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Environmentally benign copper nanoparticles supported on walnut shell as a highly durable nanocatalyst for the synthesis of propargylamines

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Abstract: This study was an attempt to prepare copper nanoparticles and to determine their catalytic activity employing walnut shell (WS) residue as a green support and a reusable material. The nanocatalyst was characterized through inductively coupled plasma optical emission spectrometry (ICP-OES), N₂-sorption analysis, X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM). The catalytic performance of CuNPs@WS was then studied in the preparation of propargylamines *via* a three-component reaction. The catalyst could be recovered and reused without a significant decrease in its activity over eight reaction cycles. The simple methodology described herein is an economic, ecofriendly and practical method accompanied by higher yields.

Keywords: walnut shell; nanoparticles; reused material; copper; propargylamine.

INTRODUCTION

The waste production on the planet Earth is growing in mass and toxicity in consequence of economic development and population growth.¹ A solution to this problem is moving toward zero waste as a suitable approach to waste management that focuses on minimizing waste, reducing superfluous consumption, extending recycling, and the manufacture of materials that could be reused, reprocessed, or recycled.² Nowadays, there is growing concern about environmental problems resulting from chemical processes and materials, which has drawn much attention to the preparation of valuable and practical materials from residues as a relatively novel area.³ A solution to the problem of waste from chemical processes in the industry is replacement of classical stoichiometric reagents with efficient catalytic

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alternatives. Catalysts, as the most beneficial and practical substances, would be an appropriate subject for the application of reused waste in the context of green chemistry.⁴ The design of catalysts that have the advantages of being reusable, biodegradable and renewable, and which are readily available, cheap and of low toxicity is extremely challenging.

In recent years, heterogeneous catalysts containing metal nanoparticles have found a wide range of applications due to their high efficiency, emanating from their large surface-to-volume ratio, and because they are potentially environmentally friendly.⁵ Transition metal nanoparticles have already proven their utility in a multitude of industrial applications. In this regard, catalysis by copper is an area of substantial scientific exploration, especially with respect to developing new environmentally friendly catalysts.^{6–10}

Versatile heterogeneous copper catalysts immobilized by various supports, such as hydroxyapatite,¹¹ zeolite,¹² magnetic nanoparticles,¹³ carbon nanotubes,¹⁴ silica,¹⁵ mesoporous silica,¹⁶ titania,¹⁷ clay,¹⁸ graphene,¹⁹ functionalized polystyrene,²⁰ and metal–organic framework derived nanoporous carbon²¹ have been efficiently used to access propargylamines, which are key intermediates in the preparation of several biologically active nitrogen compounds.^{22–26} However, most of the supported catalysts have some disadvantages, such as low catalytic efficiency, complex preparation methods, disordered distribution of the active sites, and environmental problems.

One of the most significant advances to increasing environmental consciousness has been the immobilization of reagents and catalysts on biomaterial supports because of their renewability and biodegradability. Various natural polymers, such as cellulose,^{27,28} agarose,²⁹ chitosan³⁰ and starch,³¹ have been used as supports and stabilizers for copper compounds.

As part of ongoing interest in the development of new preparative routes in the use of recyclable and degradable heterogeneous catalysts based on biomaterials, herein a new approach to the synthesis, characterization, and application of copper nanoparticles supported on walnut shell (CuNPs@WS) was developed with green chemistry in mind. Walnut shell, as an agricultural by-product, is available in abundance from the walnut-processing industry and is used in abrasion,³² oil removal³³ and adsorption.^{34–36}

Copper nanoparticles supported on widely available, economic, renewable, biocompatible, and biodegradable matrices could be used as a green catalyst with potential industrial applications, particularly in organic synthesis. It is shown that the resulting nanocomposite, CuNPs@WS, has a catalytic effect on the reaction of various aldehydes, secondary amine, and the terminal alkyne in the generation of propargylamines *via* the A³ coupling reaction.

EXPERIMENTAL

Materials

All chemicals were purchased from Sigma–Aldrich or Merck chemical companies. Deionized water was used to prepare the chemical solutions and for rinsing. Purification was performed *via* column chromatography on silica gel 60 (*n*-hexane/ethyl acetate as eluent). For thin-layer chromatography (TLC), silica gel 60 F₂₅₄ plates were used to follow the reaction progress.

