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FULL PAPER

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C-S cross-coupling reaction using novel and green synthesized CuO nanoparticles assisted by *Euphorbia maculata* extract

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In the present study, biosynthesis of CuO nanoparticles using a rapid, eco-friendly, cost-effective and efficient method has been reported employing aqueous *Euphorbia maculata* extract as mild, renewable and non-toxic reducing and capping agents without adding any surfactants. The biogenic and green method has some benefits compared to conventional physical and chemical methods. It is simple, cheap and environmentally friendly.

The biosynthesized CuO NP displayed a color change pattern (from sky blue to black) on preparation and presented its respective broad peak at 365 nm, which was analyzed by UV–Vis spectroscopy. Using the FT-IR analysis, biomolecules in *E. maculata* extract which are responsible for bioreduction activity and synthesize of CuO NP, were identified. The XRD, EDX and FESEM results confirmed the successful synthesis of CuO nanoparticles of 18 nm sizes, with spherical and sponge crystal structure.

The catalytic activity of biosynthesized CuO NPs was studied in C-S cross-coupling reaction. This method has the advantages of high yields, easy work-up, and simple reusability. The recovered CuO NP can be reused four times without any considerable loss of its catalytic activity.

KEYWORDS
catalyst, copper oxide nanoparticles, C-S cross-coupling, *Euphorbia maculata*, green synthesis

1 | INTRODUCTION

Nanotechnology is a novel scientific field that concerns materials at the nanoscale.[1] In recent decades, many types of research in different fields such as biotechnology, physics, chemistry, engineering, and medicine have focused on nanotechnology.[2–4] Metal nanoparticles (MNPs) have received significant interest regarding their considerable efficiency in catalytic reactions including cross-coupling, hydrogenation, multi-component,and oxidation.[5–7]

CuO NP is one of the metal nanoparticles that was found to be very beneficial in extensive applications regarding its singularity. CuO NPs were widely utilized as catalysts and biological activity agents.[8,9] They also can be used in solar cells,[10] lithium-ion batteries and gas sensors.[11] Copper oxide nanoparticles have been synthesized by various methods, usually classified as physical and chemical procedures. Although these two

Abbreviations: DMF, Dimethylformamide; DMSO, Dimethyl Sulfoxide; EDX, Energy Dispersive X-ray Spectrometry; FESEM, Field Emission Scanning Electron Microscopy; FT-IR, Fourier Transforms Infrared Spectroscopy; MNPs, Metal Nanoparticles; NPs, Nanoparticles; TG-DTA, Thermo Gravimetric-Differential Thermal Analysis; TLC, Thin Layer Chromatography; UV–VIS, Ultraviolet–Visible; XRD, X-ray Diffraction

methods are widely used for the synthesis of CuO NPs, issues such as expensive reagent, longer reaction time, and dangerous reaction condition for separating synthesized nanoparticles can make these methods difficult.[12] These difficulties can be solved by green chemistry.[13]

Phytonanotechnology is a biological method for the synthesis of highly stable and small sized metal nanoparticles. Lately, this method has drawn much attention in researches.[14,15] This synthetic method is a rapid, stable, reliable, reproducible, and effective procedure to create highly active copper oxide nanoparticles using plant extracts.[16,17] The pollutant-free solvent and eco-friendly reducing and capping agents are the three fundamental elements for a perfect green synthesis technique.[18,19] Green chemistry is a branch of chemistry based on the production of chemical products without using or generating dangerous and toxic substances.[20,21]

Catalysts are generally classified into two types of homogeneous and heterogeneous. Homogeneous catalysts, have limited use in the industry due to the difficulties in separating the products contaminated with residual unstable complexes and expensive recycling process of the catalysts.[22] Heterogeneous catalysts have the advantages of superior catalytic activity, low detriment and cost, simple recyclability, reusability, and ease of handling.[23,24] These heterogeneous catalysts can be separated by centrifugation and filtration procedures for the consecutive reuse.[25] Recently, the utilization of heterogeneous catalysts, especially metal oxide nanoparticles, as catalysts in organic reaction has attracted much attention regarding their great surface-to-volume ratio, highly active surface, and easy recovery and recyclability of the catalysts.[26–29] Therefore, several procedures have been developed to synthesize durable and reusable heterogeneous catalysts for the organic reaction. These catalysts are very useful from a sustainablility point of view.[30] The significance of heterogeneous catalysts in terms of enviro-economical and practical aspects for performing synthetic transformations has caused an exponential growth in their applications in organic reactions.[31] In green chemistry, biosynthesized metal nanoparticles have been used in various organic reaction especially cross-coupling reaction as effective and environmentally friendly catalysts.[32–36] Nowadays, nanocatalysis is an attractive and highly demanding area of research which involves the use of nanomaterials as catalysts in a variety of organic transformations.[37,38] This may be due to their unique characteristics like smaller size, high surface area, high density of defect sites, increased efficiency and selectivity and reusability.[39] Biosynthesized metal nanoparticles have a combination of the two complementary properties: the inorganic properties like mechanical/thermal/structural stability and the properties of organic pendant moieties such as flexibility in solution (like homogeneous catalysts) and therefore, high reactivity of the catalyst.[40] Cross-coupling reactions have been used as powerful and useful synthetic tools in novel synthetic chemistry.[5,41–43] The formation of C − S bonds is momentous in synthetic organic chemistry for the structure of different synthetics, a large number of drugs for diseases such as diabetes, cancer, Alzheimer's, Parkinson's, or inflammatory HIV diseases, and natural biologically active compounds (Figure 1).[44–46]

