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Application of Biosynthesized CuO Nanoparticles Using *Rosa canina* Fruit Extract as a Recyclable and Heterogeneous Nanocatalyst for Alkyne/Aldehyde/Amine A^3 Coupling Reactions

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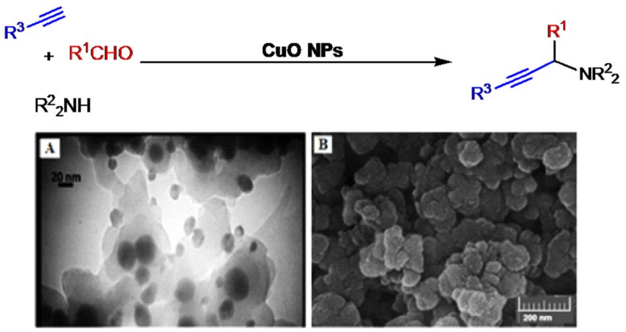
Abstract

Copper oxide (CuO) nanoparticles (NPs) were prepared through a biological procedure where the *Rosa canina* fruit extract was used as a capper and reductant agent. For the three-component reaction of amines, aldehydes and alkynes (A^3 coupling), these CuO NPs were used as an effective heterogeneous nanocatalyst. Various propargylamines were obtained in a good yield. Additionally, the reuse and separation of CuO NPs was extremely effective, economical and simple.

Graphical Abstract



Keywords A^3 coupling · Propargylamines · CuO NPs · *Rosa canina*

1 Introduction

In most cases, propargylamines are used in organic chemistry as useful construction blocks and precursors to prepare various nitrogen-containing heterocyclic materials and main intermediates to synthesize natural products and biologically active drugs [1–3]. Furthermore, a number of propargylamines have been used to treat neuropsychiatric illnesses such as Parkinson's and Alzheimer's disease [4, 5]. Their importance leads to developing various synthetic approaches [6–8]. Though, the most direct and effective technique for preparing propargylamines is via transition-metal catalyzed three-component coupling of an aldehyde, an amine and a terminal alkyne, which is identified as an A^3 coupling reaction [9, 10]. Various heterogeneous and homogeneous catalysts have recently been used to synthesize propargylamine through A^3-coupling reaction based on transition metals such as Zr [11], Mn [12], Re [13], Fe [14, 15], Ru [16, 17], Co [18], Ir [19, 20], Ni [21, 22], Pd [23] Cu [24–28], Ag [29–31], Au [32–35], Zn [36, 37], Cd [38] and Hg [39]. Among the different transition metals, copper has mostly been examined as it is cheap, abundant, high reactive and nontoxic. Although many of the catalytic systems are homogeneous, their loss at the reaction end reduces their efficacy, especially in industrial applications. Currently,

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metal NPs are regarded as heterogeneous catalysts with a high surface-to-volume ratio. They could be appropriate substitute for traditional catalysis owing to their higher selectivity and activity [40–45].

Different chemical transformations have recently been performed under the heterogeneous catalysis. Among heterogeneous catalysts, metal NPs such as CuO have been extensively used as efficient catalysts in organic reactions owing to their great surface areas, small dimensions, simplicity, excellent catalytic activity, benign character and recoverability [46–50]. Furthermore, copper oxide NPs and copper are cheap in comparison to Au, Ag, Pd, Pt, Ru and Rh, which have been extensively applied as catalysts for organic transformations.

Various ways exist to synthesize CuO NPs like sonochemical [51], microwave irradiations [52], sol–gel method [53], one step solid-state reaction technique at ambient temperature [54], electrochemical approaches [55], precipitation–pyrolysis [56], thermal decomposition of precursor [57] or by combining electro deposition and self-catalytic mechanism. Poisonous substances (e.g. hydrazine hydrate, sodium borohydride, dimethylformamide, ethylene glycol and so on) in chemical techniques are highly reactive with many biological and ecological difficulties. As a result, a challenge existed for finding a mild, harmless, suitable and a natural product to produce metal/metal oxides in an aqueous environment. In different natural materials used to construct NPs, herbs appear to be the most appropriate candidates as the NPs made using herbs are more stable and the synthesis speed is high. At present, simplicity, inexpensiveness and environmentally-friendliness of green synthesis of NPs have made it extremely important. Several reports, including those of Aloe *barbadensis Miller* [58, 59] and *Gum Karaya* [60] are available about biosynthesis of CuO NPs using herbs.

