FULL PAPER

Applied Organometallic Chemistry

Anchoring Cu nanoparticles on functionalized multi-walled carbon nanotube for regioselective synthesis of 1,2,3-triazoles via click reaction

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Ferdowsi University of Mashhad, Grant/ Award Number: 3/47784 Unique properties of 1,2,3-triazoles on the one hand and necessity of usage of an efficient catalyst with fidelity in principles of green chemistry on the other hand impelled us to design and synthesis of a novel heterogeneous nanocatalyst (Cu@Arg-MWCNTs) with simple synthesis, immense power, high regioselectivity, and easy separation and recyclability. The Cu@Arg-MWCNT structure is characterized by different analyses and used for the synthesis of various triazoles. Its high catalytic activity is confirmed by high yields and short reaction times under mild conditions in click reaction.

K E Y W O R D S click, Cu@MWCNT, heterogeneous nanocatalyst, Huisgen, triazole

1 | INTRODUCTION

A wide range of benefits in medicinal chemistry,^[1] organic chemistry and synthesis as building blocks,^[2] catalysis and material science,^[3–5] polymer science,^[6] bioconjugation,^[7,8] drug discovery,^[9,10] industry,^[11] and agrochemical^[12] are the main reasons of inconsiderable interest to the 1,2,3-triazole family. According to this extensive utility, development of various synthetic methods is obvious.

Huisgen's 1,3-dipolar cycloaddition reaction of azides and alkynes^[13] as classical process for synthesis of 1,2,3-triazoles^[9,14] has high applicability and adaptability potentials. Simultaneously, deficiencies such as long reaction times at high temperature and low reaction rate and selectivity had restricted their use.^[15] In 2002, Tornøe et al.^[16] and Rostovtsev et al.^[17] independently used Cu(I) salts as a homogeneous catalyst in this reaction, which resulted in enormous transformation in this click reaction.^[18]

The copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) version of Huisgen reaction rectified most deficiencies of non-catalyzed version,^[18,19] among which are improvement of reaction conditions, promotion of

regioselectivity, and yield enhancement,^[20,21] but still demands more revision. Direct use of Cu(I) salts as homogeneous catalyst has been restricted not only for difficulty of their separation which results in contamination of product and recovery^[22] but also because of their instability and formation of alkyne homocoupling by-product.^[23] Furthermore, it would be better to do the reaction via an in situ multicomponent one-pot azidation in the presence of alkynes, sodium azide, and epoxide/ alkyl or aryl halides, instead of utilization of hazardous and toxic alky/aryl azides.^[24]

Inevitable interest of scientists to the synthesis of triazole derivatives has resulted in the emersion of vast and variable Cu catalysts,^[25] and as it was mentioned before, direct utilization of Cu(I) salt is not an intellectual choice. Instead, in situ preparation of active Cu(I) by reduction and oxidation of Cu(II) salts and Cu(0) metal, respectively, or combination of Cu (II)/Cu(0) seems to be much better elections.^[26] Wide range of ligands containing N, P, and S ^[27,28] or mixed of NN/NO/NS ^[29] and various supporting matrices such as zeolites,^[20,30] charcoals,^[24] montmorillonite,^[31] activated carbon nanotubes,^[32,33] graphene oxides,^[34,35] silica,^[36] and polymers^[37] have been used for preparation of an effective, easily recoverable, and reusable heterogeneous catalysts.^[12]

In recent decades, chemists' endeavor is fidelity in principles of green chemistry and utilization of them in reactions like click chemistry,^[38] so design and synthesis of a heterogeneous nanocatalyst as heart of the reaction is the most important factor to achieve this goal.^[39] Based on the investigations, supported copper nanoparticles (CuNPs) are considered to be much more effective catalysts for CuAAC reaction.^[40,41] According to these points, we became interested in design and synthesis of an efficient, eco-friendly, and novel heterogeneous nanocatalyst by means of a simple and inexpensive material and method in the presence of multi-walled carbon nanotubes (MWCNTs) and arginine and reduction of copper acetate monohydrate by using sodium borohydride in ethanol.

After synthesis and detection of the catalyst (Cu@Arg-MWCNT), its catalytic activity, regioselectivity, stability, easy recoverability, reusability, and alignment with green chemistry in click reaction (in the presence of sodium azide, phenylacetylene, and epoxide/alkyl or aryl halides in water medium and under mild condition) (Scheme 1) was evaluated, and acceptable results were obtained.

2 | EXPERIMENTAL

2.1 | Materials

MWCNTs (>95%, OD: 20–30) were obtained from US Research Nanomaterials, Inc. (3302 Twig Leaf Lane, Houston, TX 77084, USA). FeSO₄·7H₂O, H₂O₂, K₂CO₃, Cu(OAc)₂·H₂O, sodium borohydride, arginine, alkyl halides, epoxides, sodium azide, and EtOH and other solvents were manufactured by Merck and Sigma-Aldrich, and no more purification was needed.

2.2 | Equipment

The ultrasound energy was employed by using PARSONIC 15S (Pars Nahand Engg. Co., Iran) ultrasonic