Instruments and measurements

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine metal concentrations. Fourier transform infrared (FTIR) spectra were obtained using a Bruker Vector 22 FTIR spectrophotometer under ambient conditions in KBr/Nujol mull in the wavenumber range 400–4000 cm⁻¹. The powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-ray powder diffractometer based on the CuK α line and in increment 2θ scanning steps of 0.07°. Nitrogen physisorption analysis was performed at the normal boiling point of liquid nitrogen using a BELSORP-max system. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were realized using a Tescan Vega system. For sample preparation, the powder samples were deposited on a carbon tape, and then mounted on an aluminum stub. The size and morphology of the particles were determined using a Philips CM120 electron spectroscopic microscope operated at 120 kV. ¹H- and ¹³C-NMR spectra were recorded at 250 and 62.9 MHz, respectively, in CDCl₃ using a Bruker Avance 250 MHz NMR spectrometer.

Preparation of CuNPs@WS

Walnut shells, collected from local fruit, were crushed and the resulting product was sieved to the desired particle size of < 88 μ m. In order to eliminate dust and soluble components, the residues were subsequently washed with deionized water and organic solvents. The prepared walnut shells were dried in an oven at 65 °C for 24 h and then stored in a desiccator.

In the next step, walnut shells (1.0 g) in deionized water (10.0 mL) were placed in a Schlenk flask under an argon atmosphere. The suspension was then subjected to sonication at 60 W for 45 min. Then, Cu(CH₃COO)₂·H₂O (0.15 mmol, 0.03 g) dissolved in 2.0 mL of H₂O was added gently to the suspension, and the slurry was stirred for 4 h at 750 rpm at room temperature. Then, a solution of NaBH₄ (0.45 mmol, 0.017 g) in water (25 mL) was added dropwise under an argon atmosphere, and the reaction mixture was stirred at 45 °C for 12 h. Finally, the material was collected by filtration, washed with deionized water, and dried under vacuum overnight.

General synthetic procedure for the A³ coupling reaction of aldehyde, amine, and the terminal alkyne

A mixture of aldehyde (1.0 mmol), secondary amine (1.2 mmol), terminal alkyne (1.5 mmol) and the nanocatalyst (0.3 g, 3 mol %) in 2.0 mL of acetonitrile was placed in a round-bottomed flask. The reaction mixture was stirred at 80 °C for 20 h under an argon atmosphere. After completion of the reaction, the catalyst was filtered, and the solvent was evaporated off under reduced pressure. The residue was purified *via* column chromatography on silica gel (*n*-hexane/ethyl acetate) to obtain the corresponding propargylamine. All products were verified based on their spectral analysis.

RESULTS AND DISCUSSION

Initially, walnut shell that is readily available in Iran³⁷ was prepared. The resulting support was then mixed with an appropriate concentration of copper(II) acetate. Next, the prepared slurry was reduced with sodium borohydride to afford the corresponding CuNPs@WS. The nanocatalyst was then characterized using multiple techniques to obtain insight into the structural features of the material.

The ICP-OES of CuNPs@WS shows the presence of 0.1 mmol g⁻¹ of copper. The porosity data of the WS and CuNPs@WS samples are given in Table I. The liquid nitrogen adsorption–desorption analysis of the samples demonstrated that walnut shell has a Brunauer–Emmett–Teller (BET) surface area of 10.09 m² g⁻¹ and a total pore volume of 0.029 cm³ g⁻¹ prior to the immobilization of nanoparticles. The average pore diameter is around 11.42 nm. The introduction of Cu species into the biomaterial matrix reduces its total pore volume and average pore diameter. This is in agreement with porosimetry results: a reduction to 0.020 cm³ g⁻¹ in the pore volume and an average pore diameter of approximately 5.46 nm. Moreover, the surface area is around 14.80 m² g⁻¹, which is more than that of the parent walnut shell (Figs. S-1 and S-3 of the Supplementary material to this paper). Nitrogen adsorption–desorption analysis of the catalyst exhibited a type III isotherm, which is generally observed for non-porous materials³⁸ (Figs. S-2 and S-4 of the Supplementary material).

