FULL PAPER



Impregnated copper ferrite on mesoporous graphitic carbon nitride: An efficient and reusable catalyst for promoting ligand-free click synthesis of diverse 1,2,3-triazoles and tetrazoles

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Funding information Shiraz University, Grant/Award Number: 97GRD1M235307 Magnetic CuFe₂O₄/g-C₃N₄ hybrids were synthesized through a facile method and their catalytic performances were evaluated in click chemistry for the first time. The structural and morphological characterization of prepared materials was carried out by different techniques such as X-ray diffraction, highresolution transmission electron microscopy, field emission scanning electron microscopy, Fourier infrared spectroscopy, vibrating sample magnetometry, thermogravimetric analysis, and N₂ adsorption-desorption analysis (Brunauer-Emmett-Teller surface area). The utilization of magnetic CuFe₂O₄/g-C₃N₄ enabled superior performance in the one-pot azide-alkyne cycloaddition reaction in water using alkyl halides and epoxides as azide precursors without the need of any additional agents. The present system is broad in scope and especially practical for the synthesis of macrocyclic triazoles and also tetrazoles. In addition, the catalytic system highly fulfills the demands of "green click chemistry" with its convenient conditions, especially easy access to a variety of significant products in low catalyst loading and simple workup and isolation procedure.

KEYWORDS

carbon nitride, click chemistry, CuFe2O4, ligand-free, triazole

1 | INTRODUCTION

Triazoles are an extremely important class of compounds in chemistry^[1-3] and biology^[4–9] that are widely used in medicinal,^[10–12] combinatorial, and material chemistry.^[13,14] Therefore, new practical methods directing the synthesis of triazole nucleus have inspired organic chemists. Huisgen was the first to investigate the thermal synthesis of triazoles in the 1960s, a reaction now termed "Huisgen cycloaddition." This reaction involves a 1,3dipolar cycloaddition between an organic azide and alkyne to produce a regioisomeric mixture of both 1,4and 1,5-disubstituted 1,2,3-triazoles (Scheme 1).^[15] Following Huisgen's pioneering work, in 2002, coppercatalyzed azide–alkyne cycloaddition (CuAAC) through the 'click chemistry' concept has been developed independently by Sharpless et al.^[16] and Meldal et al.^[17] to exclusively synthesize 1,4-disubstituted 1,2,3-triazoles. Later, ruthenium-assisted azide–alkyne cycloaddition was introduced to facilitate the formation of 1,5regioisomer.^[18]

Conventionally, CuAAC click transformation is performed using Cu(I) salts, Cu(II) salts in combination with a reducing agent,^[19] or by comproportionation of a Cu⁰/ Cu^{II} couple^[20] under various reaction conditions. Because of the detrimental features associated with

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Cu(I) species such as thermodynamic instability and initiation of undesired diacetylenes, the direct use of Cu(I) salts has been restricted.^[21] To solve these problems, auxiliary ligands should be added to protect and stabilize the copper catalyst during cycloaddition. Recently, it has been demonstrated that Cu(II) salts can accelerate click reaction under non-reductive conditions using *N*containing ligands.^[22]

Nevertheless, these systems are usually homogeneous and suffer from inherent drawbacks: difficulty in separating the catalyst and product, environmental concern, and recyclability. Recent research in this area has focused on beneficial heterogeneous catalysis which can address these problems and has several advantages such as easier separation of catalyst and product(s), better recovery, allowing for reuse of the catalyst systems, and reduced metal contamination in the final products.^[23-33] In this context, magnetic nanoparticles (MNPs) are considered promising catalysts because of their response to an external magnetic field and are thus extensively used in a variety of important organic reactions.^[34-37] Among various MNPs, spinel ferrites such as CuFe₂O₄ have acquired a special place in the field because of their successful application in a variety of catalytic transformations,^[38–47] especially in click chemistry.^[48–51]

Moreover, copper ferrite nanoparticles have been shown to be suitable candidates for a wide range of technologically important applications, such as fuel processing,^[52] high-energy-storage materials,^[53] and gas

SCHEME 1 Regioselectivity of the 1,3dipolar cycloaddition between an azide and an alkyne in the synthesis of triazoles

sensors,^[54] and also for photo-Fenton reactions^[55] and photocatalytic water splitting.^[56] High activity and stability, low preparation cost, efficient recovery, and good recyclability are other specific features of $CuFe_2O_4$ NPs.^[57] Graphitic carbon nitride (g-C₃N₄) with marked surface properties^[38,42] is believed to be one of the oldest artificial layered polymers and is applied in different arenas including organosynthesis, energy storage, and environmental purification.^[39–41] It is accepted that among the various C₃N₄ phases, tri-*s*-triazine ring is the basic tectonic unit required to establish C₃N₄ allotropes and the most stable phase of C₃N₄ at ambient conditions (Scheme 2).^[41]

The ordered mesostructure of $g-C_3N_4$ is responsible for its successful application as a catalyst or catalyst support because it allows the assembly of active species such as



SCHEME 2 Tri-s-triazine ring structure of g-C₃N₄

metals into porous structures. The nitrogen richness of g-C₃N₄ and the threefold N-bridge connecting the triazine structures provide a variety of nitrogen pots in the plane of g-C₃N₄ that supply abundant anchoring sites for metallic nanoparticles. Therefore, g-C₃N₄ can easily capture the metal cations through strong interactions between the cations and the negatively charged nitrogen atoms, which mainly results from lone pairs of electrons in the nitrogen pots of g-C₃N₄.^[41] Recently, the introduction of different transition-metal cations into the g-C₃N₄ network without destroying the actual structure of graphitic carbon nitride has been reported.^[58,59] g-C₃N₄ exhibits high catalytic capacities and is used in diverse applications including fuel cells,^[60] heterogeneous catalysis,^[61-67] photocatalysis,^[41,68,69] water splitting,^[70] and energy storage.^[71] Motivated by the attractive structure of g-C₃N₄ and its ability to chelate Cu^[41,43] and also by the outstanding work of Zhu et al.,^[22] it is envisioned that g-C₃N₄ can be used as the matrix to load large amounts of CuFe₂O₄ without deliberate addition of a reducing agent in azide-alkyne cycloaddition. We hypothesized that the abilities of nitrogen pots of $g-C_3N_4$ to chelate Cu(II) and to subsequently reduce it to the highly catalytic Cu(I) species can facilitate CuAAC click transformation. This is similar to the argument put forth for the effect of auxiliary ligands on the CuAAC reaction.^[22] The modification of g-C₃N₄ with a bimetallic system can provide an opportunity to make huge strides in the field of catalyst chemistry owing to its extraordinary structural properties. In this work, we describe the facile one-pot preparation of magnetic CuFe₂O₄/g-C₃N₄ hybrids as a heterogeneous catalyst, and perform a preliminary evaluation of its application in Huisgen [3 + 2] cycloaddition of azides and terminal alkynes/nitriles, without any sacrificial reducing agents. Moreover, the organic azides are generated in situ from the appropriate halides or epoxides and sodium azide and thus safety issues associated with the handling of the potentially explosive pre-prepared azides are avoided. Our method is also applicable for the synthesis of anthraguinone and aza-crown ether derivatives of triazole and tetrazole scaffolds. Finally, it was found that this heterogeneous catalytic system exhibited much better catalytic activity and reusability in comparison with CuFe₂O₄.^[49,50]