Indeed, green synthesis of NPs has been enhanced as a novel nanobiotechnology to produce economical and eco-friendly synthetic method for extremely stable NPs. For the first time, owing to our considerable interest in the biosynthesis of metal NPs and heterogeneous catalysts [61–73], we intend to report application of green synthesized CuO NPs as an effective heterogeneous nanocatalyst for the three-component reaction of amines, aldehydes and alkynes (A^3 coupling) using *Rosa canina* fruit extract [74]. Moreover, the CuO NPs can be recovered and recycled several times without much activity loss.

2 Experimental

2.1 CuO NPs Green Synthesis Using *Rosa canina* Fruit Extract

After carefully cleaning and washing the fresh *Rosa canina* fruits with double-distilled water several times, to 100 mL of deinonized water, 10 g of the fruits were added and boiled in a water bath for 15 min. This mixture was cooled off and filtered using Whatman filter paper No. 1 to obtain an aqueous extract. The extract was then stored at 4 °C in a refrigerator for later use as a reducing and stabilizing agent. A 10 mL extract quantity was added dropwise to 100 mL of 1 mM aqueous $Cu(OAc)_2$ solution refluxed at a temperature of 100 °C for 1 h to obtain the CuO NPs. Owing to the heating process, the mixtures coloration slowly changed to a dark brown hue over time. This issue is owing to the surface plasmon resonance excitation signaling the antioxidant phenolics hydrogen donation behavior and CuO NPs creation within the plant. Then, the obtained precipitation was rinsed three times with chloroform and ethanol, respectively. Afterward, it was air dried for 48 h at room temperature. The concentration of copper oxide was 5.6 mmol/g, which was determined by ICP-AES.

2.2 General Procedure for the Synthesis of Propargylamine Derivatives

The CuO NPs catalyst (10 mg) was poured to a mixture of aldehyde (1 mmol), phenylacetylene (1.2 mmol) and amine (1 mmol) in toluene (3 mL), and the mixture was agitated at 100 °C. The reaction development was controlled through TLC. After converting the substrate fully, the mixture was centrifuged after cooling down to ambient temperature. The crude product was obtained after isolation of the catalyst and evaporation of the solvent. For purification, silica gel column chromatography (70:30, Hexane/EtOAc) was utilized. Through melting points or spectral analysis, all the compounds were identified and their characterization was carried out [75–88].

3 Results and Discussion

The FESEM and TEM measurements were applied to verify the nanostructure of green synthesized CuO NPs using *Rosa canina* fruit extract that was synthesized again according our previously report [74]. The FESEM image indicated that the CuO nanoparticles were encapsulated by biopolymers (Fig. 1a), and surface morphology of the CuO NPs had more regular stacked structure. TEM image of CuO NPs showed that this nanoparticle formed evenly dispersed nano-sized encapsulated in membranous light gray biopolymers shells (Fig. 1b). Most of these particles are in the 20–25 nm range. The EDX showing the presence of C, N, O, and Cu in Fig. 1c also confirmed the existence of biopolymers layers on the surface of CuO NPs.

The polyphenolic compounds have been demonstrated as reducing agent during the biological extract mediated preparation of nanomaterials [48, 49]. The *Rosa canina* extract