bath. The PTFE MEMBRANES 0.22 µm (MF047PT022, filtraTECH, France) was used for filtration. UNIVERSAL 320 centrifuge from (Pole Ideal Tajhiz Co., Iran) was used for centrifugation. Melting points of the products were determined with a Thermo Scientific IA9200 (Electrothermal Engineering) melting point apparatus. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 precoated silica gel plate (0.2 mm thickness) and examined under ultraviolet (UV) light. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Fourier spectrophotometer (USA) using KBr discs. The mass spectra of compounds were recorded on a 5973Network Mass Selective Detector. The LC/MS/MS system AB SCIEX 3200 QTRAP was used for identification of the product (Table 2, Entry 7). Morphology studies of the prepared samples were carried out using a LEO-1450VP microscope (Germany) scanning electron microscope (SEM). Field emission scanning electron microscope (FE-SEM) images and energy-dispersive X-ray spectroscopy (EDX) were recorded using a TES-CAN BRNO-Mira3 LMU with gold coating equipped to determine the elemental compositions. The Zeiss Leo 912 OMEGA (120 kV) transmission electron microscope (TEM) (Germany) was used to record TEM images and determine the shape and morphology of the synthesized Cu@Arg-MWCNT nanocatalyst. ¹H and ¹³C NMR spectra were measured, respectively, at 300 and 75 MHz with tetramethylsilane (TMS) as internal reference (CDCl₃ and acetone-d6) on Bruker DRX300 AVANCE spectrometer. The content of the metal cations was recorded by inductively coupled plasma optical atomic emission spectrometer (ICP-AES) analysis with a Varian Vista-PRO CCD (Australia). Powder X-ray diffraction (XRD) patterns were obtained by use of X-ray diffractometer (Bruker D4 Endeavor) with Ni-filtered Cu K_{α} radiation in the angle 20 ranging from 20 to 80° (40 kV, 30 mA). Nanoparticle size dispersion was determined by applying a particle size analyzer (Vasco3, Cordouan, France), which can measure the dispersion between 0.5 nm and 6 µm. Thermogravimetric analysis (TGA) measurements were carried out on a Shimadzu TGA-50 under air atmosphere at a heating rate of 10°C/min.





2.3 | Preparation of catalyst

2.3.1 | Functionalization of MWCNT-OH with epibromohydrin (EP-MWCNT)

At the first step, synthesis of hydroxylated MWCNTs (MWCNT-OH) was performed according to method discussed in previously reported article.^[42]

MWCNT-OH (0.5 g) and epibromohydrin (2.5 mL) in the presence of absolute EtOH (50 mL) were sonicated for 20 min at room temperature; then, the mixture was stirred at 60°C, and after 24 h, the produced EP-MWCNTs were centrifuged and washed truly with absolute EtOH and dried in the oven at 50° C.

2.3.2 | Functionalization of MWCNTs with L-arginine (Arg-MWCNT)

A mixture of EP-MWCNT (0.5 g), K_2CO_3 (4 mmol), and L-arginine (5 mmol) in the presence of absolute EtOH (250 mL) in a round-bottom flask was first sonicated 20 min for better dispersion, and then, the flask content was refluxed for about 40 h. Finally, Arg-MWCNT was separated by centrifugation, washed exactly with EtOH, and dried under vacuum at 50°C.

2.3.3 | Synthesis of Cu@Arg-MWCNT

In a two-neck round-bottom flask, Arg-MWCNT (0.5 g) in the presence of absolute EtOH (70 mL) was dispersed via sonication for 20 min. Then, $Cu(OAc)_2 \cdot H_2O$ (1.5 mmol) was added, and the mixture was stirred under argon atmosphere at room temperature for 4 h; in follow-up, NaBH₄ (0.5 g) suspension in ethanol (10 mL) was injected drop by drop to the flask content and let it magnetically stirred under argon atmosphere for 48 h. Finally, the residue was centrifuged and washed with EtOH to remove excess NaBH₄; then, the produced Cu@Arg-MWCNT was dried under vacuum at 50°C.

3 | GENERAL PROCEDURE FOR SYNTHESIS OF 1,4-DISUBSTITUTED 1,2,3-TRIAZOLES

3.1 | General procedure for synthesis of triazoles in the presence of epoxides

In a model reaction, a mixture of phenylacetylene (1 mmol), sodium azide (1.1 mmol), and epoxides (1 mmol) in the presence of Cu@Arg-MWCNT (0.01 g or

2 mol% Cu) in water (0.5 mL) was sonicated for 2 min, and the suspension was stirred at 70°C for appropriate time. Upon the completion of the reaction, which was defined by TLC, catalyst simply was removed from the reaction mixture by centrifugation. The separated catalyst was washed with hot methanol (3 \times 10 mL) and dried in the oven (50°C) to be ready for the next run. The resulting mixture was diluted with distilled water (10 mL) and extracted with EtOAc (3×10 mL), and then, the organic layer was washed with saturated brine and finally dried over anhydrous Na₂SO₄. The solvent removal in the following and recrystallization of the crude product with EtOH:H₂O (3:1) resulted in pure β-hydroxy-1,4-disubstituted 1,2,3-triazole derivatives (Table 2, Entries 1–10). Melting point, FT-IR, mass, ¹H NMR, and ¹³C NMR spectroscopies were used for identification and characterization of the products. The synthesized new compound (4 g) was also characterized successfully by use of ¹H NMR, ¹³C NMR, FT-IR, and LC/MS/MS studies, which are readily available in Figures S1-S6

3.1.1 | Spectral data of representative compounds

2-(4-Phenyl-1H-1,2,3-triazol-1-yl)cyclohexan-1-ol (Table 2, Entry 1) (**4a**)



White solid, m.p.: $177-179^{\circ}$ C (Lit.^[32] $179-180^{\circ}$ C). FT-IR (KBr, ν , cm⁻¹): 698 (s), 769 (s), 978 (w), 1055 (s), 1080 (s), 1236 (s), 1463 (s), 1609, 1579 (s), 2864 (w), 2942 (s), 3122 (m), 3309 (br). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.82 (s, 1H), 7.79 (d, 2H, J = 7.2), 7.46–7.41 (m, 2H), 7.38–7.33 (m, 1H), 4.27–4.08 (m, 2H), 3.19 (s, 1H, OH), 2.30–2.26 (m, 2H), 2.04–1.93 (m, 2H), 1.61–1.44 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 146.9, 130.2, 128.7, 128.0, 125.5, 119.7, 72.6, 67.2, 33.7, 31.5, 24.8, 24.0. MS (m/z): 243 (M⁺).