2 | EXPERIMENTAL

2.1 | Preparation of $g-C_3N_4$

Mesoporous carbon nitride was synthesized according to the reported literature using 1:1 hydrogen-bonded supramolecular aggregates of the melamine-cyanuric acid complex.^[44] In a typical synthesis, melamine (1 g) and cyanuric acid (1.02 g) were dissolved in 35 and 17 mL of dimethyl sulfoxide (DMSO), respectively. After completion of the dissolution process, both solutions were mixed together for 15 min to obtain a white precipitate. Subsequently, the obtained precipitate was separated from the solution by filtration and washed with ethanol. The resulting white powder was dried at 50 °C and calcined at 550 ° C for 4 hr at the heating rate of 2.5 °C min⁻¹ under an argon atmosphere.

2.2 | Synthesis of CuFe₂O₄/g-C₃N₄

In brief, 0.5 g of $g-C_3N_4$ was dispersed in a deionized water–ethanol (1:1) (5 mL) solution by sonication for 30 min. Then 1 equivalent of $Cu(NO_3)_2 \cdot 3H_2O$ and 2 equivalents of Fe $(NO_3)_3 \cdot 9H_2O$ were dissolved in distilled water and added into the aforesaid suspension. Next, a solution containing 20 mmol of NaOH (20 mL) was added dropwise to the mixture with vigorous stirring for 30 min. After the addition of NaOH solution, the mixture was continuously stirred for 10 min. Finally, the solution was transferred into a Teflon-lined stainless steel autoclave and heated at 140 °C for 14 hr. After cooling the mixture, the catalyst was separated by centrifugation and washed with excessive deionized water and ethanol, and dried in a vacuum oven at 60 °C.

2.3 | General procedure for the synthesis of 1,4-disubstituted 1,2,3-triazoles

A mixture of alkyne (1.1 mmol), alkyl halide/epoxide (1.2 mmol), sodium azide (1.2 mmol), and CuFe₂O₄/g- C_3N_4 (5 mg) was vigorously stirred in water (3 mL) at 80 °C for the appropriate time specified in Tables 2 and 3. After the completion of the reaction, as detected by thin-layer chromatography (TLC), and separation of the catalyst using an external magnet, the reaction mixture was diluted with H₂O (5 mL), followed by extraction with EtOAc (3 × 10 mL). The acquired organic phases were washed with saturated brine and dried with anhydrous Na₂SO₄. Removal of the solvent under vacuum, and purification by flash column chromatography on silica gel using *n*-hexane–ethyl acetate (10:5) as the eluent produced the desired 1,2,3-triazole derivatives.

2.4 | General procedure for the synthesis of 5-substituted 1*H*-Tetrazoles

In a round-bottomed flask, $CuFe_2O_4/g-C_3N_4$ (15 mg) was added to a mixture of nitrile (1 mmol) and sodium azide (1.2 mmol) in dimethylformamide (DMF; 3 mL) and mixture was stirred at 110 °C until TLC indicated no further progress in the conversion. After cooling the reaction mixture to room temperature, the catalyst was removed magnetically and the reaction mass was quenched with water (5 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried (anhydrous Na₂SO₄) and evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel using *n*-hexane–ethyl acetate (10:5) as the eluent to afford the desired 1*H*-tetrazole derivatives. All the compounds were identified and characterized by the comparison of their spectral data with those reported in the literature.

2.5 | Characterization of the products

1-Benzyl-4-phenyl-1H-1,2,3-triazole (**3a**): Yellowish white solid, melting point (mp) = 128–130 °C. infrared (IR; KBr, cm⁻¹): v = 3093, 3031, 1458, 1218, 1072, 972, 736. ¹H nuclear magnetic resonance (NMR; 250 MHz, CDCl₃) δ : 5.55 (s, 2H), 7.24–7.44 (m, 8H), 7.67 (s, 1H), 7.79 (d, J = 6.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): 148.2, 134.6, 130.4, 129.2, 128.8, 128.2, 128.1, 125.7, 119.5, 54.3. Anal. Calcd. for C₁₅H₁₃N₃: C, 76.57; H, 5.57; N, 17.86; Found: C, 76.49; H, 5.55; N, 17.96.

2-Phenyl-2-(4-phenyl-1H-1,2,3-triazole-1-yl)ethanol (**5a**): White solid, mp = 126-128 °C. IR (KBr, cm⁻¹):

υ = 3423, 3217, 2862, 1651, 1504, 1402, 1342, 1242, 1095, 1041, 833, 524. ¹H NMR (250 MHz, CDCl₃) δ: 4.23 (dd, <math>J = 12.7, 3.5 Hz, 1H), 4.63 (dd, J = 12.6, 8.2 Hz, 1H), 5.66–5.70 (m, 1H), 7.27–7.33 (m, 3H), 7.35–7.40 (m, 5H), 7.70 (s, 1H), 7.77–7.80 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): 147.7, 136.1, 130.2, 129.2, 129.0, 128.8, 128.3, 127.2, 125.7, 120.6, 67.4, 65.1. Anal. Calcd. For C₁₆H₁₅N₃O: C, 72.43; H, 5.70; N, 15.84; Found: C, 72.57; H, 5.58; N, 15.96.

5-Phenyl tetrazole (**7a**): White solid, mp = 215–217 °C, IR (KBr, cm⁻¹): υ = 3363, 3062, 1658, 1573. ¹H NMR (250 MHz, CDCl₃): δ (ppm) = 6.31 (br, 1H), 7.40–7.56 (m, 3H), 7.80–7.84 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): 156.1, 131.4, 129.6, 126.9. 124.4. Anal. Calcd. For C₇H₆N₄: C, 57.53; H, 4.14; N, 38.34; Found: C, 57.64; H, 4.22; N, 38.14.

3 | RESULTS AND DISCUSSION

Doughnut-like mesoporous graphitic carbon nitride (mpg- C_3N_4) was obtained according to the literature^[44] by precipitating a 1:1 mixture of melamine and cyanuric acid in DMSO and subjecting it to calcination under an argon atmosphere at 550 °C for 4 hr (Scheme 3).