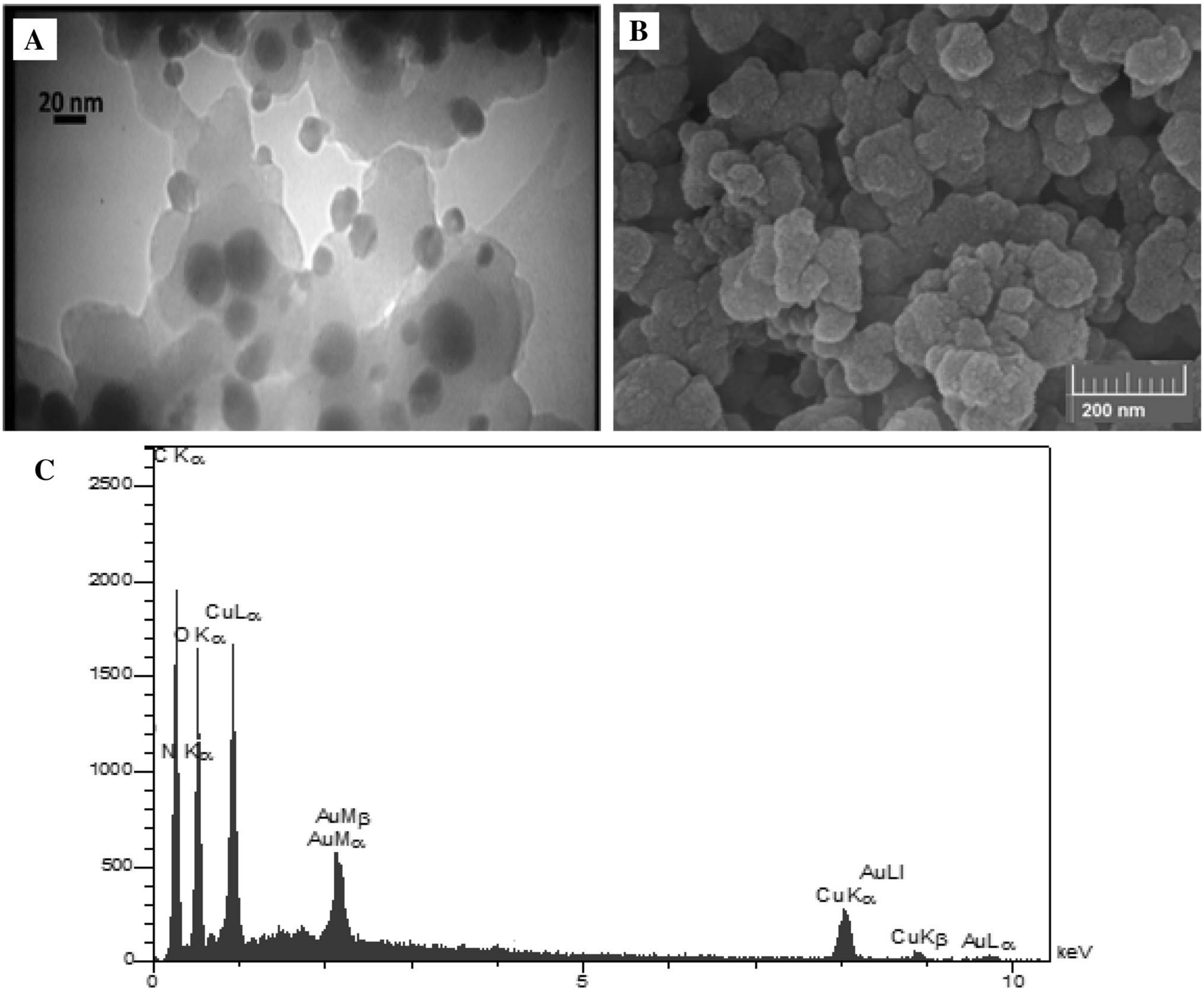


Fig. 1 **a** FESEM, **b** TEM, and **c** EDX data of biosynthesized CuO NPs

is also a rich source of the polyphenolic compounds and flavonoidic groups. These entire polyphenolic compounds may act as reducing agent for the reduction of Cu^{2+} ion. Scheme 1 shows the schematic representation of probable mechanism. In the first step, when extract mixed with the metal salt solution, the hydroxyl groups of the polyphenolic compounds formed the complex with the Cu^{2+} and reduced it into the Cu. Thus formed metallic copper atoms react with the available atmospheric oxygen to form most stable oxide i.e. CuO. In the next, formed CuO molecules come together to nucleate followed by further growth which results the formation of nanoparticles.