1-(4-Phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 2, Entry 2) (**4b**)

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White solid, m.p.: 114–116°C (Lit.^[43] 114–116°C). FT-IR (KBr, ν , cm⁻¹): 517 (m), 697 (s), 762 (s), 819 (m), 981 (m), 1088 (s), 1139 (s), 1230 (m), 1370 (w), 1429 (m), 1465 (m), 1612 (w), 2964 (m), 3145 (m), 3263 (b). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.90 (s, 1H), 7.83 (d, 2H, J = 6.9 Hz), 7.47–7.42 (m, 2H), 7.38–7.34 (m, 1H), 4.52 (dd, 1H, ¹J = 13.3, ²J = 2.1), 4.43–4.27 (m, 2H), 2.11 (s, broad, OH), 1.35 (d, 3H, J = 6.3 Hz). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 147.0, 130.3, 128.8, 128.2, 125.7, 121.1, 66.7, 57.2, 30.9. MS (m/z): 203 (M⁺).

1-(4-Phenyl-1H-1,2,3-triazol-1-yl)butan-2-ol (Table 2, Entry 3) (**4c**)



White powder m.p.: 111–113°C (Lit.^[34] 110–112°C). FT-IR (KBr, ν , cm⁻¹): 695 (s), 764 (s), 826 (w), 981 (m), 1091 (s), 1137 (s), 1229 (m), 1467 (m), 1633 (m), 2872 (m), 2933 (m), 2960 (m), 3140 (m), 3255 (s), 3411 (b). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.88 (s, 1H), 7.81–7.78 (m, 2H), 7.45–7.35 (m, 3H), 4.55 (dd, 1H, ¹J = 13.8 Hz, ²J = 2.7 Hz), 4.34–4.27 (m, 1H), 4.14–4.08 (m, 1H), 3.03 (broad, 1H, OH), 1.68–1.57 (m, 2H), 1.1 (t, 3H, J = 7.41 Hz). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 147.3, 130.3, 129.2, 128.8, 128.2, 125.6, 71.8, 55.8, 27.5, 9.8. MS (m/z): 217 (M+).

1-(*Allyloxy*)-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (*Table 2*, *Entry 4*) (**4d**)



White solid, m.p.: 70–72°C (Lit.^[32] 70–72°C). FT-IR (KBr, ν , cm⁻¹): 696 (s), 767 (s), 827 (m), 921 (m), 1090 (s), 1110 (s), 1364 (m), 1433 (m), 1647 (w), 2930 (m), 3140 (m), 3239 (b). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.94 (s, 1H), 7.85 (dd, 2H, ¹J = 8.4, ²J = 1.5), 7.48–7.43 (m, 2H), 7.39–7.35 (m, 1H), 6.00–5.87 (m, 1H), 5.35–5.24 (m, 2H), 4.64 (dd, 1H, ¹J = 14.1 Hz, ²J = 3.6 Hz), 4.49 (dd, 1H, ¹J = 14.1 Hz, ²J = 8.4 Hz), 4.34–4.25 (m, 1H), 4.06 (td, 2H, ¹J = 5.7 Hz, ²J = 1.2 Hz), 3.57 (dd, 1H, ¹J = 9.6 Hz, ²J = 4.8 Hz), 3.45 (dd, 1H, ¹J = 9.6 Hz, ²J = 6 Hz), 2.14 (s, broad, 1H, OH). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 147.7, 139.9, 130.3, 128.8, 128.2, 125.7, 121.2, 117.8, 72.4, 70.8, 69.3, 53.0. MS (m/z): 259 (M⁺).

1-Butoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 2, Entry 5) (**4e**)



White solid, m.p.: $64-66^{\circ}$ C (Lit.^[43] $66-68^{\circ}$ C). FT-IR (KBr, ν , cm⁻¹): 697 (s), 766 (s), 826 (m), 981 (m), 1089 (s), 1115 (s), 1229 (m), 1467 (m), 1611 (w), 2866 (s), 2929 (m), 2953 (s), 3139 (m), 3257 (b). ¹H NMR (300 MHz, acetoned6) δ ppm: 8.34 (s, 1H), 7.94–7.91 (m, 2H), 7.48–7.31 (m, 3H), 4.66 (dd, 1H, ¹J = 13.8 Hz, ²J = 3.6 Hz), 4.46 (dd, 1H, ¹J = 13.8 Hz, ²J = 7.5 Hz), 4.21 (broad, 1H), 3.54–3.44 (m, 4H), 1.63–1.53 (m, 2H), 1.48–1.36 (m, 2H), 0.94 (t, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 147.4, 130.4, 128.8, 128.1, 125.7, 121.2, 71.5, 71.4, 69.2, 53.0, 31.6, 19.2, 13.8. MS (m/z): 275 (M⁺).

1-Isopropoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 2, Entry 6) (**4f**)



White powder, m.p.: $62-64^{\circ}C$ (Lit.^[44] $62-64^{\circ}C$). FT-IR (KBr, ν , cm⁻¹): 695(w), 766 (m), 1086 (s), 1125 (s), 1383 (m), 1466 (m), 1647 (w), 2971 (w), 3411 (b). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.95 (s, 1H), 7.89–7.86 (m, 2H), 7.49–7.44 (m, 2H), 7.39–7.36 (m, 1H), 4.63 (dd, 1H, ¹*J* = 14.1 Hz, ²*J* = 3.9 Hz), 4.50 (dd, 1H, ¹*J* = 14.1 Hz, ²*J* = 6.6 Hz), 4.27–4.20 (m, 1H), 3.68–3.60 (m, 1H), 3.55 (dd, 1H, ¹*J* = 9.4 Hz, ²*J* = 4.8 Hz), 3.38 (dd, 1H, ¹*J* = 9.4 Hz, ²*J* = 6.3 Hz), 2.20 (s, broad, 1H, OH), 1.20 (dd, 6H, ¹*J* = 6 Hz, ²*J* = 1.8 Hz). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 146.9, 130.4, 128.8, 128.1, 125.7, 72.5, 69.4, 68.8, 53.1, 22.0. MS: m/z (%): 261 (M⁺).