The one-pot modified calcination method was then used to synthesize the magnetic $CuFe_2O_4/g-C_3N_4$ nanocomposite.^[45] The structure and morphology of the prepared mpg-C₃N₄ and $CuFe_2O_4/g-C_3N_4$ hybrids were

Melamine-cyanoric acid supramolecular aggregates (MCAs)



SCHEME 3 Mesoporous graphitic carbon nitride (mpg- C_3N_4) formation. DMSO, dimethyl sulfoxide; r.t., room temperature



characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) patterns, field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), and



FIGURE 1 Fourier transform infrared spectra of mpg- C_3N_4 (green), CuFe₂O₄ nanoparticles (blue), and CuFe₂O₄/g- C_3N_4 (red)

Brunauer-Emmett-Teller (BET) surface area analysis to establish their characteristics. The FT-IR spectra of CuFe₂O₄ NPs, mpg-C₃N₄, and CuFe₂O₄/g-C₃N₄ hybrids are presented in Figure 1. For the pure CuFe₂O₄ NPs, a distinct absorption band at 572 cm^{-1} belongs to the symmetric stretching vibration of the Fe-O band.^[46] The band at 410 cm⁻¹ is attributed to the octahedral metal stretching of Cu-O. The absorption bands at 3440 and 1635 cm⁻¹ represent the stretching and bending mode of -OH groups of H₂O which absorbed on the surface of ferrite. In the case of mpg-C₃N₄, characteristic bands at 1244, 1319, 1427, 1566, and 1642 cm^{-1} result from the stretching modes of aromatic C-N heterocycles. The sharp peak at 813 cm⁻¹ was ascribed to the out-of-plane bending vibration of the triazine units. A broad band, arising from -NH2 vibrations of uncondensed amine groups, is detectable around 3200–3400 cm⁻¹. The FT-IR spectrum of magnetic CuFe₂O₄/g-C₃N₄ shows characterization peaks in the region of 400-600 cm⁻¹ for Fe-O (550 cm^{-1}) and Cu-O (427 cm⁻¹), which indicate the presence of copper ferrites, and 1200–1650 cm⁻¹ for the C-N group, which indicates the presence of copper ferrite and carbon nitride in the composite (Figure 1). As shown in Figure 1, the intensity of band located at 1407 cm^{-1} (aromatic C-N stretching bond) decreased in CuFe₂O₄/ g-C₃N₄ compared with that in mpg-C₃N₄, which is regarded as a strong evidence for the interaction between copper ferrite and the C–N bond of mpg-C₃N₄.^[72]

The crystalline structures of the as-synthesized $CuFe_2O_4$, mpg- C_3N_4 , and $CuFe_2O_4/g$ - C_3N_4 hybrids were studied by XRD (Figure 2). For pure $CuFe_2O_4$ NPs, typical diffraction peaks at $2\theta = 20.6$, 29.9, 35.5, 38.9, 42.8, 56.9, and 62.4° are ascribed to the (101), (112), (103), (211), (202), (220), (321), and (224) planes of the tetragonal $CuFe_2O_4$ NPs (JCPDS card no: 77–0427), respectively.^[73]

mpg-C₃N₄ exhibits two well-resolved peaks centered at $2\theta = 12.8$ and 27.7, corresponding to the (100) and (002)



FIGURE 2 X-ray diffraction pattern of g-C₃N₄, CuFe₂O₄, and CuFe₂O₄/g-C₃N₄

plane arising from the in-plane arrangement of nitrogenlinked triazine units and interlayer spacing of the graphite-like structure, respectively (JCPDS 87-1526).^[73] For the CuFe₂O₄/g-C₃N₄ nanocatalyst, the main peaks of both mpg-C₃N₄ and CuFe₂O₄ are discernible, confirming that the CuFe₂O₄ NPs have been successfully loaded onto mpg- C_3N_4 . The location of the (002) peak down shifts from 27.7° (C_3N_4) to a lower angle direction of 27.1° ($CuFe_2O_4$ / g-C₃N₄), indicating the increase of the corresponding interplanar distance from 0.321 to 0.328 nm. The BET surface area was calculated using N₂ adsorption isotherms at 77 K which indicated that an average pore diameter of around 16.6 nm is generated at 550 °C, where mpg-C₃N₄ had a BET surface area of 52 $m^2 g^{-1}$ and a pore volume of $0.3 \text{ cm}^3 \text{ g}^{-1}$. The total pore volume and specific BET surface area of the resulting $CuFe_2O_4/g-C_3N_4$ were 0.3 cm³ g⁻¹ and 81 m^2/g , respectively.

As expected, the BET surface areas gradually decreased after modification, probably because the copper ferrites blocked the pores partially. Moreover, the Barrett–Joyner–Halenda pore-size distribution of $CuFe_2O_4/g-C_3N_4$ calculated from the adsorption branch further shows that the pore-size distribution fluctuates between 10 and 50 nm, with the maximal value centered

at 15.9 nm. The morphology and structural details of the synthesized samples were characterized by FESEM (Figure 3) and HRTEM (Figure 4).

FESEM analysis of carbon nitride at low and high magnification shows a well-developed "doughnut-like" mesopore architecture with an average diameter of around 1–3 μ m and a narrow size distribution. The FESEM image of CuFe₂O₄/g-C₃N₄ reveals that the Cu NPs have been well dispersed on the carbon nitride surfaces. Compared with Figure 3a, the "doughnut-like" structure cannot be seen, because it is now covered by copper ferrite nanoparticles. In addition, the energy-dispersive X-ray spectroscopy (EDS) spectrum of the CuFe₂O₄/g-C₃N₄ hybrid in Figure 3e confirmed the presence of Cu, Fe, O, C, and N.

TEM images show that the pores with diameters in the range of 30–40 nm are embedded in the nanosheet structure of carbon nitride. HRTEM of the $CuFe_2O_4/g-C_3N_4$ hybrid demonstrates that after hybridization, the surface of carbon nitride is decorated finely with $CuFe_2O_4$ particles to form an excellent heterojunction and interface between $CuFe_2O_4$ and mpg- C_3N_4 .

To obtain a quantitative idea of the surface chemical nature of the as-synthesized composite, XPS



FIGURE 3 Structural evolution of $g-C_3N_4$ by field-emission scanning electron microscopy: (a) $g-C_3N_4$ (low magnification), (b) $g-C_3N_4$ (high magnification), (c) field emission scanning electron microscopy image of $CuFe_2O_4/g-C_3N_4$; and energy-dispersive X-ray spectroscopy analysis: (d) $g-C_3N_4$ and (e) $CuFe_2O_4/g-C_3N_4$



FIGURE 4 High-resolution transmission electron microscopy images of (a,b) g-C₃N₄ and (c,d) CuFe₂O₄/g-C₃N₄

measurements were performed for the $CuFe_2O_4/g-C_3N_4$ hybrid (Figure 5).