Owing to our constant interest in the biosynthesis of metal NPs and heterogeneous catalysts [61–73], after structural characterization of the prepared CuO NPs, their catalytic activity was studied in the three-component coupling reaction of amines, aldehydes and alkynes (A^3 coupling). Using benzaldehyde, morpholine and phenylacetylene, primary tests were conducted to optimize different factors such as time, temperature, solvents and catalyst loading. Table 1 presents the outcomes. In this regard, the effect of catalyst was first studied, and as expected, desired product was not obtained without catalyst presenting the dispensable role of CuO NPs in the reaction mechanism (Table 1, entry 1). Using a 10 mg catalyst in toluene at 80 °C, the reaction yield was obtained 85% (Table 1, entry 2). In addition, the reaction quantitatively occurred using 10 mg of catalyst at 100 °C (Table 1, entry 3). By decreasing the catalyst level to 7 and 5 mg, lower yields were achieved (Table 1, entries 4 and 5). However, using 10 mg of catalyst in other solvents such as CH_2Cl_2, DMF, EtOH, H_2O, CH_3CN and neat, resulted in lower reaction yields (Table 1, entries 6–11). As a result, we opted toluene as the best solvent, 10 mg catalyst and 100 °C reaction temperature as the most optimum and

Scheme 1 Probable mechanism for formation of CuO NPs using *Rosa canina* extract

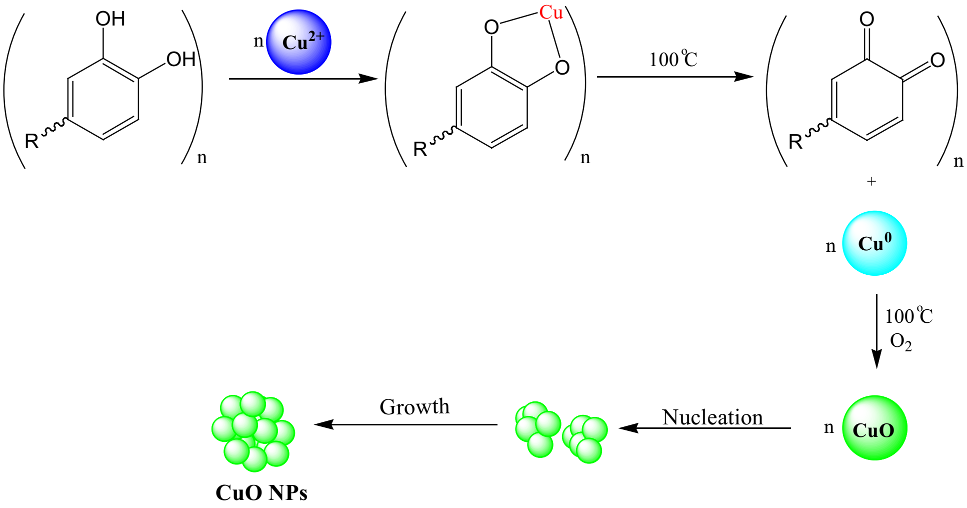
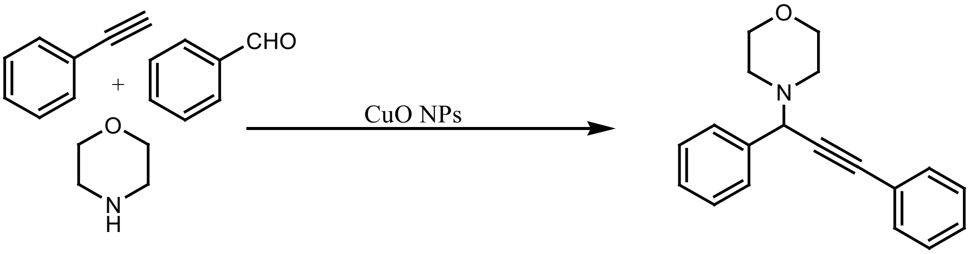


Table 1 Optimization of various conditions in the model reaction using biosynthesized CuO NPs catalyst