1-(tert-Butoxy)-3-(4-phenyl-1H-1,2,3-triazol-1-yl) propan-2-ol (Table 2, Entry 7) (**4g**)



Pale yellow crystal, m.p.: 77-79°C (new) FT-IR (KBr, ν , cm⁻¹): 694 (s), 765(s), 1080 (s), 1100 (s), 1196 (s), 1227 (m), 1362 (s), 1440 (m), 1465 (m), 1484 (m), 1613 (w), 2973 (s), 3133 (w), 3344 (b). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.97 (s, 1H), 7.87 (d, 2H, J = 7.2 Hz), 7.48-7.43 (m, 2H), 7.39–7.34 (m, 1H), 4.63 (dd, 1H, ${}^{1}J = 13.9$, Hz $^{2}J = 3.9$ Hz), 4.48 (dd, 1H, $^{1}J = 14.1$ Hz, $^{2}J = 6.9$ Hz), 4.24–4.16 (m, 1H), 3.49 (dd, 1H, ${}^{1}J = 9.1$, ${}^{2}J = 4.8$ Hz), 3.36 (dd, 1H, ${}^{1}J = 9.1$ Hz, ${}^{2}J = 6$ Hz), 2.55 (s, broad, 1H, OH), 1.23 (s, 9H $[3 \times CH_3]$). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 147.2, 130.4, 128.7, 128.0, 125.5, 121.3, 73.5, 69.5, 62.9, 53.5, 27.4. MS (m/z): 275 (M⁺). LC/MS/MS studies on compound (4g) were done, and its mass spectra has been shown in Figure S6. Compound (4g) gave $[M + H]^+$ ion at m/z = 276.165 and $[M + Na]^+$ adduct ion at m/zz = 298.148.

1-(3-Methoxyphenoxy)-3-(4-phenyl-1H-1,2,3-triazol-1-yl) propan-2-ol (Table 2, Entry 8) (**4**h)



White powder, m.p.: 97–99°C (Lit.^[35] 99–100°C). FT-IR (KBr, ν , cm⁻¹): 688 (m), 764 (s), 1048 (s), 1154 (s), 1201 (s), 1265 (m), 1288 (s), 1492 (s), 1602 (s), *2834* (m), *2871* (m), 2930 (m), *2961* (m), 3144 (w), 3382 (b). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.91 (s, 1H), 7.76 (d, 2H, J = 7.2 Hz), 7.44–7.32 (m, 3H), 7.25–7.20 (m, 1H), 6.60– 6.52 (m, 3H), 4.79–4.72 (m, 1H), 4.64–4.46 (m, 2H), 4.16 (s, 1H), 4.06–3.95 (m, 2H), 3.81 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 160.9, 159.5, 159.3, 147.8, 130.2, 130.1, 128.8, 128.2, 125.6, 107.1, 106.6, 101.2, 68.9, 67.8, 55.3, 53.1. MS (m/z): 325 (M⁺).

1-Phenoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (Table 2, Entry 9) (**4i**)



White crystal, m.p.: 124–126°C (Lit.^[35] 124–127°C). FT-IR (KBr, ν , cm⁻¹): 692 (s), 752 (s), 1043 (m), 1079 (m), 1173 (w), 11248 (s), 1496 (s), 1599 (s), 2933 (w), 3084 (w), 3397 (br). ¹H NMR (300 MHz, CDCl₃) δ ppm:

7.92 (s, 1H), 7.78 (d, 2H, J = 7.2 Hz), 7.45–7.40 (m, 2H), 7.37–7.31 (m, 3H), 7.03 (t, 1H), 6.95 (d, 2H), 4.79–4.73 (m, 1H), 4.63–4.55 (m, 2H), 4.11–4.03 (m, 2H), 2.98 (broad, 1H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 158.09, 147.60, 129.67, 129.55, 128.87, 128.25, 125.70, 121.62, 121.40, 114.57, 68.95, 68.8, 53.13. MS (m/z): 295 (M⁺).

2-Phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-ol (Table 2, Entry 10) (**4j**)



Pale yellow solid, m.p.: $123-125^{\circ}$ C (Lit.^[13] 125-127°C). FT-IR (KBr, ν , cm⁻¹): 690 (s), 763 (s), 1074 (s), 1235 (m), 1454 (m), 1482 (m), 1605 (w), 2928 (m), 3155 (m), 3215 (br). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.82 (d, 2H), 7.75 (s, 1H), 7.56 (dd, 1H, ¹J = 6 Hz, ²J = 3 Hz), 7.46-7.36 (m, 6H), 7.31 (s, 1H), 5.73-5.71 (m, 1H), 4.67 (dd, 1H, ¹J = 12 Hz, ²J = 8.1 Hz), 4.28-4.24 (m, 1H), 2.86 (broad, 1H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 147.6, 136.0, 132.9, 129.2, 129.1, 128.8, 128.3, 127.1, 125.7, 67.3, 65.3. MS (m/z): 265 (M⁺).

3.2 | General procedure for synthesis of triazoles in the presence of alkyl halides

In a model reaction, a mixture of phenylacetylene (1 mmol), sodium azide (1.1 mmol), and alkyl halides (1 mmol) in the presence of Cu@Arg-MWCNT (0.01 g or 2 mol% Cu) in water medium (0.5 mL) was sonicated for 2 min, and the suspension was stirred at 70°C for appropriate time. Upon the completion of the reaction, which was defined by TLC, catalyst simply was removed from the reaction mixture by centrifugation. The separated catalyst was washed with hot methanol (3 \times 10 mL) and dried in the oven (50°C) to be ready for the next run. The resulting mixture was diluted with distilled water (10 mL) and extracted with EtOAc (3 \times 10 mL), and then, the organic layer was washed with saturated brine and finally dried over anhydrous Na₂SO₄. The solvent removal in the following and recrystallization of the crude product with EtOH:H₂O (3:1) resulted in pure 1,4-disubstituted 1,2,3-triazole derivatives (Table 2, Entries 11–16). Melting point, FT-IR, mass, ¹H NMR, and ¹³C NMR spectroscopies were used for identification and characterization of the products.