The XPS survey spectrum reveals that besides the three lines corresponding to the carbon, nitrogen, and oxygen of carbon nitride, signals of Cu and Fe can be found in the composite, which further confirms the incorporation of CuFe₂O₄ into mpg-C₃N₄. The corresponding highresolution spectra of C1s, N1s, O1s, Cu2p, and Fe2p are also presented. The C1s spectra can be mainly divided into three peaks located at about 284.8, 286.2, and 288.3 eV, respectively. As shown in Figure 5, the C1s peaks at 284.7 and 286.2 eV can be ascribed to sp² C-C bonds in carbon species and C-O species on the surface of the material, respectively, whereas the peak at 288.3 eV corresponds to sp²-bonded carbon (N-C=N).^[73] The N1s spectra (Figure 5) is divided into three sub-bands centered at 398.8, 399.9, and 401.6 eV, which correspond to the sp^2 nitrogen bonded to carbon involved in triazine rings, the three coordinated nitrogen bonded to carbon atoms in the form of N-(C)3, and terminal amino groups (N-H), respectively.^[74] In O1s spectra, two peaks can be distinguished to be centered at 529.6 and 531.2 eV, which are exclusively assigned to the O_2^- in CuFe₂O₄ lattice and surface hydroxyl group, respectively.^[73] The peaks at 933.5 and 953.8 eV (with a satellite at 961.7 eV) in the spectrum of Cu2p can be assigned to Cu $(2P_{3/2})$ and Cu $(2P_{1/2})$, spinorbital components, respectively. The deconvoluted Cu $(2P_{3/2})$ XPS spectrum (Figure 5) shows two peaks at 933.4 and 934.8 eV which could be attributed to Cu⁺ and

 Cu^{2+} , respectively.^[45,72] This may be due to the transformation of Cu²⁺ into Cu⁺ during the formation of the CuFe₂O₄/g-C₃N₄ composite. These are in conformity with the results reported elsewhere.^[45,75,76] The highresolution narrow scan for the Fe2p spectrum reveals Fe $(2p_{1/2})$ and Fe $(2p_{3/2})$ binding energy peaks related to the oxidized Fe species, which can be deconvoluted into five peaks (Figure 5). The peak centered at 724.9 eV is attributed to the binding energies of $2p_{1/2}$ of Fe³⁺ and Fe²⁺ ions, and the peak centered around 723.2 eV corresponds to the binding energies of $2p_{1/2}$ of Fe²⁺ ion. The peaks at 712.0 and 710.3 eV are assigned to $2p_{3/2}$ of the Fe³⁺ and Fe²⁺ ions, respectively, with a satellite peak at 718.5 eV, which indicates the coexistence of Fe^{3+} and Fe^{2+} in the catalyst. The obtained results are in agreement with published work on the CuFe₂O₄/g-C₃N₄ hybrid.^[73] The magnetic behavior of the CuFe₂O₄/g-C₃N₄ hybrid was also examined using a vibrating sample magnetometer.

Figure 6 displays the hysteresis loop formed by the $CuFe_2O_4/g-C_3N_4$ hybrid at room temperature (300 K). The observed magnetic parameters of the $CuFe_2O_4/g-C_3N_4$ hybrid such as relatively high saturation magnetization ($M_s = 17.2 \text{ emu g}^{-1}$) and low remnant magnetization and coercivity revealed that the synthesized $CuFe_2O_4/g-C_3N_4$ composites show soft magnetic behavior and can be easily separated by an external magnetic field. The lower M_s value in the $CuFe_2O_4/g-C_3N_4$ hybrid materials is possibly due to the strong counteraction between the $CuFe_2O_4$ MNPs and mpg- C_3N_4 .



FIGURE 5 X-ray photoelectron spectroscopy spectra of CuFe₂O₄/g-C₃N₄: (a) survey, (b) C1s, (c) N1s, (d) O1s, (e) Cu2p, and (f) Fe2p



FIGURE 6 Vibrating sample magnetometry curve of $CuFe_2O_4/g-C_3N_4$

The thermal stability of the fresh $CuFe_2O_4$, mpg- C_3N_4 , and $CuFe_2O_4/g-C_3N_4$ hybrid is studied by TGA and their corresponding TGA profiles are shown in Figure 7.

These results demonstrate that pure $CuFe_2O_4$ NPs are stable and do not lose any weight from 30 to 800 °C, whereas mpg-C₃N₄ loses almost all of its weight from 500 to 600 °C. For the CuFe₂O₄/g-C₃N₄ hybrid sample,



FIGURE 7 Thermogravimetric analysis graph: (a) $CuFe_2O_4$, (b) mpg-C₃N₄, and (c) $CuFe_2O_4/g$ -C₃N₄

the slight weight loss below 150 °C likely results from the evaporation of absorbed water in the sample, but the significant weight loss above 550 °C results from the direct thermal decomposition of the mpg- C_3N_4 phase. This result shows that thermal stability of the mpg- C_3N_4 phase in the CuFe₂O₄/g-C₃N₄ nanocomposite is less than that in pure mpg- C_3N_4 , which may be due to a catalytic effect of the Cu–Fe mixed oxide on the oxidation of the carbon nitride support or the weakening of cross-linked rings of mpg-C₃N₄ resulting from the introduction of CuFe₂O₄.^[73]

In our quest to develop aqueous medium organic synthesis of triazoles,^[77,78] we employed $CuFe_2O_4/g-C_3N_4$ hybrids as a catalyst in the click reaction of phenylacetylene **1a** (1.1 mmol), benzyl bromide **2a** (1.2 mmol), and sodium azide (1.2 mmol) in H₂O without using any reducing agent (Table 1).

The control experiment in the absence of the catalyst showed that a trace amount of desired product **3a** was formed at 80 °C even after prolonged reaction time (entry 1). This result clearly highlights the role of Cu NPs as catalysts in the click reaction. Another copper promoter, $CuFe_2O_4$, was also examined in this reaction and the yield of triazole **3a** was 80% after 3 hr (entry 2). According to Table 1, the $CuFe_2O_4/g-C_3N_4$ hybrids with 5-mg loading showed high catalytic activity to give 1-benzyl-4-phenyl-1*H*-1,2,3-triazole in excellent yield (entry 3). The effect of reaction temperature was also investigated (entries 4 and 5). The results indicated that the yield of the product was not changed obviously by raising the temperature. Decreasing the reaction temperature to

TABLE 1 Optimization of the parameters for click reacti	ion
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60 °C also resulted in the decrease of yield of the desired triazole. Next, the optimal amount of CuFe₂O₄/g-C₃N₄ nanocatalyst to be used in the synthesis was examined. It is clear from Table 1 that an increase in the amount of the nanocatalyst had no positive effect on the overall yield of triazole 3a while decreasing the amount of catalyst to 2.5 mg led to a lower yield (entries 6 and 7). Among the different solvents screened, water was recognized to be the best for the model reaction (entries 8-12). In addition, a comparative study on the reactivity of the CuFe₂O₄/g-C₃N₄ nanocatalyst with heterogeneous Cu catalysts such as Cu, CuO, and Cu₂O was performed, but the results were not encouraging (entries 13-15). Therefore, the CuFe₂O₄/g-C₃N₄ nanocatalyst (5 mg, entry 3) proved to be the best choice among the screened heterogeneous catalysts under the reaction conditions. To assess and broaden the scope of the present methodology, a series of triazole derivatives were prepared under the optimized reaction conditions, with the results presented in Table 2 (See supporting information).

