne afforded only 31% product yield due to its low reactivity. It is noticeable that diethylamine and aniline gave no products because they are hard to underwent A<sup>3</sup> couplings.

### 3.4 | Application of CuSO<sub>4</sub>NPs@CMC/ PANI composites in one-pot catalytic CuAAC reactions

In order to furtherly explore the application universality of CuSO<sub>4</sub>NPs@CMC/PANI composites, CuAAC reactions



**FIGURE 8** XPS of recovered catalyst from CuAAC reaction (a), recovered catalyst from A<sup>3</sup> reaction (b, c), recovered catalyst from A<sup>3</sup>-cycloisomerization tandem reaction (d, e), SEM images of recovered catalyst from CuAAC reaction (f), TEM images of recovered catalyst from CuAAC reaction (g) and nanoparticles diameter histogram of recovered catalyst from CuAAC reaction (h)

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### TABLE 1 CuSO<sub>4</sub>NPs@CMC/PANI-catalyzed A<sup>3</sup> couplings to synthesis of propargylamines<sup>[a]</sup>



<sup>a</sup>Reaction conditions: aldehyde/ketone (1.0 mmol), alkyne (1.5 mmol), amine (1.2 mmol), CuSO<sub>4</sub>NPs@CMC/PANI (6.0 mol% of Cu), 120°C, solvent-free condition. All yields are isolated.

 $^{\mathrm{b}}\mathrm{1}$  ml of toluene as solvent was added in this reaction.

<sup>d</sup>Imine intermediate was determined by GC-MS.

<sup>e</sup>No desired product and imine intermediate were determined by GC-MS.

<sup>&</sup>lt;sup>c</sup>Detected by TLC.

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#### TABLE 2 CuSO<sub>4</sub>NPs@CMC/PANI-catalyzed A<sup>3</sup>-cycloisomerization tandem reactions to synthesis of benzofurans<sup>[a]</sup>



<sup>a</sup>Reaction conditions: aldehyde (1.0 mmol), alkyne (1.5 mmol), amine (1.2 mmol), CuSO<sub>4</sub>NPs@CMC/PANI (6.0 mol% of Cu), DMAP (0.5 mmol), toluene (1.0 ml), 120°C. All yields are isolated.

<sup>b</sup>Detected by TLC.

<sup>c</sup>Imine intermediate was determined by GC-MS.

<sup>d</sup>No desired product was determined by GC-MS.

had been performed in the presence of  $CuSO_4NPs@CMC/PANI$  catalytic system to prepare corresponding 1,2,3-triazoles. The model reaction of benzyl bromide (1.0 mmol), NaN<sub>3</sub> (1.2 mmol), and phenylacetylene (1.0 mmol) was exerted to search of the optimal reaction conditions (Table S3). The optimal condition for model reaction involved the usage of benzyl bromide (1.0 equiv.), NaN<sub>3</sub> (1.2 equiv.), phenylacetylene (1.0 equiv.), and 20 mg CuSO<sub>4</sub>NPs@CMC/PANI (4 mol % of Cu) in 3 ml aqueous methanol (H<sub>2</sub>O/MeOH = 1:1, v/v) at 70°C.

Having optimized reaction conditions, we explored the generality of the CuSO<sub>4</sub>NPs@CMC/PANI composite catalyst for the CuAAC reaction of structurally diverse benzyl (alkyl) halides and alkynes, and the results are summarized in Table 3. All the substrates bearing with TABLE 3 CuSO<sub>4</sub>NPs@CMC/PANI-catalyzed CuAAC reactions to synthesis a variety of 1,2,3-triazoles<sup>[a]</sup>

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<sup>a</sup>Reaction conditions: halide (1.0 mmol), alkyne (1.0 mmol), NaN<sub>3</sub> (1.2 mmol), CuSO<sub>4</sub>NPs@CMC/PANI (4.0 mol% of Cu), H<sub>2</sub>O/MeOH (v:v = 1:1, 3 mL), 70 °C. All yields are isolated.

electron-donating and electron-withdrawing groups produced the expected cycloaddition product in good to excellent yields with high selectivity. By comparison with benzyl bromide, a longer reaction time was required for benzyl chloride due to its lower reactivity. Furthermore, it was observed that the yield of phenylacetylene containing electron-donating substituents were higher than those with electron-withdrawing groups, which probably attributed to the higher reactivity promoted by electrondonating substituents which increase the electron cloud density of the terminal alkynyl. Additionally, it was worth noting that 1-octyne and 2-bromo-1-phenylethanone also achieved good yields, which meant this composite catalyst was compatible of wide scope of substrates.