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3.2.1 | Spectral data of representative compounds

1-Benzyl-4-phenyl-1H-1,2,3-triazole (Table 2, Entries 11, 14) (**4**k)

White crystal, m.p.: 128–130°C (Lit.^[44] 127–129°C). FT-IR (KBr, ν , cm⁻¹): 695 (s), 730 (s), 768 (s), 1044 (m), 1074 (m), 1223 (m), 1361 (w), 1450 (m), 2973 (w), 3141 (w). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.85–7.82 (m, 2H), 7.69 (s, 1H), 7.46–7.39 (m, 5H), 7.37–7.33 (m, 3H), 5.6 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 148.2, 134.7, 130.5, 129.1, 128.8, 128.1, 128.0, 125.7, 119.4, 54.2. MS (m/z): 235 (M⁺).

1-(3-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (Table 2, Entry 12) (**4**)



White solid, m.p.: $148-150^{\circ}$ C (Lit.^[45] $148-152^{\circ}$ C). FT-IR (KBr, ν , cm⁻¹): 692 (m), 725 (s), 764 (s), 811 (w), 1075 (w), 1353 (s), 1465 (w), 1518 (s), 1612 (w), 2953 (w), 3084 (w), 3141 (w). ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.27-8.25 (m, 2H), 7.86–7.84 (m, 2H), 7.81 (s, 1H), 7.68–7.61 (m, 2H), 7.48–7.43 (m, 2H), 7.39–7.35 (m, 1H), 5.73 (s, 1H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 145.9, 136.8, 133.8, 130.3, 128.9, 128.4, 125.7, 123.8, 122.8, 119.5, 53.2. MS (m/z): 280 (M⁺).

1-(4-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (Table 2, Entries 13, 15) (**4m**)



Yellow solid, m.p.: $154-156^{\circ}$ C (Lit.^[23] 156-157°C). FT-IR (KBr, ν , cm⁻¹): 692 (m), 732 (m), 763 (m), 1045 (w), 1078 (w), 1222(w), 1351 (s), 1519 (s), 1465 (w), 1607 (w), 3084 (w), 3125 (w). ¹H NMR (300 MHz, CDCl₃) δ ppm: 8.28 (d, 2H, J = 8.4 Hz), 7.86 (d, 2H, J = 6.9 Hz), 7.78 (s, 1H), 7.50–7.46 (m, 3H), 7.43–7.39 (m, 2H), 5.74 (s. 2H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 148.1, 141.7, 130.1, 128.9, 128.5, 128.5, 125.7, 124.3, 121.0, 119.7, 53.7. MS (m/z): 280 (M⁺).

1-(4-Chlorobenzyl)-4-phenyl-1H-1,2,3-triazole (Table 2, Entry 16) (**4n**)



Pale yellow cottony solid, m.p.: 141–143°C (Lit.^[46] 143–144°C). FT-IR (KBr, ν , cm⁻¹): 694 (s), 764 (s), 809 (s), 1018 (s), 1095 (s), 1217 (s), 1411 (m), 1460 (s), 1492 (s), 1597 (m), 1687 (w), 2998 (w), 3084 (m), 3125 (m). ¹H NMR (300 MHz, CDCl₃) δ ppm: 7.85 (d, 2H, J = 7.2 Hz), 7.75 (s, 1H), 7.46–7.37 (m, 5H), 7.35–7.29 (m, 2H), 5.57 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 148.2, 134.8, 133.2, 130.4, 129.3, 129.1, 128.8, 128.3, 125.7, 53.5. MS (m/z): 269 (M⁺).

4 | RESULTS AND DISCUSSION

4.1 | Characterization of Cu@Arg-MWCNT

Cu@Arg-MWCNT was synthesized, through the pathway defined completely and shown in Scheme 2, as a novel, green, powerful, recoverable, and reusable nanocatalyst. After hydroxylation of MWCNTs via Fenton reaction followed by reaction with epibromohydrin, utilization of L-arginine amino acid as a natural ligand was our next strategy in approaching to principles of green chemistry. As the final step in the synthesis of our desired nanocatalyst, we should immobilize Cu(0) nanoparticles (CuNPs) on the Arg-MWCNTs by means of reduction of Cu(II) salt in the presence of NaBH₄. Results from different characterization techniques such as FT-IR, XRD, EDX, TGA, inductively coupled plasma (ICP), element maps analysis (elemental mapping), a particle size analysis (PSA), scanning electron microscopy (SEM), FE-SEM, and TEM confirmed the successful synthesize of the Cu@Arg-MWCNT catalyst.

Figure 1 shows comparative FT-IR spectral data of pristine MWCNT (p-MWCNT), MWCNT-OH, EP-MWCNT, Arg-MWCNT, and Cu@Arg-MWCNT, respectively, from bottom to top. As it can be seen in Figure 1a, the FT-IR spectrum of the p-MWCNT showed a band at

SCHEME 2 Preparation of Cu@Arg-MWCNT



FIGURE 1 Comparative FT-IR spectra of (a) p-MWCNT, (b) MWCNT-OH, (c) EP-MWCNT, (d) Arg-MWCNT, and (e) Cu@Arg-MWCNT



 3444 cm^{-1} , which can be assigned to the -OH stretching vibrations of adsorbed water. The bands that appeared at 2925 and 2856 cm^{-1} can be assumed for C–H stretching vibrations, and a peak at 1631 cm^{-1} is referred to C=C stretching vibrations due to the graphitic structure of MWCNTs. Appearance of a broad peak at 3428 cm^{-1} in Figure 1b corresponds to the stretching vibrations of the OH group, which is a confirmation on great hydroxylation of the p-MWCNTs. Comparison of the peak area of NH or OH, as it can be seen in Figure 1, reveals logical increase or decrease in peak area depending on their functionalization. In Figure 1c, peaks at 2902 and 1376 cm⁻¹, respectively, belong to the C-H stretching of methylene groups of 2-methyloxirane and C-H bending, the peak at 1552 cm^{-1} corresponds to C=C stretching of the MWCNTs, and a strong peak 1022 cm⁻¹ corresponds to C–O stretching of aliphatic ether. In Figure 1d, appearance of a peak with intense absorption at 3439 cm^{-1} is assigned to the N–H stretching, and a peak at 2920 cm^{-1} is referred to C-H stretching. COO⁻ asymmetric and symmetric stretching vibrations at 1645 and 1551, respectively, confirm that the L-arginine has been attached from its guanidinium part. A peak at 1065 corresponds to stretching vibration of secondary alcohol. Appearance of a new peak at 586 in the spectrum of the final catalyst (Figure 1e) that refers to Cu-N stretching vibration confirms the coordination of copper with organic ligand.