Entry	Catalyst (mg)	Solvent	T (°C)	Yield (%)[a]
1	–	Toluene	80	–
2	10	Toluene	80	85
3	10	Toluene	100	96
4	7	Toluene	100	65
5	5	Toluene	100	50
6	10	CH_2Cl_2	70	30
7	10	DMF	100	65
8	10	EtOH	80	60
9	10	H_2O	100	50
10	10	CH_3CN	70	60
11	10	–	100	35

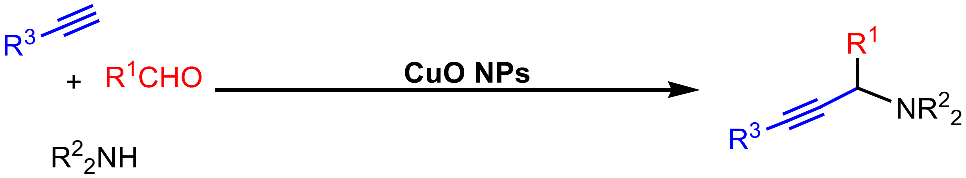
Reaction conditions: Benzaldehyde (1.0 mmol), morpholine (1 mmol), phenylacetylene (1.2 mmol), CuO NPs, solvent (3.0 mL) for 10 h

[a] Yields are based on ^1H NMR

effective reaction conditions to study the scope of this A^3 coupling.

Under optimal reaction conditions, other aldehydes reacted with various phenylacetylene and aliphatic amines, resulted in the A^3 coupling product with good yield (Table 2). At the primary study of the aldehyde substrate scope, phenylacetylene and morpholine were used as model substrates and various aldehydes were studied for the A^3-coupling reactions (Table 2, entries 1–14). The results demonstrate that aromatic aldehydes behavior such as functional groups as –Cl, –Br, –OH, –Me, or –OMe can affect the A^3-coupling. Furthermore, minor electronic influence was found that is associated with reaction of aryl aldehydes with electron-withdrawing groups (Table 2, entries 2–4) and generation of the relevant products in excellent yields, whereas replacement of electron rich groups (Table 2, entries 5–7) on the benzene ring lowered the performance and caused less yields. Furthermore, reaction of challenging heterocyclic

Table 2 The reactions of aldehydes, amines and alkynes in the presence of CuO NPs catalyst



Entry	R^1	Amine	R^3	Yield (%)[a]	Refs.[b]
1	Ph	Morpholine	Ph	96	[75]
2	4-ClC_6H_4	Morpholine	Ph	90	[85]
3	3-ClC_6H_4	Morpholine	Ph	95	[88]
4	4-BrC_6H_4	Morpholine	Ph	92	[78]
5	4-OHC_6H_4	Morpholine	Ph	88	[86]
6	4-MeC_6H_4	Morpholine	Ph	90	[75]
7	4-$OMeC_6H_4$	Morpholine	Ph	85	[86]
8	2-Thiophenyl	Morpholine	Ph	92	[86]
9	2-Furfuryl	Morpholine	Ph	90	[75]
10	Cyclohexyl	Morpholine	Ph	90	[86]
11	C_3H_7	Morpholine	Ph	80	[86]
12	Ph	Piperidine	Ph	92	[86]
13	Ph	Pyrrolidine	Ph	90	[87]
14	Ph	Aniline	Ph	0	[86]

Reaction conditions: Aldehyde (1.0 mmol), amine (1 mmol), alkyne (1.2 mmol), CuO NPs (10 mg) were stirred in toluene (3.0 mL) at 100 °C for 10 h

[a] Yields are based on ^1H NMR

[b] Earlier reference of the corresponding product

compounds like thiophene-2-carbaldehyde or furan-2-carboxaldehyde with morpholine and phenylacetylene efficiently proceeded, and the corresponding propargylamines were obtained in good yields (Table 2, entries 8, 9). Moreover, under this optimum condition, the aliphatic aldehyde (cyclohexanecarbaldehyde/butanaldehyde) indicated good yields (Table 2, entries 10, 11). A mixture of benzaldehyde-phenylacetylene-amine was selected to expand the scope of amine substrates, and various amines were examined (Table 2, entries 1 and 12–14). The results show that under optimal reaction conditions, cyclic, heterocyclic (piperidine/pyrrolidine/morpholine) provided high yields of products (Table 2, entries 1 and 12, 13). However, no product was achieved by using aniline as a substrate (Table 2, entry 14).