FIGURE 9 Recycling of CuSO<sub>4</sub>NPs@CMC/PANI composites in A<sup>3</sup> coupling reaction

catalyst $cl$ $cl$ $r$						
Entry	Catalyst (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref
1	CuSO <sub>4</sub> @CMC/PANI (6)	Solvent free	120	1	95	This work
2	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Se-T/CuI (20 mg)	Solvent free	100	2.3	93	Rangraz et al. <sup>[38]</sup>
3	Cu <sup>0</sup> NPs@CMC (7.5)	Neat	120	2	80	Liu et al. <sup>[39]</sup>
4	CuI/HTNT-5 (20 mg)	Solvent free	70	1.5	96	Reddy et al. <sup>[40]</sup>
5	CMC-Cu (II) (5)	Solvent free	100	15	88	Liu et al. <sup>[41]</sup>
6	Cu-MCM-41 (40 mg)	Solvent free	90–100	2	85	Abdollahi-Alibeik and Moaddeli <sup>[42]</sup>
7	Cu <sup>I</sup> / <sup>II</sup> @Cys-MGO (0.01 g)	Toluene	110	1	85	Rafiee and Khavari <sup>[43]</sup>
8	Cu <sup>II</sup> @PAA/PVC mesoporous fibers (3)	Toluene	120	36	95	Jiang et al. <sup>[44]</sup>
9	Cu/Al oxide mesoporous sponges (12)	Toluene	100	22	94	Dulle et al. <sup>[45]</sup>
10	Cu-P <sub>S</sub> -ala (0.01 g)	$H_2O$	Reflux	6	85	Islam et al. <sup>[46]</sup>
11	Cu nanoparticles (15)	CH <sub>3</sub> CN	100-110	5.5	98	Kidwai et al. <sup>[47]</sup>

#### TABLE 4 Comparison of the A<sup>3</sup> coupling reaction using CuSO<sub>4</sub>NPs@CMC/PANI catalyst and other reported Cu-catalysts

# 3.5 | Recyclability and heterogeneity test of CuSO<sub>4</sub>NPs@CMC/PANI composites in A<sup>3</sup> three-component coupling reactions

For practical application, the recyclability of the CuSO<sub>4</sub>NPs@CMC/PANI composites was evaluated using the A<sup>3</sup> model reaction under the afore-mentioned optimal condition. The results shown in Figure 9 demonstrated that the composite catalyst could be effectively reused for more than 15 consecutive runs with marginal dropping its catalytic activity. The Cu content of the recovered catalyst after 15 cycles was determined using ICP-AES analysis to be 1.374 mmol/g, which is slightly lower than 2.006 mmol/g of Cu content in fresh catalyst. The average loss of Cu in each run was calculated to be 2%, which make us to further investigate the homogeneity/heterogeneity of CuSO<sub>4</sub>NPs@CMC/PANI catalysts. Then, hot filtration test was performed using the  $A^3$ model reaction. The reaction was quenched in 10 min (18% conversion) by adding excessively ethyl acetate to separate the solid catalyst. After entire removal of ethyl acetate, the residues were then continued to react for 1 h at 120°C, and only a slight improvement in conversation (18% to 22%) was observed, suggesting that the catalysis was characteristically heterogeneous in nature.

# 3.6 | Comparison of catalytic activity in A<sup>3</sup> coupling reaction between CuSO<sub>4</sub>NPs@CMC/PANI composite and other reported catalysts

То illustrate the merits and applicability of CuSO<sub>4</sub>NPs@CMC/PANI catalyst, it has been compared with other previously reported copper catalysts using the A<sup>3</sup> model reaction as a reference. The comparative results presented in Table 4 clearly demonstrate that the present composite catalyst indeed has some significant benefits over other solid copper catalysts in terms of superior catalytic activity, low catalyst loading, short reaction time, excellent yield, easy separation, and recycling of catalyst. The superior catalytic performance of CuSO<sub>4</sub>NPs@CMC/ PANI composites can be presumably attributed to the coordination and stabilizing effect of CMC and PANI which make the high dispersity of CuSO<sub>4</sub> NPs on CMC/PANI framework and thus prevent aggregation.

# 4 | CONCLUSIONS

An easy template method for the fabrication of  $CuSO_4NPs@CMC/PANI$  composites has been developed via in situ interfacial oxidative polymerization of aniline

using  $CuSO_4$  as initiator and CMC—Na as template in which quasi-spherical  $CuSO_4$  nanoparticles with 5.78 nm average diameter are successfully loaded on the CMC/PANI matrix. This as-prepared composites were well characterized by ICP, XPS, TEM, SEM, EDS, FTIR, and TGA analyses. It was proven that  $CuSO_4NPs@CMC/PANI$  composite was a highly efficient catalyst for A<sup>3</sup> coupling reactions, A<sup>3</sup>-cycloisomerization tandem reactions, and CuAAC reactions in terms of low catalyst loading, remarkable catalytic performance, tolerance of wide scope of substrates, recyclability, robustness, and benign to environment. These salient features of this catalytic process make it more competitive for practical applications.

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#### **AUTHOR CONTRIBUTIONS**

**Zhian Xu:** Conceptualization; investigation; methodology. **Jinxi Xu :** Investigation; methodology. **Yiqun Li:** Conceptualization; funding acquisition; project administration; resources; supervision.

#### **CONFLICT OF INTEREST**

The authors declare no competing interest.

#### DATA AVAILABILITY STATEMENT

The data that support the finding of this study are available in the supporting information in this article.

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