Recently, aryl sulfides and their derivatives have drawn much attention in molecular precursors for the development of this materials because of their biological, pharmaceutical properties.[47–51] Therefore, transition-metal-catalyzed C-S bond formation has been the subject of many studies in the last few decades.[52–55] The advantages of using copper oxide nanoparticles (CuO NPs) in the cross-coupling reactions are the availability inexpensive catalyst, recyclability, and lack of exterior ligands as compared to the usual catalytic systems.[56–60]

In this study for the first time, we synthesized CuO NP using aerial parts extract of *Euphorbia maculata* (a member of the *Euphorbiaceae* family). This process is faster than most of the existing chemical methods. We have developed an economical, green and simple procedure to synthesize heterogeneous catalyst for organic reaction. In continuation of this research, a new protocol has been presented for the procurement of CuO NPs by *Euphorbia maculata* extract (new reducing/capping agents) and Characterizations of the obtained nanoparticles were analyzed by various standard techniques. The CuO nanoparticles as a novel heterogeneous catalyst provide excellent catalytic activity for the synthesis of thioether under ligand-free conditions. In addition, the recyclability and reusability of nanocatalyst was investigated for C-S cross coupling reaction at least four times without a considerable loss of its catalytic activity.

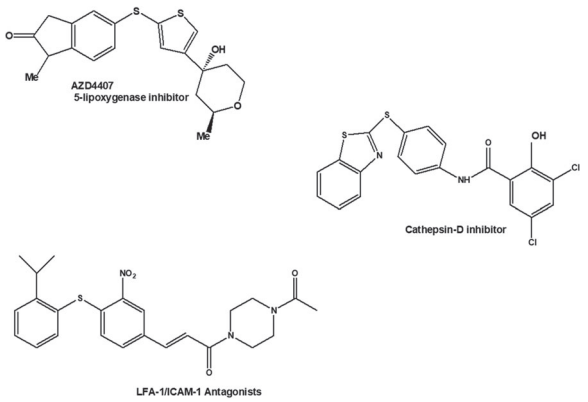


FIGURE 1 Biologically active thioethers used as drugs

2 | MATERIAL AND METHODS

2.1 | Preparation of extract

Euphorbia maculata aerial parts were collected within the Mazandaran region in Iran, during the month of July 2017. Healthful aerial parts were selected and separated from the remains. Then, the collected aerial parts of *Euphorbia maculata* was cleaned with distilled water frequently to pick up the impurities, then were dried and powdered these parts using a kitchen blender.

In a 250 ml flask, 10 g of powdered aerial parts of *Euphorbia maculata* was added to 100 ml of double distilled water and well stirred using a magnetic heater stirrer at 90 °C for 45 min to prepare the aqueous extract. The extract was filtered and was kept at 4 °C for further use.[61]

2.2 | Synthesis of copper oxide nanoparticles

Capped CuO nanoparticles with *Euphorbia maculata* extract were synthesized by the green method. 100 ml of copper (II) sulfate pentahydrate (1 M, $CuSO_4.5H_2O$) was blended in 10 ml of *E. maculata* aqueous extract at 50 °C for 2 hours. The reaction showed a change of color in the solution from sky blue to black. In the following, synthesized copper oxide nanoparticles were centrifuged at 7000 rpm for 30 mins and washed with deionized water (3 × 15 ml) and ethanol (3 × 15 ml). Then, these nanoparticles were dried at 60 °C in an oven.[62]

2.3 | Characterization of copper oxide nanoparticles

The optical properties and the crystalline nature of the CuO nanoparticles were studied by UV–Visible spectroscopy (SPEKOL 2000 Analytik Jena) and X-ray diffractometer (PHILIPS, PW1730), respectively. The particle size and morphology of biosynthesized CuO nanoparticles were analyzed through Field-emission scanning electron microscopy analysis (FESEM,TESCAN) and the composition of the elements present in CuO nanoparticles was determined using energy dispersive spectrophotometer (EDS, TESCAN, MIRA) attached to the Map. FT-IR spectra were obtained through Fourier-transform infrared spectrophotometer (Bruker model Tensor 27 spectrometer) in the spectral region of 4000–400 cm^{-1} using dry KBr pellet as a standard reference and thermogravimetric-differential thermal analysis (TG-DTA) was performed by the means of STA 1500 Rheometric Scientific. The surface area, pore volume and pore size distribution of the support and the catalyst were determined by adsorption–desorption of N_2 using BELSORPII instrument.