Recovery of heterogeneous new catalysts is particularly essential in terms of economic and sustainable chemistry views. As a result, we studied the recovery of the CuO NPs catalyst for the reaction of benzaldehyde, morpholine and phenylacetylene under optimum reaction conditions. For this purpose, at the end of the reaction, through centrifugation and rinsing with water and ethanol twice, the catalyst was isolated from the reaction solution. Afterward, the catalyst was recycled for seven times with observing no significant change in the catalytic performance (Fig. 2). This reusability demonstrates the excellent turnover and stability of the catalyst under working conditions.

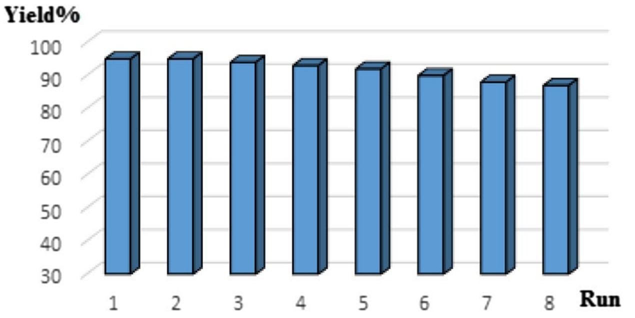


Fig. 2 Recycling of catalyst for the reaction of benzaldehyde, morpholine and phenylacetylene

In addition, to stablish the catalyst heterogeneity, for the reaction of benzaldehyde, morpholine and phenylacetylene, a hot filtration examination was performed using CuO NPs under the optimized conditions. After 5 h a 65% yield could be achieved from the reaction, and subsequently the catalyst was separated to be reapplied. No increase in yield of the

Table 3 Comparison efficiency of CuO NPs with some reported methods for the A^3 coupling reaction between benzaldehyde and piperidine with phenylacetylene

Entry	Reaction conditions	Time (h)	Yield %	Refs.
1	CuO NPs, toluene, 100 °C	10	96	This work
2	AgI, H_2O, 100 °C, N_2	14	70	[76]
3	CuSBA-15, toluene, 90 °C	6	80	[77]
4	Au@PMO-IL, $CHCl_3$, 60 °C	12	87	[78]
5	$FeCl_3$, 70 °C	14	34	[79]
6	Ag NPs, PEG, 100 °C	20	77	[80]
7	Nano Co_3O_4, 130 °C	15	87	[81]
8	Fe_3O_4, toluene, 80 °C	16	75	[82]
9	Fe_3O_4@SBA-15, toluene, 110 °C	8	76	[83]
10	$NiCl_2$, toluene, 111 °C	9	87	[84]
11	Ag-NaY, neat, 100 °C	15	73	[85]
12	Ag NPs/plant extract, PEG, 90 °C	18	83	[48, 49]
13	MNP@Au/NNN-pincer, H_2O, 85 °C	7	90	[86]
14	[CuCl{2,5-bis(2-thienyl)-1-phenylphosphole}$_2$], 100 °C	5	92	[87]
15	$InBr_3$, toluene, 80 °C	6	80	[88]

product was observed and when the reaction for another 5 h was sustained following the catalyst was separated, approving the catalyst's heterogeneous property.

Table 3 presents a comparison of a number of chosen procedures in the literature and current procedure, showing that CuO NPs is similarly or more effective catalyst in terms of yield and reaction time than previously-reported ones.

4 Conclusion

In summary, a cost-effective, green, simple effective, technique was developed to synthesize CuO NPs with *Rosa canina* fruit extract as a stabilizer and reductant. It was determined that CuO NPs were an air stable, effective and cost-effective catalyst to synthesize propargylamines using a one-pot three-component A^3-coupling reaction of aldehydes, amines and alkynes. The products were obtained in good to high yields, and the catalyst can be reutilized up to seven cycles with almost no performance change.

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