As can be seen from Table 2, the reactions of all substrates could be completed at 80 °C to provide the corresponding triazoles in good to excellent yields. As expected, benzyl halides bearing electron-withdrawing

	Ph−C≡CH + PhCH ₂ t	Br + NaN ₃ <u>catalyst (mg)</u> Solvent, T(°C)	N	
	1a 2a		3a	
Entry	Catalyst (mg)	Solvent (condition)	Time (hr)	Yield of 3a (%) ^b
1	_	H ₂ O, 80 °C	6	Trace
2	$CuFe_2O_4(5)$	H ₂ O, 80 °C	3	80
3	$CuFe_2O_4/g-C_3N_4$ (5)	H ₂ O, 80 °C	1	95 °
4	$CuFe_2O_4/g-C_3N_4$ (5)	H ₂ O, 100 °C	1	94
5	$CuFe_2O_4/g-C_3N_4$ (5)	H ₂ O, 60 °C	1	79
6	$CuFe_2O_4/g-C_3N_4$ (10)	H ₂ O, 80 °C	1	93
7	$CuFe_2O_4/g-C_3N_4$ (2.5)	H ₂ O, 80 °C	3	75
8	$CuFe_2O_4/g-C_3N_4$ (5)	EtOH, reflux	1	84
9	$CuFe_2O_4/g-C_3N_4$ (5)	CH ₃ CN, reflux	1	67
10	$CuFe_2O_4/g-C_3N_4$ (5)	Dioxane, reflux	3	51
11	$CuFe_2O_4/g-C_3N_4$ (5)	THF, reflux	6	13
12	$CuFe_2O_4/g-C_3N_4$ (5)	Toluene, 80 °C	6	42
13	Cu	H ₂ O, 80 °C	6	49
14	CuO	H ₂ O, 80 °C	6	70
15	$Cu (OAc)_2.H_2O$	H ₂ O, 80 °C	3	77

^aReactions were performed with phenylacetylene (1.1 mmol), benzyl bromide (1.2 mmol), NaN₃ (1.2 mmol), solvent (3 mL), and catalyst (type and amount indicated).

^bYields of isolated pure products.

^cBold value signifies the best reaction conditions.

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 $\label{eq:TABLE 2} \textbf{TABLE 2} \quad \text{Substrate scope for } CuFe_2O_4/g\text{-}C_3N_4\text{-}catalyzed \ triazole \ formation^a$



^aReactions were performed with terminal alkyne (1.1 mmol), alkyl halide (1.2 mmol), NaN₃ (1.2 mmol), 3 mL of H₂O as a solvent, and CuFe₂O₄/g-C₃N₄ (5 mg) at 80 °C.

²Yield of isolated pure products.

and electron-donating groups were rapidly converted to the respective products using only 5 mg of the catalyst for 1–3 hr at 80 °C (entries 1–5). Allyl bromide could also be applied to the reaction successfully (entry 6). The primary and secondary aliphatic alkyl halides could be used as the azide precursors in the reaction with phenylacetylene, which provided the best results (entries 7–10). The usefulness of this reaction was further verified with another terminal alkyne, 2-(prop-2-yn-1-yloxy)naph-thalene, with the results indicating that it worked well and afforded the desired triazoles in good to excellent yields (entries 11–15). Following reports of the catalytic

TABLE 3 Multicomponent synthesis of β -hydroxy-1,2,3-triazoles from epoxides catalyzed by CuFe₂O₄/g-C₃N₄^a



^aReactions were performed with terminal alkyne (1.0 mmol), epoxide (1.2 mmol), NaN₃ (1.2 mmol), 3 mL of H₂O as a solvent, and CuFe₂O₄/g-C₃N₄ (5 mg) at 80 °C.

^bYield of isolated pure products.

effect of copper catalysts in the Huisgen reaction, interest in the synthesis of macrocycles possessing triazole moieties has increased significantly.^[79,80] Hence, we scrutinized the possibility of using macrocyclic halide substrates in the click reaction which, being reconcilable with the optimized reaction conditions, could extend the versatility of the catalyst (Scheme 4). For this purpose, the aza-crown ether bearing an acetylenic moiety was synthesized in a four-step procedure starting from catechol. The resulting acetylenic aza-crown ether was finally subjected to CuAAC to afford the corresponding 1,4disubstituted triazole. The yield of product **3p** was 73% by this method.

The pre-synthesized anthraquinone 2-(bromomethyl)-1-hydroxy-9,10-anthracenedione was also tested in this click reaction and it was possible to transform it into desired product 3q under the reaction conditions (Scheme 5).

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Having successfully established the CuFe₂O₄/g-C₃N₄catalyzed one-pot click reaction for the synthesis of 1,4disubstituted triazoles, it was suggested that β -hydroxy-1,2,3-triazoles might also be synthesized under the same reaction conditions by replacing alkyl halides with epoxides.

To explore the feasibility of using epoxides in the CuAAC reaction, we carried out coupling between phenylacetylene **1a** (1 mmol), sodium azide (1.2 mmol), and styrene oxide (1.2 mmol) in the presence of catalytic amounts of $CuFe_2O_4/g-C_3N_4$ (5 mg) (See supplementary data). This reaction provided exclusively primary



SCHEME 4 CuFe₂O₄/g-C₃N₄-catalyzed synthesis of macrocycles possessing the triazole moiety. r.t., room temperature



SCHEME 5 Anthraquinone derivative as a substrate in click reaction. NBS = N-Bromosuccinimide

 β -hydroxy triazole **5a** as the major product in 90% yield (Table 3, entry 1), without the formation of another regioisomer. This regioselectivity can be justified by preferential ring opening of the benzylic position.^[81]

In the same way, more hindered attack was found with 4-chlorostyrene oxide as an aryl-substituted epoxide (entry 2). Bicyclic epoxides such as cyclohexene oxide are shown to be more disinclined to react and took more time to produce a high yield of the corresponding triazole 5c (entry 3). Alkyl-substituted epoxides were also made to react under the stipulated conditions to afford β -hydroxy triazoles with opposite regioselectivity to that displayed by the aryl-substituted epoxides (entries 4-6). Ethyloxirane, glycidyl phenyl ether, and glycidyl allyl ether showed similar reactivity, providing the corresponding triazoles **5d-f** in good yields. The present methodology was proven to be equally effective for other terminal alkynes such as 2-methyl-3-butyn-2-ol and 2-(prop-2-yn-1-yloxy)naphthalene, which manifested the same reactivity pattern (entries 7-11). A similar trend on governed regiochemistry is observed in major products 5g-k obtained from the reaction of monoalkyl-/ monoaryl-substituted oxiranes. This result is in good agreement with the previously reported azidolysis of aryl-/alkyl-monosubstituted oxiranes.^[81] Finally, further experiments were performed to verify the recovery potential of the catalyst in the cycloaddition reaction of phenylacetylene, sodium azide, and benzyl bromide under

the optimized reaction conditions. After the first use, the $CuFe_2O_4/g-C_3N_4$ catalyst was simply separated using a magnet and washed several times with EtOAc, dried in an oven, and subsequently reused directly in the next cycle for further catalytic reactions. No significant change in activity was observed up to six rounds (Table 4).