2.4 | General procedure for aryl-sulfur coupling

In a round bottom flask, a mixture of aryl halide (1.1 mmol), thiol (1 mmol), CuO nanoparticles (0.015 g), and KOH (1.5 mmol) was well-stirred at 110 °C under a nitrogen atmosphere in DMSO (1 ml). The progress of the reaction was monitored by a thin layer chromatography (n-hexane/ethyl acetate, 9:1). After the end of the reaction, the reaction mixture was cooled at the room temperature and the catalyst was separated by centrifugation and subsequently washed with ethanol (15 ml) and used for a consecutive cycle. Then, the reaction was diluted with 15 ml of water and was extracted with ethyl acetate (3 × 10 ml). The organic phase was purified on a short pad of silica gel using hexane and ethyl acetate to give the corresponding coupling product. All organic products were recognized easily by spectroscopy techniques such as ^1H NMR, ^{13}C NMR (BRUKER ULTRASHIELD 400 AVANCE III NMR), and FT-IR (Bruker model Tensor 27 spectrometer).

3 | RESULTS AND DISCUSSION

3.1 | XRD analysis

Figure 2 displays the X-ray diffraction patterns of the CuO nanoparticle. The peak positions with 2θ values of 32.8°, 35.9°, 39.1°, 46.3°, 49.1°, 52.9°, 58.7°, 66.6°, 68.3°, 72.6° and 75.5°, were assigned to (−111), (002), (111), (−112), (−202), (020), (202), (−311), (113), (311) and

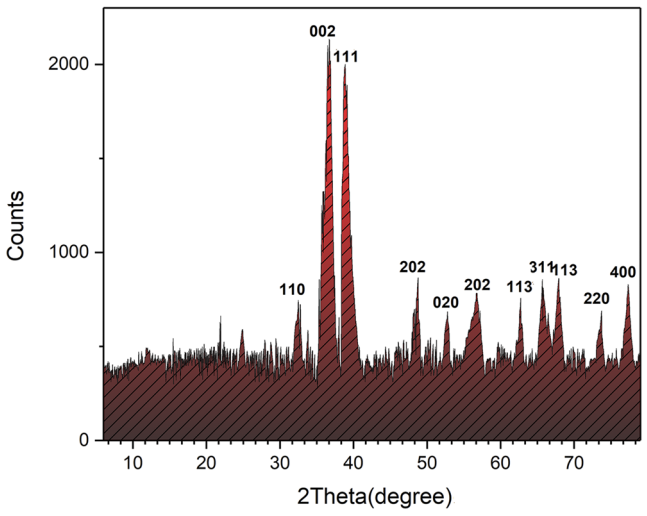


FIGURE 2 XRD powder pattern of CuO NP synthesized using the aqueous extract of the aerial parts of Euphorbia maculata

(400) planes, respectively. Therefore, the formation of CuO nanocrystal synthesized from the *E. maculata* extract was clearly demonstrated by XRD studies, which is in agreement with previous studies.

3.2 | UV–vis analysis

UV–Vis Spectroscopy is generally used to confirm the synthesis of the CuO nanoparticle (Figure 3). The absorption spectrum of UV–Vis spectroscopy for the CuO (NP) was investigated in the range of 280–420 nm. The absorption peak at a wavelength of 360 nm corresponds to the formation of the copper oxide nanoparticles.

3.3 | FT-IR analysis

The FT-IR analysis was performed to recognize the biomolecules which are likely to be involved in the biosynthesis of CuO nanoparticles. The FT-IR analysis of the *Euphorbia maculata* extract (Figure 4) showed some significant peaks at 3430 and 2938, dedicated to the OH group resulting from phenolic stretching and the C–H stretching vibrations of the $-CH_2$ functional group respectively. The presence of the peaks at 1626 and 1414 are related to the carbonyl group (C = O) and the stretching C = C aromatic ring. The peak observed at 1218 to 1075 cm^{-1} corresponds to C-O stretching frequency of C-OH stretching vibrations. The FT-IR analysis confirmed the presence of phenolic compounds in the plant extract. The FT-IR spectrum of CuO NPs (Figure 4) demonstrates that the 3430, 2938, 1626, 1414, 1218, and 1075 cm^{-1} peaks were respectively shifted to new positions of 3462, 2935, 1637, 1359, and 1058, in