TABLE I. Nitrogen adsorption–desorption characterization of the WS and CuNPs@WS samples

Entry	Catalyst	$a_s / \text{m}^2 \text{g}^{-1}$	Diameter, nm	Total pore volume, cm ³ g ⁻¹
1	WS	10.09	11.42	0.029
2	CuNPs@ WS	14.80	5.46	0.020

The FTIR spectra of WS and CuNPs@WS are shown in Fig. 1. A comparison of the spectra showed that all the vibrations of the support remained. The vibration peak at 3420 cm⁻¹ could be assigned to the vibration range of intra- and inter-molecular hydrogen bonded OH-groups. The vibration peaks associated with C–H, C=O, and C–O stretching were observed at 2902, 1743, and 1023 cm⁻¹, respectively. In addition, the peaks appearing at around 1600 and 1506 cm⁻¹ may be attributed to aromatic skeleton vibrations of lignin. A comparison of the spectra revealed that many characteristic bands shifted, or the signal intensity increased when the walnut shell powder was loaded with copper. These changes in FTIR spectra confirm the role of functional groups in metal binding.

The XRD pattern of the nanocatalyst exhibited the characteristic diffraction peaks of Cu at 2 θ positions of 34.7 and 42.1° (Fig. 2). The diffraction peaks are characteristic peaks of Cu₂O (JCPDS No. 05-0667) and Cu (JCPDS No. 04-0836), which indicate the presence of both Cu(0) and Cu(I) species in the sample. Reduction using a strong reducing agent NaBH₄ yielded both Cu(0) and Cu₂O.²⁸ The

broad peak appearing at around a 2θ value of 22.1° is attributable to cellulose (JCPDS No. 03- 0289).²⁷

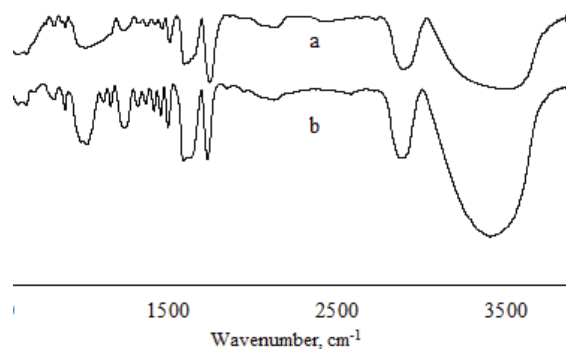


Fig. 1. FTIR spectra of: a) the WS biomaterial and b) the CuNPs@WS nanocatalyst.

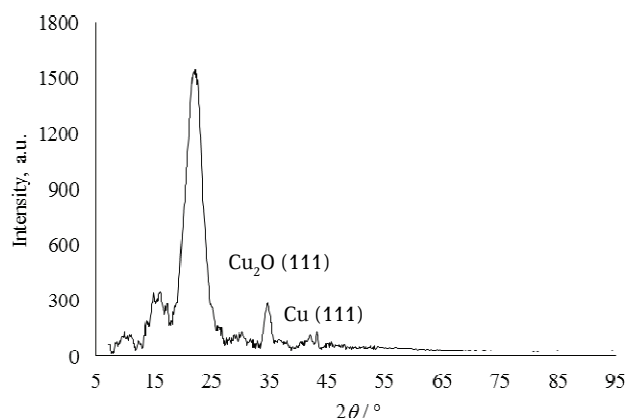


Fig. 2. X-Ray diffraction pattern of CuNPs@WS.

Furthermore, the EDS analysis of the CuNPs@WS catalyst showed carbon, oxygen, calcium and sodium peaks, which were derived from the walnut shell. As could be seen, the presence of the copper peaks proved that Cu had been successfully loaded onto the biomaterial (Fig. 3).

The TEM image of CuNPs@WS confirmed the presence of the CuNPs with an average diameter of 10–15 nm on the support (Fig. 4).

To study the catalytic performance of the CuNPs@WS nanocatalyst in the A³ coupling reaction, a model reaction of benzaldehyde, piperidine, and phenylacetylene was further optimized on the reaction parameters such as the solvent, temperature, and catalyst loading.