To further illustrate the detailed chemical structure of the catalyst, TEM analysis of the recycled catalyst after the fourth run was performed. Interestingly, there was no significant change of the catalyst before and after recycling (Figure 8).

To determine the heterogeneity/leaching of the catalytic system, a hot filtration test was also carried out using the model reaction and it was found that no further consumption of phenyl acetylene occurred after the catalyst was filtered off at the conversion of 61%. In addition, inductively coupled plasma analysis showed that no Cu species were released in the course of the reaction which

TABLE 4Catalyst reusability study^a

Run	1	2	3	4	5	6
Yield of 3a ^b	95	93	93	92	91	91

^aReaction conditions: Phenyl acetylene (1.1 mmol), benzyl bromide (1.2 mmol), NaN₃ (1.2 mmol), and CuFe₂O₄/g-C₃N₄ (5 mg each) in H₂O (3 mL) at 80 °C.

^bIsolated yield.



FIGURE 8 Transmission electron microscopy image of the recycled catalyst after the fourth run

proves the hot filtration test results. These analyses demonstrated that the CuFe₂O₄/g-C₃N₄ catalyst is heterogeneous in nature and CuAAC truly promoted the reaction under heterogeneous conditions. A brief look at the mechanism of this azide–alkyne click chemistry and an analysis of the XPS data revealed that the catalytic Cu(I) species which partially exist in the structure of the catalyst can be responsible for efficient CuAAC click transformation.^[22,23] After the generation of Cu(I) species, the cycloaddition is performed according to a reaction mechanism proposed previously by Sharpless et al. (Scheme 6).^[16] WILEY Organometallic 13 of 17

By contrast, tetrazole scaffolds with impressive functionality have attracted unprecedented interest over the last decade mainly due to their distinct applications in various areas of science.^[82] The wide applicability of tetrazoles has prompted extensive attempts toward the development of new and practical strategies for their synthesis, $[^{[83-85]}]$ however, the [3 + 2] cycloaddition of organic nitriles with an azide anion remain by far the most efficient and sustainable route for the synthesis of diverse 5-substituted 1*H*-tetrazoles.^[83,84,86–88] The investigation was initiated using 1 mmol of benzonitrile (6a) and NaN_3 (1.2 mmol) as model substrates in the presence of the catalyst under various conditions (Table 5). In the absence of the catalyst, the reaction led to the target 5phenyl-1H-tetrazole 7a in a very low yield of 17% using DMF as a solvent (Table 5, entry 1).

It was observed that 15 mg of the CuFe₂O₄/g-C₃N₄ catalyst was found to be optimum after evaluating various amounts of the catalyst from 5 to 20 mg (entries 2–4). The efficiency of the reaction system at different reaction temperatures was also examined, with 110 °C found to be the best choice (entries 5–6). Subsequently, the influence of solvent on the reaction outcome was investigated and it was found that DMF was superior to other tested solvents such as H₂O, EtOH, CH₃CN, and DMSO. Under the optimized reaction conditions described earlier, various 5-substituted 1*H*-tetrazoles were synthesized using this novel protocol. The results are summarized in Table 6.

The results furnished in Table 6 reveal that a smooth conversion of aryl nitriles occurred in all the cases. Variation of the aryl unit within a series of nitriles was investigated, with the incorporation of both electrondonating and electron-deficient substituents providing 5-



SCHEME 6 Plausible mechanism of one-pot copper-catalyzed azide–alkyne cycloaddition using CuFe₂O₄/g-C₃N₄

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TABLE 5 Optimization of the reaction^a

	6a CN + Na	N ₃ CuFe₂O₄/g-C Solvent, T(°C	$\frac{HN^{-N}}{N}$		
Entry	Amount of CuFe ₂ O ₄ /g-C ₃ N ₄ (mg)	Solvent	Temperature (°C)	Time (hr)	Yield (%) ^b
1	_	DMF	110	12	17
2	5	DMF	110	6	52
3	10	DMF	110	4	80
4	15	DMF	110	3	87
5	20	DMF	110	3	84
6	15	DMF	80	8	66
7	15	DMF	120	3	85
8	15	H ₂ O	90	8	75
9	15	EtOH	Reflux	8	69
10	15	CH ₃ CN	Reflux	8	51
11	15	DMSO	110	3	78

 a Reactions were performed with benzonitrile (1.0 mmol), NaN₃ (1.2 mmol), solvent (3 mL), and CuFe₂O₄/g-C₃N₄.

^bYields of isolated pure products.

^cBold value signifies the best reaction conditions.

DMF, dimethylformamide; DMSO, dimethyl sulfoxide.



TABLE 6 Synthesis of 5-substituted tetrazoles using CuFe2O4/g-C3N4^a

^aReaction conditions: Nitrile (1.0 mmol), NaN₃ (1.2 mmol), dimethylformamide (3 mL), and CuFe₂O₄/g-C₃N₄ (15 mg) stirred at 110 °C for 3–5 hr. ^bIsolated yields.





substituted 1H-tetrazoles 7a-7i in good to excellent yields. Aryl nitriles containing electron-donating groups such as -OCH₃ and -CH₃ at the para position afforded 82% and 78% of products 7b and 7c, respectively (Table 6, entries 2 and 3). The reaction of nitrile having an electronwithdrawing group such as $-CF_3$ at the para position gave better yield (entry 4). Halogen-substituted substrates could also be employed to give the corresponding tetrazoles 7e-7g in high yields (entries 5-7). Moreover, aryl nitriles holding -NO₂ as an electron-withdrawing group were also found to be suitable reaction partners with sodium azide in the reaction (entries 8 and 9). Furthermore, the reusability of the catalyst was investigated in the reaction for the preparation of 5-phenyl-1H-tetrazole 7a starting with benzonitrile and sodium azide; after six consecutive cycles only a slight loss of activity was observed which is consistent with slight leaching of the active catalyst species and indicated that the catalyst has great potential for the development of green processes (Figure 9).