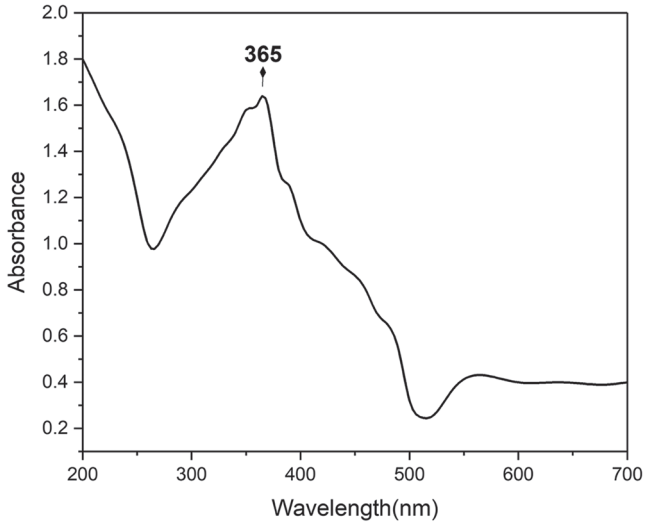


FIGURE 3 UV–vis spectrum of green synthesized CuO NP using Euphorbia maculata

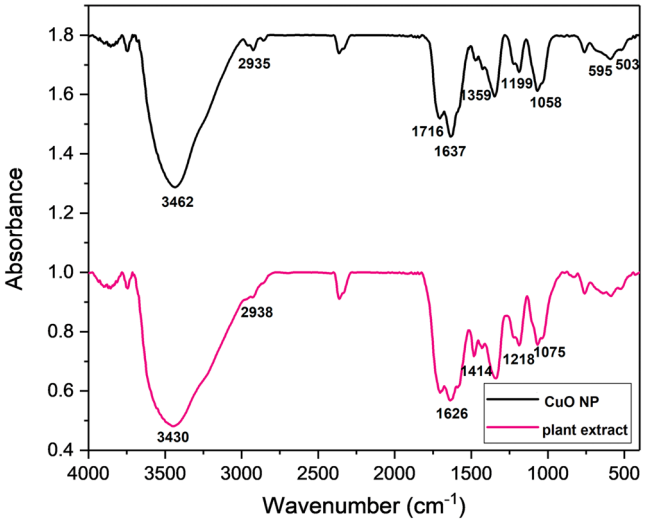


FIGURE 4 FT-IR spectra of (a) plant extract (b) CuO NP with plant extract

the region of 400–4000 cm^{-1}. The existence of the peaks at 1716 cm^{-1} confirmed the formation of ketone as a capping agent. The formation of CuO is characterized by two peaks at 595 and 503 cm^{-1} which correspond to the Cu-O stretching bond. The FT-IR results confirm the presence of phytochemical compounds in the *E. maculata* extract, which further act as reducing/capping agents for the synthesis of CuO NPs.

3.4 | EDS and FESEM analysis

The composition of biosynthesized CuO NPs has been analyzed by studying the energy-dispersive X-ray spectroscopy (EDS), as shown in Figure 5. The EDS spectrum represents the existence of copper and oxygen with carbon, which indicates the presence of stabilizing agents, originated from *Euphorbia maculata* extract (Figure 5).

Figure 6 indicates the field-emission SEM (FESEM) image of the biosynthesized CuO NPs. This image reveals the spherical form of the produced CuO NP, also indicates that the average size of nanoparticle by FESEM was 18 nm. It can be considered that the green synthesis of CuO NPs using *Euphorbia maculata* extract produces spherical particles in nano sizes.

3.5 | Specific surface area and porosity studies

The particle size, morphology, and density parameters depend on the specific surface area measurements ($m^2.g^{-1}$). The specific surface area determined by the BET method is 36.75 m^2/g and the estimated average pore diameter is approximately 27 nm. Also, the nitrogen