The effect of the solvent was studied under reflux conditions. The coupling reaction in CH₃CN at 80 °C was found to produce the best yield (Table II, Entry

4), the use of other solvents, such as CHCl_3 , CH_2Cl_2 , and THF, produced lower yields under the same reaction conditions (Table II, Entries 1–4). The effect of the reaction temperature was examined and it was found that reducing the temperature resulted in lower yields (Table II, Entries 4 and 5). A study of the three variations of catalyst loading (1–3 mol %) revealed that increasing the loading of the catalyst significantly enhanced the yield (Table II, Entries 4, 6 and 7). Moreover, no detectable product was found for the reaction in the presence of walnut shell alone, *i.e.*, not bearing copper nanoparticles, as the catalyst (Table II, Entry 8).

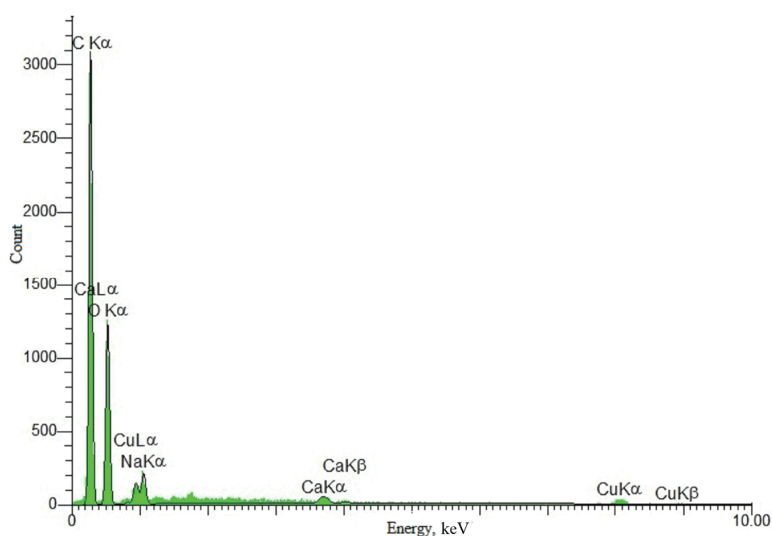


Fig. 3. Energy-dispersive X-ray spectrum of CuNPs@WS.

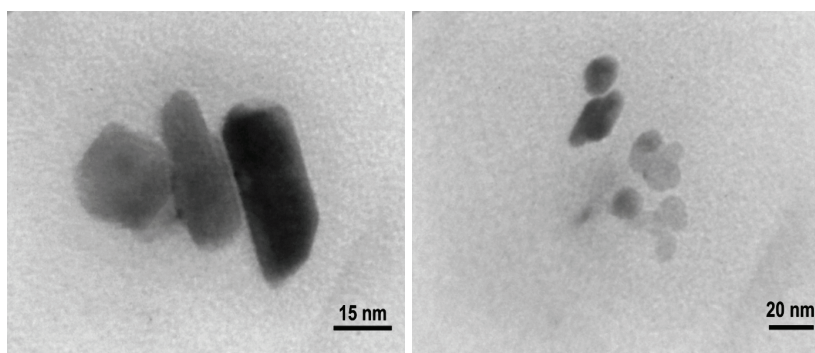
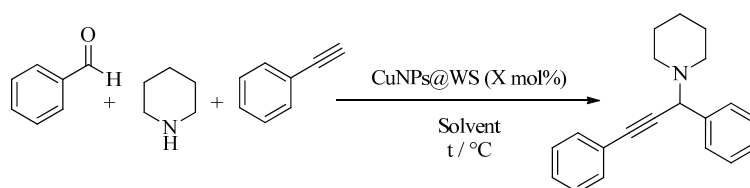


Fig. 4. Transmission electron microscopy images of CuNPs@WS.

Based on the optimized conditions, the scope and limitations of the novel nanocatalyst were examined for a variety of aldehydes and amines possessing different functional groups. As shown in Table III, the reaction with various alde-

hydes, such as aliphatic, aromatic and heterocyclic aldehydes, and cyclic amines, such as morpholine and piperidine, were found to proceed well, and propargylamines were produced in high yields without the generation of any traceable side product.