4 | CONCLUSION

In summary, magnetic CuFe₂O₄/g-C₃N₄ hybrids were successfully synthesized by a facile one-step process and characterized by FT-IR, XRD, FESEM, EDS, HRTEM, XPS, VSM, and TGA techniques. An efficient and ligand-free catalytic system which utilized the CuFe₂O₄/ g-C₃N₄ nanocomposite was implemented for convenient access to triazoles through in situ generation of organic azides from alkyl halides and epoxides with alkynes. We also demonstrated that this catalyst system can be applied for click reactions using macrocyclic halide substrates. Moreover, this heterogeneous catalyst was used to generate a diverse range of 5-substituted 1H-tetrazoles through [3 + 2] cycloaddition of sodium azide and a wide variety of nitriles in DMF. Chemical stability, low cost, effortless recoverability, and recyclability of the catalyst, along with simple and clean workup of the products, make this catalyst an attractive candidate from an environmental standpoint.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

- [1] D. Huang, G. Yan, Adv. Synth. Catal. 2017, 359, 1600.
- [2] A. S. Felten, N. Petry, B. Henry, N. Pellegrini-Moise, K. Selmeczi, New J. Chem. 2016, 40, 1507.
- [3] Z. Chen, Z. Liu, G. Cao, H. Li, H. Ren, Adv. Synth. Catal. 2017, 359, 202.
- [4] N. Pribut, C. G. L. Veale, A. E. Basson, W. A. L. van Otterlo, S. C. Pelly, *Bioorg. Med. Chem. Lett.* 2016, *26*, 3700.
- [5] N. Nayak, J. Ramprasad, U. Dalimba, P. Yogeeswari, D. Sriram, H. S. S. Kumar, S. K. Peethambar, R. Achur, *Res. Chem. Intermed.* 2016, 42, 3721.
- [6] M. H. Shaikh, D. D. Subhedar, L. Nawale, D. Sarkar, F. A. Kalam Khan, J. N. Sangshetti, B. B. Shingate, *Med. Chem. Commun.* 2015, 6, 1104.
- [7] V. K. Tiwari, B. B. Mishra, K. B. Mishra, N. Mishra, A. S. Singh, X. Chen, *Chem. Rev.* **2016**, *116*, 3086.
- [8] H. Cheng, J. Wan, M.-I. Lin, Y. Liu, X. Lu, J. Liu, Y. Xu, J. Chen, Z. Tu, Y.-S. E. Cheng, K. Ding, J. Med. Chem. 2012, 55, 2144.
- [9] N. R. Penthala, L. Madhukuri, S. Thakkar, N. R. Madadi, G. Lamture, R. L. Eoff, P. A. Crooks, *Med. Chem. Commun.* 2015, 6, 1535.
- [10] S. A. Bakunov, S. M. Bakunova, T. Wenzler, M. Ghebru, K. A. Werbovetz, R. Brun, R. R. Tidwell, *J. Med. Chem.* **2010**, *53*, 254.
- [11] A. D. Moorhouse, J. E. Moses, ChemMedChem 2008, 3, 715.
- [12] D. Dheer, V. Singh, R. Shankar, Bioorg. Chem. 2017, 71, 30.
- [13] J. M. Holub, K. Kirshenbaum, Chem. Soc. Rev. 2010, 39, 1325.
- [14] M. Meldal, C. W. Tornøe, Chem. Rev. 2008, 108, 2952.
- [15] R. Huisgen, Angew. Chem. Int. Ed. 1963, 2, 565.
- [16] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, Angew. Chem. Int. Ed. 2002, 41, 2596.
- [17] C. W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 2002, 67, 3057.
- [18] L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G. Jia, J. Am. Chem. Soc. 2005, 127, 15998.
- [19] J. Totobenazara, A. J. Burke, Tetrahedron Lett. 2015, 56, 2853.
- [20] S. Quader, S. E. Boyd, I. D. Jenkins, T. A. Houston, J. Org. Chem. 2007, 72, 1962.
- [21] S. Chassaing, A. S. S. Sido, A. Alix, M. Kumarraja, P. Pale, J. Sommer, *Chem. – Eur. J.* **2008**, *14*, 6713.

16 of 17 WILEY Organometallic Chemistry

- [22] G.-C. Kuang, H. A. Michaels, J. T. Simmons, R. J. Clark, L. Zhu, J. Org. Chem. 2010, 75, 6540.
- [23] Y. Wang, J. Liu, C. Xia, Adv. Synth. Catal. 2011, 353, 1534.
- [24] B. Lai, Z. Huang, Z. Jia, R. Bai, Y. Gu, Catal. Sci. Technol. 2016, 6, 1810.
- [25] S. Sabaqian, F. Nemati, M. M. Heravi, H. T. Nahzomi, Appl. Organomet. Chem. 2017, 31.
- [26] C. Wang, F. Yang, Y. Cao, X. He, Y. Tang, Y. Li, RSC Adv. 2017, 7, 9567.
- [27] R. Nie, R. Sang, X. Ma, Y. Zheng, X. Cheng, W. Li, L. Guo, H. Jin, Y. Wu, J. Catal. 2016, 344, 286.
- [28] A. Nunes, L. Djakovitch, L. Khrouz, F.-X. Felpin, V. Dufaud, *Mol. Catal.* 2017, 437, 150.
- [29] M. Bhardwaj, B. Jamwal, S. Paul, Catal. Lett. 2016, 146, 629.
- [30] K. Bahrami, M. Sheikh Arabi, New J. Chem. 2016, 40, 3447.
- [31] S. Chassaing, V. Beneteau, P. Pale, Catal. Sci. Technol. 2016, 6, 923.
- [32] B. Dervaux, F. E. Du Prez, Chem. Sci. 2012, 3, 959.
- [33] T. Jin, M. Yan, Y. Yamamoto, ChemCatChem 2012, 4, 1217.
- [34] K. V. S. Ranganath, F. Glorius, Catal. Sci. Technol. 2011, 1, 13.
- [35] R. Hudson, Y. Feng, R. S. Varma, A. Moores, *Green Chem.* 2014, 16, 4493.
- [36] M. B. Gawande, P. S. Branco, R. S. Varma, Chem. Soc. Rev. 2013, 42, 3371.
- [37] L. M. Rossi, N. J. S. Costa, F. P. Silva, R. Wojcieszak, Green Chem. 2014, 16, 2906.
- [38] K. S. Lakhi, D.-H. Park, K. Al-Bahily, W. Cha, B. Viswanathan, J.-H. Choy, A. Vinu, *Chem. Soc. Rev.* 2017, 46, 72.
- [39] Y. Zheng, L. Lin, B. Wang, X. Wang, Angew. Chem. Int. Ed. 2015, 54, 12868.
- [40] J. Wen, J. Xie, X. Chen, X. Li, Appl. Surf. Sci. 2017, 391, 72.
- [41] W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chem. Rev.* 2016, 116, 7159.
- [42] P. Zhang, J. Zhang, S. Dai, Chem. Eur. J. 2017, 23.
- [43] M. Fan, C. Song, T. Chen, X. Yan, D. Xu, W. Gu, W. Shi, L. Xiao, RSC Adv. 2016, 6, 34633.
- [44] Y.-S. Jun, E. Z. Lee, X. Wang, W. H. Hong, G. D. Stucky, A. Thomas, Adv. Funct. Mater. 2013, 23, 3661.
- [45] R. Cheng, X. Fan, M. Wang, M. Li, J. Tian, L. Zhang, *RSC Adv.* 2016, 6, 18990.
- [46] S. Anandan, T. Selvamani, G. G. Prasad, A. M. Asiri, J. J. Wu, J. Magn. Magn. Mater. 2017, 432, 437.
- [47] S. Fan, W. Dong, X. Huang, H. Gao, J. Wang, Z. Jin, J. Tang, G. Wang, ACS Catal. 2017, 7, 243.
- [48] B. Sreedhar, A. S. Kumar, D. Yada, *Tetrahedron Lett.* 2011, 52, 3565.
- [49] B. S. P. Anil Kumar, K. H. V. Reddy, G. Satish, R. U. Kumar, Y. V. D. Nageswar, *RSC Adv.* 2014, 4, 60652.
- [50] B. S. P. Anil Kumar, K. H. V. Reddy, B. Madhav, K. Ramesh, Y. V. D. Nageswar, *Tetrahedron Lett.* **2012**, *53*, 4595.
- [51] R. Hudson, C.-J. Li, A. Moores, Green Chem. 2012, 14, 622.
- [52] J. J. Spivey, Catal. Today 2005, 100, 171.
- [53] J. Wang, Q. Deng, M. Li, K. Jiang, J. Zhang, Z. Hu, J. Chu, Sci. Rep. 2017, 7, 8903.