The X-ray diffraction patterns of the Arg-MWCNT and Cu@Arg-MWCNT are shown in Figure 2. XRD analysis was used in order to study the crystalline structure of Cu@Arg-MWCNT (Figure 2b). The diffraction peaks were observed in $(2\theta [^{\circ}]) = 43.3$, 51.2, and 74.6, which correspond to (111), (200), and (220) planes of FCC lattice of metallic CuNPs. CuNPs' sensitivity to the oxygen in

the air results in their oxidation to the copper(I) oxide (Cu₂O). So, according to JCPDS reference no 05-0667, weak diffraction peaks at around $(2\theta [^{\circ}]) = 29, 36.7, 42.65, 61.35, and 73.3$ could be attributed to (110), (111), (200), (220), and (311) planes of Cu₂O, respectively.^[47] MWCNT is characterized by a sharp peak with high intensity at $(2\theta [^{\circ}]) = 26^{\circ}$ corresponding to (002) plane indices of MWCNT,^[48] which is clearly notified in both XRD patterns (Figure 2a,b). The absence of peaks relates to CuNPs and Cu2O in XRD pattern of the Arg-MWCNT (Figure 2a), and their appearance in XRD pattern of the Cu@Arg-MWCNT (Figure 2b) strongly confirms the anchoring of CuNPs in the final step of catalyst synthesis.

The EDX spectrum of the Cu@Arg-MWCNT represented existence of the C, N, O, and Cu elements (Figure 3). It should be noted that the unassigned peaks related to the Au element, which has been used as topcoat for the analysis.

Thermal stability of the Cu@Arg-MWCNT was investigated by TGA technique (Figure 4a) and also its comparison with TGA graph of the Arg-MWCNT (Figure 4b), and their weight difference can be attributed to the CuNPs anchored onto the Arg-MWCNT surface. As it can be interfered from the TGA graph (Figure 4a), weight loss of the catalyst with gentle slope from 80 to 440°C has happened, which can be considered (\cong 7% weight loss, below 200°C) for evaporation of physically adsorbed water molecules and (\cong 20.5% weight loss, 200–440°C) for decomposition of functional groups like hydroxyl, carboxyl, and epoxy on the surface and inside of the MWCNTs, and a severe reduction weight loss (\cong 40.1%) at about 440–520°C is considered for complete decomposition of zwitterionic organic components. In Figure 4a,b,



FIGURE 2 XRD pattern of (a) Arg-MWCNT and (b) Cu@Arg-MWCNT



FIGURE 3 EDX spectrum of Cu@Arg-MWCNT



FIGURE 4 (a) TGA analysis of Cu@Arg-MWCNT, (b) comparison TGA analysis of Arg-MWCNT and Cu@Arg-MWCNT



FIGURE 5 Elemental mapping of Cu@Arg-MWCNT

Arg-MWCNT shows just two weight losses. Its first weight loss with gentle slope occurs at the range of 100–440°C (\cong 31% weight loss), and the second one with severe reduction weight loss (\cong 50%) occurs at about 440–520°C. The approximate molar % of the CuNPs (2.1%) were calculated by considering the weight difference of the Arg-MWCNTs with Cu@Arg-MWCNTs in 520°C and the molecular weight of the CuNPs. TGA analysis showed that 1.000 g of the catalyst contains 2.1 mmol of copper (amount of Cu is reported 13.4 wt%).

The ICP-AES analysis was used to determine the copper content of the Cu@Arg-MWCNT quantitatively. The ICP analysis showed that 1.000 g of the catalyst contains 1.83 mmol of copper (amount of Cu is reported 11.6 wt %), which can be considered as a great confirmation of CuNPs anchored to the arginine ligand linked to MWCNTs.

Distribution of elements (C, N, O, and Cu) was characterized by using elemental mapping data. Figure 5a–e reveals uniform dispersion of these elements on the surface of MWCNT and confirms no aggregation of Cu species.

Utilization of SEM/FE-SEM technique was done to define the morphology of the Cu@Arg-MWCNT surface. The FE-SEM images are shown in Figure 6, which apparently confirm high length of the MWCNTs and spherical structure of CuNPs.

The TEM images of synthesized Cu@Arg-MWCNT nanocatalyst in Figure 7, besides representation of the cylindrical shape and high length of the MWCNTs, obviously confirmed the presence of the CuNPs on MWCNTs.

Figure 8 shows the particle size distribution of the Cu@Arg-MWCNT catalyst, which determines the size ranging from 37 to 770 nm and most of the nanoparticles ranging from 37 to 300 nm. Nanoparticles with size up to 100 nm are considered to be fragmentary MWCNTs and CuNPs. NPs with size over 100 nm belong to MWCNTs, which greatly confirms high length of MWCNTs, which has been previously interfered from the FE-SEM and TEM results.