TABLE II. Optimization conditions for the three-component reaction of benzaldehyde, phenylacetylene, and piperidine using CuNPs@WS as a nanocatalyst; reaction conditions: benzaldehyde (1 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol), catalyst (X mol %), 2 mL solvent, Ar atmosphere, 20 h



Entry	X / mol %	Solvent	T / °C	Yield ^a , %
1	3	CH ₃ Cl	60	20
2	3	CH ₂ Cl ₂	40	40
3	3	THF	66	45
4	3	CH₃CN	80	91
5	3	CH ₃ CN	45	40
6	2	CH ₃ CN	80	70
7	1	CH ₃ CN	80	57
8	– ^b	CH ₃ CN	80	–

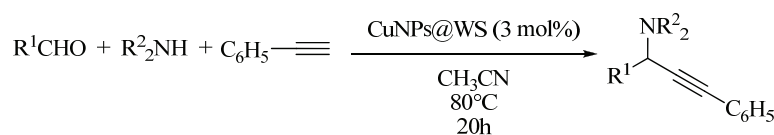
^aIsolated yield; ^bcatalyst: walnut shell (0.3 g)

Notably, this nanocatalyst had an equal effect on aromatic aldehydes bearing either electron-withdrawing or electron-donating groups, such as methoxy-, methyl-, bromo- and chloro-groups, and the respective propargylamines were produced in good to excellent yields. Moreover, heterocyclic aldehyde and 1-naphthaldehyde successfully reacted with piperidine and phenylacetylene to provide the corresponding coupling products (Table III, Entries 13 and 15). It is important to note that even an aliphatic aldehyde produced the corresponding product in high yield (Table III, Entry 16). These results strongly confirm the outstanding performance and generality of the CuNPs@WS nanocatalyst in terms of the catalysis of the three-component reactions.

The recoverability and reusability of the nanocatalyst were also examined *via* isolating the catalyst from the reaction of benzaldehyde, piperidine, and phenylacetylene under standard reaction conditions (Fig. 5). For this purpose, after the completion of the reaction, the reaction mixture was filtered and the catalyst was washed with acetonitrile. The catalyst was recovered and reused at least eight times, with its activity slowly decreasing over the repeated runs under

the same reaction conditions as before. The results proved the good durability, reusability, and recoverability of the CuNPs@WS nanocatalyst.

TABLE III. Three-component reactions of aldehydes, amines, and phenylacetylene in the presence of the CuNPs@WS nanocatalyst; conditions: aldehyde (1 mmol), amine (1.2 mmol), phenylacetylene (1.5 mmol), catalyst (3 mol %), acetonitrile (2 mL), 80 °C, Ar atmosphere, 20 h



Entry	R ¹	R ² NH	Yield ^a , %
1	C ₆ H ₅	Piperidine	91
2	C ₆ H ₅	Morpholine	85
3	4-OCH ₃ -C ₆ H ₄	Morpholine	89
4	4-CH ₃ -C ₆ H ₄	Morpholine	90
5	4-CH ₃ -C ₆ H ₄	Piperidine	86
6	4-CH ₃ -C ₆ H ₄	Pyrrolidine	76
7	3-CH ₃ -C ₆ H ₄	Piperidine	65
8	4-Br-C ₆ H ₄	Piperidine	90
9	4-Cl-C ₆ H ₄	Piperidine	83
10	2-Cl-C ₆ H ₄	Piperidine	89
11	2-Cl-C ₆ H ₄	Morpholine	87
12	2,4-Cl ₂ -C ₆ H ₃	Piperidine	84
13	1-Naphtyl	Piperidine	90
14	1-Naphtyl	Morpholine	83
15	2-Furanyl	Piperidine	85
16	Hexyl	Morpholine	87

^aIsolated yield

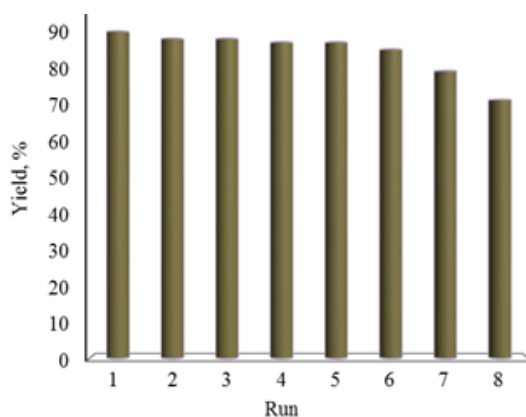


Fig. 5. Reusability of the CuNPs@WS nanocatalyst in the three-component reaction of benzaldehyde, piperidine, and phenylacetylene.

In another experiment, a filtration test was performed to determine the possibility of weakening the interaction between Cu nanoparticles and walnut shell.