- [54] M. A. Haija, A. F. S. Abu-Hani, N. Hamdan, S. Stephen, A. I. Ayesh, J. Alloys Compd. 2017, 690, 461.
- [55] K. Atacan, B. Topaloğlu, M. Özacar, Appl. Catal. A-Gen. 2018, 564, 33.
- [56] M. I. Díez-García, T. Lana-Villarreal, R. Gómez, *ChemSusChem* 2016, 9, 1504.
- [57] D. Wang, D. Astruc, Chem. Rev. 2014, 114, 6949.
- [58] Z. Ding, X. Chen, M. Antonietti, X. Wang, *ChemSusChem* 2011, 4, 274.
- [59] X. Wang, X. Chen, A. Thomas, X. Fu, M. Antonietti, Adv. Mater. 2009, 21, 1609.
- [60] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Z. Qiao, *Energy Environ. Sci.* 2012, 5, 6717.
- [61] H. Wang, Y. Wang, Y. Guo, X.-K. Ren, L. Wu, L. Liu, Z. Shi, Y. Wang, Catal. Today 2019, 330, 124.
- [62] T. Huang, Y. Fu, Q. Peng, C. Yu, J. Zhu, A. Yu, X. Wang, *Appl. Surf. Sci.* 2019, 480, 888.
- [63] X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu, A. Vinu, *Angew. Chem. Int. Ed.* **2009**, *48*, 7884.
- [64] M. Hassan, T. Liu, X. Bo, M. Zhou, J. Phys, Chem. Solids 2019, 131, 111.
- [65] H. Ghafuri, G. Jafari, A. Rashidizadeh, F. Manteghi, *Mol. Catal.* 2019, 475, 110491.
- [66] X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, J. Am. Chem. Soc. 2009, 131, 11658.
- [67] S. Sadjadi, M. M. Heravi, M. Malmir, Carbohydr. Polym. 2018, 186, 25.
- [68] K. Wang, Q. Li, B. Liu, B. Cheng, W. Ho, J. Yu, Appl. Catal. B-Environ. 2015, 176-177, 44.
- [69] Y. Gong, M. Li, H. Li, Y. Wang, Green Chem. 2015, 17, 715.
- [70] A. Mishra, A. Mehta, S. Basu, N. P. Shetti, K. R. Reddy, T. M. Aminabhavi, *Carbon* 2019, 149, 693.
- [71] M. Tahir, C. Cao, F. K. Butt, F. Idrees, N. Mahmood, Z. Ali, I. Aslam, M. Tanveer, M. Rizwan, T. Mahmood, J. Mater, *Chem.* A 2013, 1, 13949.
- [72] K. Lu, F. Yang, W. Lin, S. Zhou, T. Xi, C. Song, Y. Kong, Chem. Select. 2018, 3, 4207.
- [73] Y. Yao, F. Lu, Y. Zhu, F. Wei, X. Liu, C. Lian, S. Wang, J. Hazard. Mater. 2015, 297, 224.
- [74] L. Shi, T. Liang, L. Liang, F. Wang, M. Liu, J. Sun, J. Porous Mater. 2015, 22, 1393.
- [75] K. Takanabe, T. Uzawa, X. Wang, K. Maeda, M. Katayama, J. Kubota, A. Kudo, K. Domen, *Dalton Trans.* 2009, 10055. https://doi.org/10.1039/B910318J
- [76] S. Mohammed, A. K. Padala, B. A. Dar, B. Singh, B. Sreedhar, R. A. Vishwakarma, S. B. Bharate, *Tetrahedron* 2012, 68, 8156.
- [77] D. Khalili, New J. Chem. 2016, 40, 2547.
- [78] D. Khalili, E. Etemadi-Davan, A. R. Banazadeh, Appl. Organomet. Chem. 2017, 32, 1.
- [79] G. V. Latyshev, M. S. Baranov, A. V. Kazantsev, A. D. Averin, N. V. Lukashev, I. P. Beletskaya, *Synthesis* 2009, 9, 2605.
- [80] H. Sharghi, R. Khalifeh, M. M. Doroodmand, *Adv. Synth. Catal.* 2009, 351, 207.
- [81] F. Alonso, Y. Moglie, G. Radivoy, M. Yus, J. Org. Chem. 2011, 76, 8394.

- [82] R. N. Butler, in *Comprehensive Heterocyclic Chemistry II*, (Eds: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford **1996** 621.
- [83] A. Sarvary, A. Maleki, Mol. Diversity 2015, 19, 189.
- [84] D. S. Treitler, S. Leung, M. Lindrud, Org. Process Res. Dev. 2017, 21, 460.
- [85] K. Ishihara, M. Kawashima, T. Matsumoto, T. Shioiri, M. Matsugi, Synthesis 2018, 50, 1293.
- [86] S. B. Bhagat, V. N. Telvekar, Synlett 2018, 29, 874.
- [87] B. Yakambram, A. Jaya Shree, L. Srinivasula Reddy, T. Satyanarayana, P. Naveen, R. Bandichhor, *Tetrahedron Lett.* 2018, *59*, 445.
- [88] J. Azarnia Mehraban, K. Azizi, M. Sadat Jalali, A. Heydari, *Chem. Select* 2018, 3, 12175.

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