FIGURE 6 FE-SEM images of Cu@Arg-MWCNT with three magnifications: (a) 200 nm, (b) 500 nm, (c) 1 µm



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FIGURE 7 TEM images of Cu@Arg-MWCNT with two magnifications: (a) 50 nm, (b) 200 nm



FIGURE 8 Particle size distribution of Cu@Arg-MWCNT

4.2 | Catalytic performance of Cu@Arg-MWCNT

After being characterized thoroughly, Cu@Arg-MWCNT performance as a heterogeneous catalyst was assessed for the synthesis of 1,4-disubstituted triazole derivatives using CuAAC reaction. In order to obtain optimum condition, the reaction between phenylacetylene, benzyl bromide, and sodium azide was selected as a model reaction

and investigated under various parameters such as reaction time, temperature, and amount of catalyst and solvents (Table 1). As can be seen in Table 1 (Entries 1-5), the model reaction was carried out in water medium at various temperatures (r.t., 50, 70, 90, and 110°C), which allowed us to select 70°C as the most convenient in order to achieve maximum conversion of the reactants at shorter time reaction. As shown in Table 1 (Entries 7, 11–14), reaction in the absence of solvent and in the presence of different solvents such as acetone, acetonitrile, methanol, and water in the presence of 0.01 g Cu@Arg-MWCNT (2 mol% Cu) was estimated, and based on the results, polar solvents were more effective in this reaction, and the best result was obtained in the presence of water. Various amounts of the catalyst were tested for the model reaction (Table 1, Entries 6–10); in the absence of catalyst even after 24 h, no progress was observed in the reaction, and increase in amount of catalyst from 0.005 to 0.01 g resulted in improvement of the reaction yields. The further increase in the amount of Cu@Arg-MWCNT catalyst to 0.035 g just had negligible effects on the efficiency of the reaction. Thus, 0.01 g of catalyst in water as green solvent at 70°C was selected as optimized reaction condition, and a series of commercially available epoxides/halides with electron-donating and electron-

TABLE 1 Optimization of the reaction conditions for synthesis of 1,2,3-triazole (4k) via click reaction

_					
	لیے کے ۱ mi	$- = + \qquad Br + NaN_3$ mol 1 mmol 1.1 mmol	Cu@Arg-MWCNT		
Entry	Solvent	Catalyst (mg, mol%)	Temp. (°C)	Time (h)	Yield (%)
1	H_2O^a	5.0, 1	r.t.	2.5	20
2	H_2O	5.0, 1	50	2	63
3	H ₂ O	5.0, 1	70	1	84
4	H ₂ O	5.0, 1	90	0.58	69
5	H ₂ O	5.0, 1	110	0.5	52
6	H ₂ O	-	70	24	0
7	H ₂ O	10.0, 2	70	1	92
8	H ₂ O	15.0, 3	70	1	86
9	H ₂ O	25.0, 5	70	0.75	87
10	H ₂ O	35.0, 7	70	0.5	94
11	-	10.0, 2	70	3.5	52
12	Acetone	10.0, 2	70	3	29
13	Acetonitrile	10.0, 2	70	3	43
14	Methanol	10.0, 2	70	1.5	83

^aDeionized water.

TABLE 2 Synthesis of 1,4-disubstituted-1,2,3-triazoles (4a-4n) under optimized condition

) Deio	Epoxide/Halide - 1 (1 mmol) nized water (0.5 ml)	+Phenylacetylend 2 (1 mmol)	e + Sodium Azide 3 (1.1 mmol)	H ₂ O [] /70 °C Arg-MWCNT@C (10 mg)	→ Triazole ^u 4	
Entry	Epoxide/halide	Time (h)	Triazole		Yield (%)	TON/TOF (h^{-1})
1		3		1	38	4400/1467
	O			•OH N ^{−N} , V		

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TABLE 2 (Continued)

	Epoxide/Halide +	-Phenylacetylen	e + Sodium Azide	H ₂ O [*] /70 °C		
	l (1 mmol)	2 (1 mmol)	3 (1.1 mmol)	Arg-MWCNT@C (10 mg)	u 4	
*) De	eionized water (0.5 ml)					
Entry	Epoxide/halide	Time (h)	Triazole		Yield (%)	TON/TOF (h^{-1})
2	Å	2	НО	N-N, N	91	4550/2275
;	<u> </u>	1.5	НО	N-N, N	90	4500/3000
	~ <u>°</u>	2	HC	N N N	90	4500/2250
;	~~ <u>^</u>	1.25		N-N, HO	92	4600/3680
6	γ°	2.5	Lo~~ HO	N-N. N-N.	91	4550/1820

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TABLE 2 (Continued)

				H ₂ O [*] /70 °C		
*) ח	Epoxide/Halide - 1 (1 mmol) eionized water (0.5 ml)	-Phenylacetylend 2 (1 mmol)	e+ Sodium Azide 3 (1.1 mmol)	Arg-MWCNT@Cu (10 mg)	- Triazole 4	
	elomzed water (0.5 ml)					
Entry	Epoxide/halide	Time (h)	Triazole	Yi	eld (%)	TON/TOF (h^{-1})
7	\rightarrow°	3.25	HO	88		4400/1354
	OMe OMe	2	MeO	81		4050/2025
	C C	0.5	H	89		4450/8900
0		1.25	HO	92		4600/3680
1	Br	0.5	C	92		4600/9200

 TABLE 2
 (Continued)

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	Enoxide/Halide 4	-Phenylacetylene	+ Sodium Azide	H ₂ O [*] /70 °C		
*) Dei	(1 mmol) ionized water (0.5 ml)	2 (1 mmol)	3 (1.1 mmol)	Arg-MWCNT@C (10 mg)	Cu 4	
Enters	Enovido (bolido	Time (h)	Triogolo		Viold (01)	$TON/TOF(h^{-1})$
Entry	Epoxide/hande	Time (n)	1 riazoie		viela (%)	10N/10F (n)
12	Br NO ₂	3	O ₂ N	N-N,N	86	4300/1433
13	O ₂ N Br	1.5	O ₂ N	N N N N N N N N N N N N N N N N N N N	91	4550/3033
14	CI	1		N-N,N	90	4500/4500
15	O ₂ N CI	3	O ₂ N	N-N,N	89	4450/1483
16	CI	2.5	CI	N-N, N-N, N	88	4400/1760



withdrawing groups, sodium azide, and phenylacetylene were subjected to the azidolysis–cycloaddition reaction, which resulted in desired 1,4-disubstituted-1,2,3-triazoles in good to excellent yields within short reaction times (Table 2).