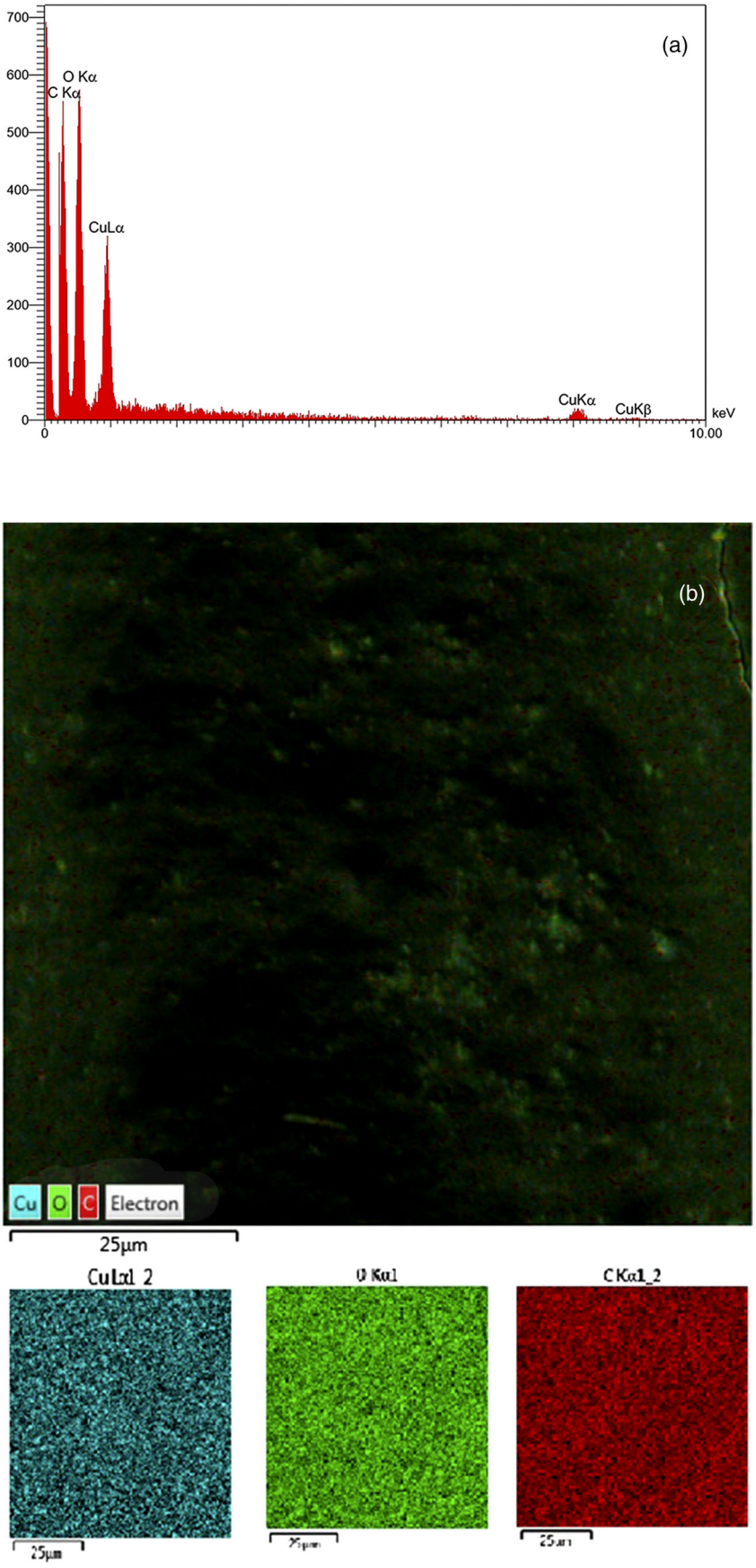


FIGURE 5 (a). Energy-dispersive X-ray (EDS) spectroscopy spectrum of Euphorbia maculata extract-mediatedsynthesized CuO NP, (b). EDS mapping analysis of CuO NP.

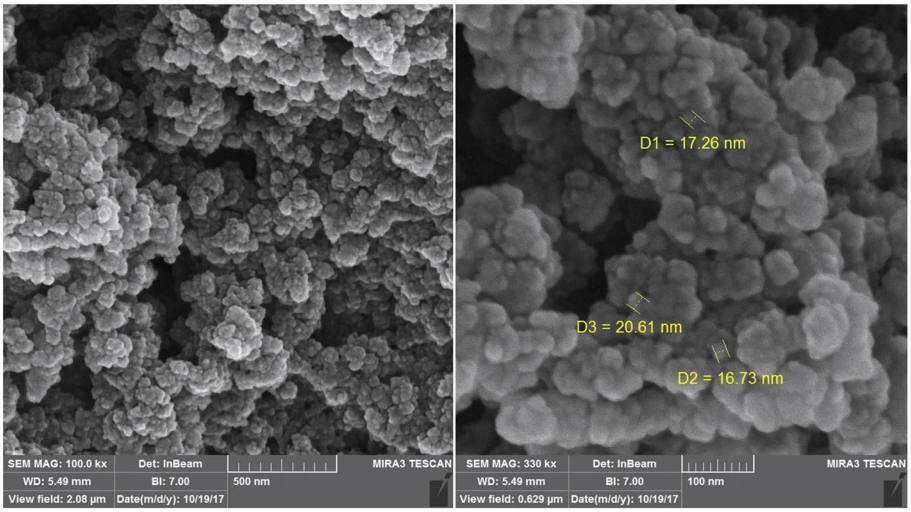


FIGURE 6 FESEM images of the green synthesized CuO NPs

adsorption–desorption isotherms for CuO NPs have been shown in Figure 7.

3.6 | TGA analysis

Thermogravimetric analysis of CuO NPs (Figure 8) shows three-step weight losses, the primary step is related to the loss of water molecules at the temperature below 150 °C. The second weight loss occurs at 150–300 °C and it is due to decomposition in a part of the organic content existing in the biosynthesized CuO NPs. The third weight loss happens at the temperature over 300 °C, and it is due to the presence of the remaining organic compounds and copper in the biosynthesized CuO NPs/plant extract.

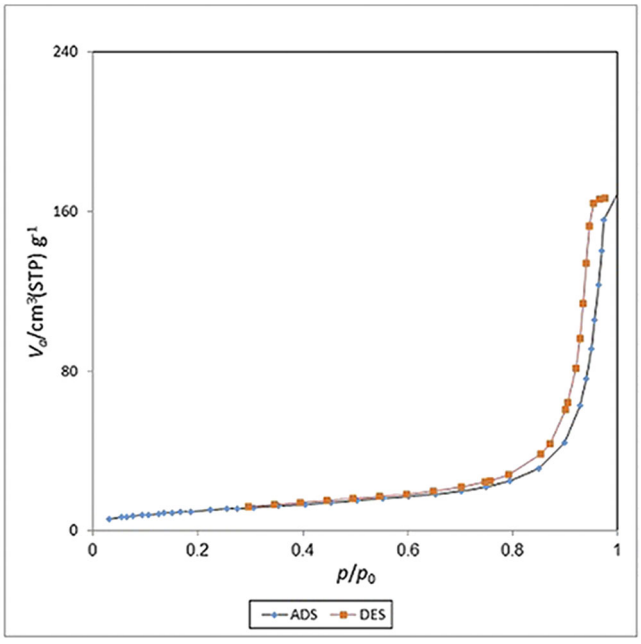


FIGURE 7 N2 adsorption/desorption isotherm of capped CuO NP by plant extract

3.7 | C-S coupling reaction

At first, 4-iodobenzene, 4-chlorothiophenol, and CuO NPs were examined as a model reaction in order to determine optimal reaction conditions. The effects of different solvents, bases and different amounts of CuO NP as a catalyst on the C-S cross-coupling reaction were investigated. Several solvents were tested, and great reaction yields were obtained using DMSO, toluene, and DMF as solvents (Table 1, entries 1, 6–9). Among these solvents, DMSO was found to be the most effective. H_2O is not a good choice for this reaction (Table 1, entry 8). It was found that potassium hydroxide gives an excellent