To this end, the above-mentioned model reaction was performed under the same conditions. After 10 h and before the complete consumption of all the starting materials, the reaction mixture was filtered. A conversion percent of 43 % was obtained at this stage. Then, the reaction was allowed to continue for another 10 h. This brought about a conversion of 60 %, indicating negligible leaching. The leaching of copper species to reaction medium was 0.18 % as determined by ICP analysis.

In a final experiment, the catalytic performance of CuNPs@WS was compared with that of a number of previously reported copper nanoparticles containing heterogeneous catalysts in the synthesis of propargylamine from benzaldehyde, piperidine, and phenylacetylene (Table IV). The recycling properties of the nanocatalyst introduced in the present study were found to be superior to those of most of the previously reported catalytic systems. Moreover, in most other cases, the reaction was realized at a temperature higher than that employed for the present study. These findings confirmed the high efficiency of the present nanocatalyst in the A³ coupling reaction.

TABLE IV. A comparison of the CuNPs@WS nanocatalyst with the previously reported copper nanoparticles catalytic systems in the synthesis of propargylamine from benzaldehyde, piperidine, and phenylacetylene

Entry	Catalyst	Conditions	Recycling times	Yield, %	Ref.
1	CuNPs	MeCN, reflux, N ₂ , 6h	4	94	39
2	SiO ₂ -NHC-Cu ^{Ia}	Neat, 70 °C, N ₂ , 4 h	5	91	40
3	CuNPs/TiO ₂	Neat, 70 °C, 7 h	4	90	17
4	Cu/NCNT ^b	THF, 70 °C, N ₂ , 7 h	4	85	14
5	Cu ⁰ -Mont ^c	Toluene, 110 °C, 6 h	3	94	18
6	Cu/G ^d	Toluene, 100 °C, Ar, 24 h	–	84	19
7	CuNPs@MOF-5-C ^e	Toluene, 110 °C, N ₂ , 6 h	–	96	21
8	CuNPs@WS	MeCN, 80 °C, Ar, 20 h	8	91	This work

^aSilica-immobilized *N*-heterocyclic carbenes Cu(I) complexes; ^bcopper nanoparticles stabilized on nitrogen-doped carbon nanotubes; ^ccopper nanoparticles stabilized on modified montmorillonite; ^dcopper nanoparticles supported on graphene; ^ecopper nanoparticles supported on metal-organic framework derived nanoporous carbon

CONCLUSIONS

The present study used empirical findings to show the potential of walnut shell residue as a representative of biomaterials and green supports. The copper nanoparticles supported on walnut shell showed superior catalytic activity in the three-component coupling reaction of a wide range of aromatic, aliphatic, and heterocyclic aldehydes with secondary amines, and a terminal alkyne. The catalyst was reused and recycled for eight consecutive runs. This new material offers the advantages of being renewable, biodegradable, and stable under the reaction conditions. Considering the results, the stated simple methodology could be extended for the preparation of a large number of new nanocatalysts.

SUPPLEMENTARY MATERIAL

Additional data and the results of the characterization of the products are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ЕКОЛОШКИ ПОВОЉАН ПОСТУПАК СИНТЕЗЕ ПРОПАРГИЛАМИНА УПОТРЕБОМ
СТАБИЛНОГ НАНОКАТАЛИЗАТОРА ДОБИЈЕНОГ ИЗ НАНОЧЕСТИЦА БАКРА НА
СПРАШЕНОЈ ЉУСЦИ ОРАХА КАО НОСАЧУ

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Током истраживања припремљене су наночестице бакра (CuNPs) на спрашеној љусци ораха (WS) као еколошки прихватљивог носача, и испитана је њихова каталитичка активност. Нанокатализатор је окарактерисан индуктивно-куплованом оптичком емисионом спектрометријом (ICP-OES), N₂-сорпционом анализом, рендгенском анализом праха (XRD), енергетски дисперзионом рендгенском спектроскопијом (EDS), и трансмисионом електронском микроскопијом (ТЕМ). Каталитичке способности CuNPs@WS су испитане у синтези пропаргиламина у трокомпонентним реакцијама. Катализатор може да се регенерише и поново користи без значајнијег пада каталитичке активности током осам реакционих циклуса. Приказани поступак је једноставан, економичан, еколошки прихватљив, практичан и даје висок принос производа.

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