4.3 | Mechanistic evaluation of the reaction in the presence of Cu@Arg-MWCNT

Compound (4a) with *trans*- β -hydroxytriazole structure that has been interfered from the ¹H NMR coupling constants suggests the proposed pathway of the reaction.

Based on the results, it is presumed that ring opening occur via S_N 2 mechanism. As can be seen in Scheme 3 at first step, aliphatic epoxides connect with CuNPs of the catalyst and then the azide as nucleophiles attack at its less hindered position. After that, formation of a π -complex between phenylacetylene and Cu@Arg-MWCNT results in a copper(I) acetylide intermediate. Nucleophilicity of the triple bond enhances the coordination of the synthesized organoazide to the copper center of the acetylide. As a result, attack of the C_{β} of the acetylide as a nucleophile to the terminal *N* atom of the synthesized organoazide as electrophile followed by a protonation finally leads in the formation of 1,2,3-triazole ring as final product.



SCHEME 3 Proposed mechanism of the reaction



FIGURE 9 Recycling of the Cu@Arg-MWCNT in the synthesis of the triazole (**4**k)

An exception has been happened at (**4j**), and primary β -hydroxytriazole has been formed as the major product instead of secondary ones. This event can be explicated that in these cases, the electronic factor overcomes the steric factor, which results in nucleophilic attack of the azide at the sterically crowded benzylic position, instead of the less substituted β -carbon.



FIGURE 10 The FT-IR spectrum of the (top) fresh and (bottom) the recycled catalyst after five times

High regioselectivity of the Cu@Arg-MWCNT was confirmed by detect of 1,4-disubstituted 1,2,3-triazoles as the only product of the click reaction in its presence. Based on a research resulting to easily distinguish 1,4-disubstituted 1H-1,2,3-triazoles from the isomeric 1,5-disubstituted 1H-1,2,3-triazoles,^[49] appearance of a ¹³C signal of at $\delta \approx 120$ ppm for compound **4k**, which is due to C₅ of the 1,4-disubstituted 1H-1,2,3-triazoles, was a great confirmation on the high regioselectivity of our catalyst. No ¹³C signal appearance at $\delta \approx 133$ ppm, which is due to C₄ of 1,5-disubstituted 1H-1,2,3-triazoles, also showed that 1,4-disubstituted 1,2,3-triazoles were the only products.

4.4 | The recyclability and stability of the Cu@Arg-MWCNT

Besides the high catalytic activity and ease of separation of this novel heterogeneous nanocatalyst (Cu@Arg-MWCNTs), it is noteworthy to mention that it is also reusable up to five runs without any noticeable decrease in its catalytic activity. For this purpose, after the completion of the first reaction, the Cu@Arg-MWCNT was separated easily from the reaction mixture by centrifugation and washed thoroughly with ethanol (3×10 mL) and dried in the oven at 50°C to be used for the next run. This



FIGURE 11 FE-SEM images of (a) fresh catalyst and (b) recycled catalyst after five runs with three magnifications (A,A' 200 nm, B,B' 500 nm, C,C' 1 μ m)

2	5 1					
Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	Cu/C	H_2O	100	1	91	[23]
2	CuAl ₂ O ₄ NPs	H_2O	90	0.75	95	[50]
3	GO-Salen-Zn	H_2O	100	2	92	[51]
4	Cu NPs	МеОН	r.t.	8	93	[52]
5	Cu-PEI@Fe ₃ O ₄ MNPs	H ₂ O/PEG	70	3	96	[45]
6	Silica-APTS-supported copper(I)	EtOH	78	24	92	[53]
7	Cu@Arg-MWCNT	H ₂ O	70	0.5	92	This work

TABLE 3 Comparison of click synthesis of 1,4-disubstituted 1,2,3-triazoles catalyzed by the Cu@Arg-MWCNT heterogeneous nanocatalyst with other catalysts reported in the literatures

process was repeated for each run. The results forcefully confirmed the recyclability of this catalyst (Figure 9).

Comparison of the FT-IR spectra of the Cu@Arg-MWCNT before being used in reaction (fresh catalyst) and after being used for five times in model reaction (recycled catalyst) as can be seen in Figure 10 greatly confirms the structure stability of the catalyst.

The FE-SEM images of the fresh Cu@Arg-MWCNT catalyst and after recycling for five runs have been shown in Figure 11. Analogy of the fresh catalyst (Figure 11a) with recycled one (Figure 11b) shows that the catalyst has preserved its long cylindrical structure, which also confirms the catalyst's structure stability.

4.5 | Comparison of Cu@Arg-MWCNT with other catalysts

In order to investigate the competency of our catalyst in comparison with other catalysts, their catalytic activity in synthesis of 1,2,3-triazole (4k) has been compared in Table 3. According to the results shown in Table 3, this new heterogeneous nanocatalyst has the ability to perform this reaction in shorter reaction time and mild green conditions, which is another confirmation on its efficiency.

5 | CONCLUSION

Cu@Arg-MWCNT catalyst was synthesized via a simple method and characterized by use of various techniques such as FT-IR, FE-SEM, ICP, XRD, EDS, and mapping. Regioselective synthesis of the 1,2,3-tiazoles via click reaction in the presence of Cu@Arg-MWCNT catalyst in mild reaction conditions and short reaction time with high to excellent yields is great confirmation on its high catalytic activity. Synthesis of 1,4-disubstituted triazoles as the only product of the click reaction in the presence of this catalyst strongly confirms its high regioselectivity. This catalyst also has the ability to be recycled and reused for several times without any significant decrease in its catalytic efficiency and yields.

In conclusion, we introduced a new regioselective and highly efficient heterogeneous nanocatalyst. High catalytic activity in water medium and its reusability and fidelity in principles of green chemistry are among its interesting features that bring Cu@Arg-MWCNT up as a unique catalyst.

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AUTHOR CONTRIBUTIONS

Mahsa Khoshnevis: Data curation; investigation. **Hossein Eshghi:** Conceptualization; data curation; methodology; supervision; validation; visualization.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the Supporting Information of this article.

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