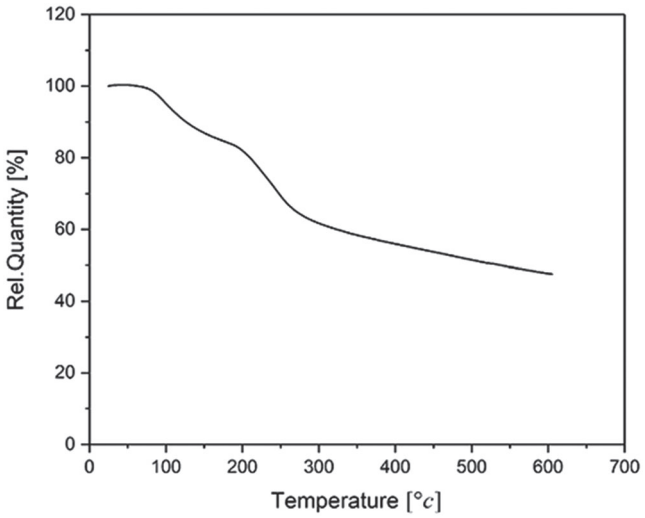


FIGURE 8 TG-DTA data measured for CuO NPs/plant extract

TABLE 1 Optimization of reaction conditions for the C-S cross-coupling reaction between 4-chlorothiophenol and iodobenzene using biosynthesized CuO NP as the catalyst

Entry	Base	Solvent	Catalyst amount(g)	Temperature(°C)	Yield (%)
1	KOH	DMSO	0.015	110	89
2	K_2CO_3	DMSO	0.015	110	45
3	Na_2CO_3	DMSO	0.015	110	30
4	Et_3N	DMSO	0.015	110	15
5	NaOH	DMSO	0.015	110	Trace
6	KOH	DMF	0.015	110	68
7	KOH	Toluene	0.015	110	<5
8	KOH	H_2O	0.015	Reflux	5
9	KOH	Ethanol	0.015	Reflux	35
10	KOH	DMSO	0.01	110	75
11	KOH	DMSO	0.007	110	45
12	KOH	DMSO	0.005	110	20
13	KOH	DMSO	0.02	110	89
14	KOH	DMSO	–	110	0
15	KOH	DMSO	0.015	80	65
16	KOH	DMSO	0.015	Room temperature	0
17	KOH	DMSO	0.015	130	89

General reaction conditions: 4-cholorothiophenol (1 mmol) and iodobenzene (1.1 mmol) were mixed together with bases (1.5 mmol) and biosynthesized CuO NP/plant extract as catalyst in various amounts in 1 ml solvent under nitrogen atmosphere. (Reaction time was 8 hrs)

reaction yield for the coupling reaction to diphenyl thioethers (Table 1, entry1); while, by using other bases, triethylamine, sodium carbonate, and potassium carbonate the reaction yields are moderate (entries 2–4); also using NaOH as a base gives a lower yield compared with other bases (entry 5).

The C-S coupling reaction was studied with various amounts of catalyst. It should be noted that a high reaction yield of 89% was achieved by using 0.015 g of CuO NP as a catalyst. It was observed that lower catalyst amounts decreased the reaction yield (Table 1, entry 12). However, increasing of catalyst amount to 0.02 g did not affect the yield of reaction (entry 13). This reaction without the catalyst was also investigated, but as expected; no product was produced (entry 14).

The temperature is effective in developing the reaction. When the reaction occurred at a high temperature (110 °C), the yield of the isolated product was 89% (Table 1, entry 1). However, increasing the temperature could not obviously improve the reaction yield (entry 17). A good reaction yield of 65% for the product was obtained when the reaction was performed at 80 °C (entry 15); while at the room temperature, no desired product was detected (entry 16). Increasing reaction time had no effect on the reaction yields and the results were similar.

Different catalysts were investigated in this model cross-coupling reaction and the results are presented in Table 2 (entries 1–9). Among these catalysts, biosynthesized CuO

TABLE 2 Screening of various catalysts for the formation of thioether under different conditions[a]

Entry	Catalyst	Base	Solvent	Yield[b] (%)	Reference
1	$CuSO_4$	Cs_2CO_3	DMSO	28	[63]
2	Cu $(OAc)_2$	Cs_2CO_3	DMSO	22	[63]
3	CuO powder	Cs_2CO_3	DMSO	24	[63]
4	CuI	K_2CO_3	DMSO	<3	[64]
5	$FeCl_3$	Cs_2CO_3	DMF	28	[65]
6	CuBr	KOH	DMF	56	[55]
7	Cu2O	KOH	DMF	42	[55]
8	CuO NP	KOH	DMSO	78	[66]
9	Biosynthesized CuO NP/plant extract	KOH	DMSO	89	This work

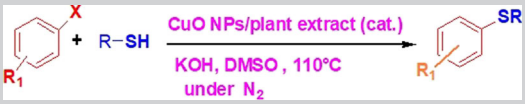
[a]Reaction conditions: thiophenol (1 mmol) and iodobenzene (1.1 mmol) were mixed together with bases (1.5 mmol) and various catalysts in 1 ml solvent under nitrogen atmosphere.

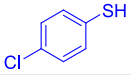
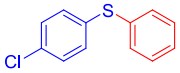
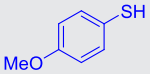
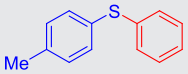
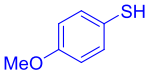
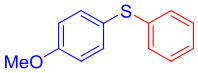
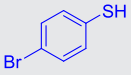
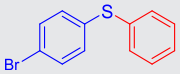
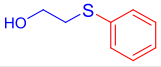
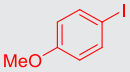
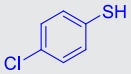
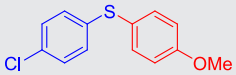
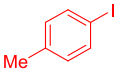
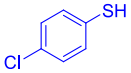
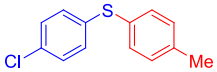
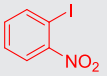
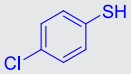
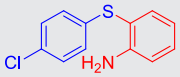
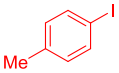
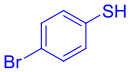
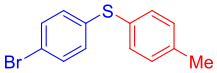
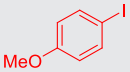
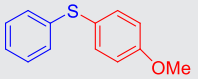
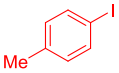
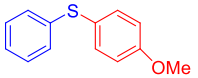
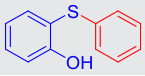
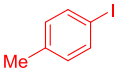
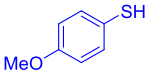
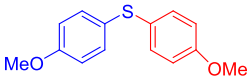
[b]Isolated yield.

NP/plant extract is an exceptionally efficient catalyst for C-S cross-coupling reaction. With this catalyst, a higher yield for the reaction is obtained compared to other catalysts.

After optimizing the reaction conditions, various aryl halides with different aryl and alkyl thiols were coupled in the presence of biosynthesized CuO NP as a catalyst (Table 3). Generally, it was observed that the C-S

TABLE 3 C-S cross-coupling reaction of thiols with aryl halides[a]



Entry	Aryl halide	Thiol	Product	Time (hr)	Yield[b] (%)
1				8	89
2				8	88
3				7	92
4				8	85
5				12	67
6				10	70
7				8	80
8				11	75
9				8	75
10				14	75
11				14	78
12				12	79
13				8	82
14				14	10
15				14	15
16				18	–

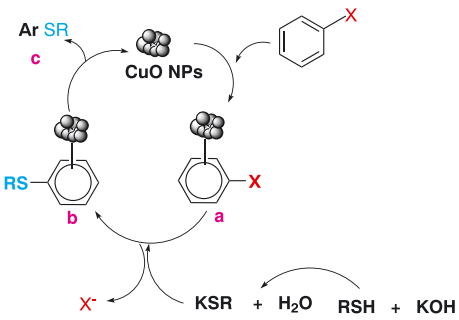
[a]Reaction conditions: Aryl halides (1.1 mmol), thiols (1 mmol), KOH (1.5 mmol), and biosynthesized CuO NP as catalyst (0.015 g) were mixed in DMSO (1 ml) at 110 °C under nitrogen atmosphere.

[b]Isolated yield.

cross-coupling reaction was performed with good to excellent yields. The results have indicated that the quiddity of functional groups plays the main role in reactivity of the coupling substrate. When electron-donating groups on thiols were used, the reaction yield was dramatically increased to 92% (Table 3, entries 2,3). Additionally, substrates with electron-donating groups in the aryl iodide were not appropriate partners for the C-S cross-coupling reaction, so the products were obtained with moderate yields (Table 3, entries 6–11).

As expected, the reactivity of aliphatic thiol with aryl iodide was not remarkable (entry 5). Furthermore, lower yields were observed when 4-iodobenzene was replaced by 4-bromobenzene under the same reaction condition (entries 14,15). On the other hand, a similar coupling reaction with chlorobenzenes was not successful (entry 16).

Finally, a feasible mechanism for the C-S coupling reaction was proposed.[67] This mechanism is described in Scheme 1. We hypothesize that prior coordination of the copper catalyst to the aromatic ring may provide intermediate (a). The aryl halide then undergoes a polarization that facilitates the substitution of the halide on the ring and brings about the formation of a copper-product complex. In the next step, the base removes the proton of thiol so a nucleophilic attack by thiol happens quickly. Moreover, the intermediate (a) reacts with the thiol to form an intermediate (b). In the final step, the release of the coupling product (c) restores the copper (II) catalyst.



SCHEME 1 A plausible mechanism for the c-s cross-coupling reaction using biosynthesized CuO NPs

3.8 | Catalyst reusability

Easy separation and steady reusability are two important factors for an effective heterogeneous catalytic system. The reusability of a catalytic system is necessary to develop a cost-effective and stable catalyst. Recycling capacity of this catalyst was examined for C-S cross-coupling reaction under the optimized reaction conditions of iodobenzene with 4-chlorothiophenol. After completion of the reaction; the catalyst was recovered by centrifugation techniques, washed with ethanol, dried under vacuum and then reused in the next cycle. The catalyst could be recycled four times with high activity and consistent activity as shown in Figure 9. Catalytic activity was approximately the same in the two initial cycles, but in the third cycle, the yield of reaction reduced to 82%. The catalytic activity of the CuO nanoparticle in the fourth cycle was also studied and an 80% yield was obtained.

We characterized the CuO NPs/plant extract heterogeneous catalyst by XRD and FESEM after performing the catalytic reaction as shown in Figure 10. The average size of the CuO NPs/plant extract after recycled four times was found to be ~26 nm which is very close to the 18 nm, the average size of the nanoparticles before the reaction. Therefore, the XRD, as well as FESEM analysis, plainly indicate clearly that the size and morphology of the CuO NPs/plant extract catalyst remain unchanged after performing the catalytic reaction.

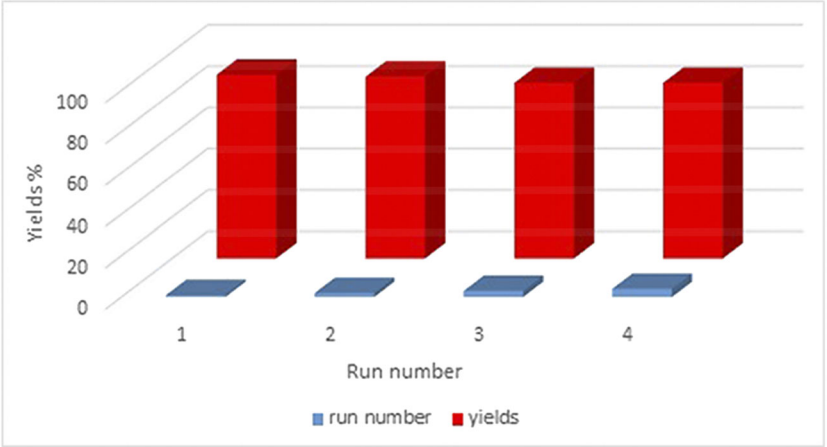


FIGURE 9 Reusability study of biosynthesized CuO NP/plant extract catalyst in C-S cross-coupling reaction. Reaction conditions: 4-choloro thiophenol (1 mmol), iodo benzene (1.1 mmol), KOH (1.5 mmol), biosynthesized CuO NP as catalyst (0.015 g) were mixed in DMSO (1 ml) at 110 °C under nitrogen atmosphere

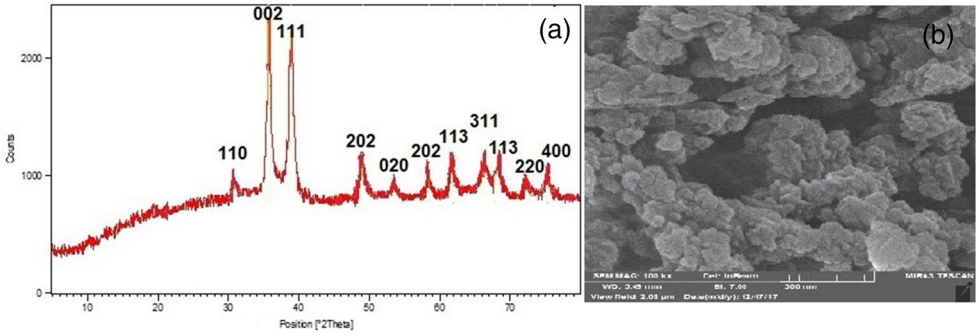


FIGURE 10 Characterization of the CuO NPs/plant extract catalyst after performing the reaction (a) XRD pattern, (b) FESEM image

The results confirm that biosynthesized CuO NP/plant extract is a versatile and efficient heterogeneous catalyst for the C-S cross-coupling reaction.

4 | CONCLUSION

In this study, an effective, easy, and cost-effective method for the biosynthesis of CuO NP by utilization the *Euphorbia maculata* aerial parts extracts as a reducing and stabilizing agent was presented. The plant extract was employed as an efficient and economic substitute of the chemical reagent or surfactant template, and also provided the bioprocess with the advantage of being environment-friendly. FESEM image of CuO NPs/plant extract confirmed the spherical shape and the nanoparticle size were found to be in the range of 18 nm. This novel copper oxide nanoparticle which was synthesized by the green method was used as a heterogeneous catalyst in a C-S cross-coupling reaction due to its high surface to volume ratio. The CuO NPs/plant extract was described to be inexpensive, air-stable, and highly efficient in C-S cross coupling. The cross-coupling of different thiols with aryl halides and their derivatives produced the coupling products in good or excellent yields in short reaction time. In addition, the catalyst could be easily separated from the catalytic system and it also could be recycled at least four times without a considerable loss of its catalytic activity as a heterogeneous system.

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