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# Immobilized polytriazole complexes of copper(I) onto graphene oxide as a recyclable nanocatalyst for synthesis of triazoles

Hossein Naeimi 问 | Zahra Ansarian

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Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan 87317IR, Iran

#### Correspondence

Hossein Naeimi, Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan 87317, IR Iran. Email: naeimi@kashanu.ac.ir

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An efficient solid-supported catalyst for the Huisgen [3 + 2] cycloaddition reaction between azides and alkynes was prepared from copper(I) iodide and 1,2,3-triazolefunctionalized graphene oxide. This catalyst was then used for the efficient synthesis of  $\beta$ -hydroxy-1,2,3-triazoles giving access to these products in excellent yields. In this protocol, the catalyst was shown to have high activity, air-stability and recyclability. The formation of copper triazolide is very straightforward and energetically desirable. The catalyst can be isolated from copper-catalysed azide–alkyne cycloaddition reactions.

#### **KEYWORDS**

azides, catalyst, click reaction, graphene oxide, triazole

# **1** | **INTRODUCTION**

1,2,3-Triazoles are nitrogen-containing heterocyclic molecules that have attracted increasing interest due to their wide range of applications. These molecules are commonly employed in many fields of chemistry such as drug discovery,<sup>[1,2]</sup>, fungicides, herbicides, corrosion-retarding agents, solar cells and dyes.<sup>[3,4]</sup>

In 2002, Sharpless and co-workers<sup>[5]</sup> and Meldal and co-workers<sup>[6]</sup> independently reported the Huisgen [3 + 2] cycloaddition of terminal alkynes and organic azides catalysed by homogeneous Cu(I) salts, the so-called click reaction. The click reaction can also be catalysed by heterogeneous Cu(I),<sup>[7]</sup> such as copper nanoparticles on activated carbon,<sup>[8–11]</sup> copper zeolites,<sup>[12,13]</sup> CuBr on graphene oxide/Fe<sub>3</sub>O<sub>4</sub><sup>[14]</sup> and copper nitride nanoparticles supported on mesoporous SiO<sub>2</sub>.<sup>[15,16]</sup> Also, CuI was applied in a highly optimized protocol for repetitive triazole formation on a solid support.<sup>[17,18]</sup>

Graphene is a typical solid support employed in the preparation of heterogeneous catalysts. Graphene oxide (GO), an oxidized form of graphene, has appeared as a significant material owing to its unique nanostructure and a diversity of fascinating characteristics such as very high specific surface area with natural low mass, excellent mechanical strength<sup>[19,20]</sup> and abundant hydrophilic oxygencontaining groups including hydroxyl, epoxy, carboxyl and carbonyl groups, leading to its easy modification and widespread application.<sup>[21]</sup> The chemical modification of GO has been demonstrated to be an efficient method which renders it a more versatile precursor for a wide range of applications.

Functionalization of GO is necessary for various applications such as carbocatalysis. In addition, carbocatalysts are commonly inexpensive, stable and readily available. Another advantage of carbocatalysts relates to their desirable surface to volume ratio which increases the contact between reactants and catalyst support and in turn enhances catalytic activity.<sup>[22]</sup> Also, carbocatalysis provides a bridge to heterogeneous catalysis.<sup>[23]</sup>

Special ligands are often employed both to increase the rate of reaction and to protect Cu(I) from oxidation in the presence of adventurous oxygen.<sup>[24]</sup> These ligands containing nitrogen atoms with special structure are able to chelate copper. Oligotriazole ligands are advantageous in protecting Cu(I) ions from aerobic aqueous conditions and therefore improve the copper-catalysed azide–alkyne cycloaddition (CuAAC) reaction rate.<sup>[25,26]</sup> They are oligotriazole derivatives branching from propargylamine cores. This new class of ligands is capable of binding to metals by forming a

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chelate between the nitrogen atoms of the triazole and the amine. The nitrogen atom of tertiary amine is supposed to bind constantly to the metal centre, while the triazole ligands might provisionally dissociate from the Cu(I) ion to permit the formation of copper acetylide as starting point of the catalytic cycle of the CuAAC reaction.<sup>[26]</sup> In continuation of our ongoing work towards the synthesis of triazoles,<sup>[27,28]</sup> herein we report a GO-supported copper catalyst, containing 1,2,3-triazoles as Cu(I)-stabilizing ligands, for use in the preparation of triazole derivatives.

# 2 | EXPERIMENTAL

#### 2.1 | Materials and apparatus

The chemicals used in this work were purchased from Fluka and Merck and used without purification. Fourier transform infrared (FT-IR) spectra were obtained as KBr pellets with a PerkinElmer 781 spectrophotometer and a Nicolet Impact 400 FT-IR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solvent with a Bruker DRX-400 spectrometer using tetramethylsilane as internal reference. X-ray diffraction (XRD) patterns were recorded using an X'Pert Pro (Philips) instrument with an X-ray beam of 1.54 Å wavelength and Cu anode material, at a scanning speed of  $2^{\circ}$  min<sup>-1</sup> from  $10^{\circ}$  to  $80^{\circ}$  (2 $\theta$ ). Scanning electron microscopy (SEM) images of the prepared catalyst were obtained with an FE-SEM S4160 instrument (Hitachi). Atomic force microscopy (AFM) images of GO nanosheets and functionalized GO were measured using a scanning probe microscope (SPM-9600, Shimadzu). Thermogravimetric analysis (TGA) was performed with a Mettler TA4000 system TG-50 at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Melting points were obtained with a Yanagimoto micro melting point apparatus. Purity determination of substrates and reaction monitoring were accomplished by TLC using silica-gel Polygram SILG/UV 254 plates (Merck).

#### 2.2 | Preparation of catalyst

#### 2.2.1 | Preparation of GO

GO was synthesized from natural graphite using the Hummers method.<sup>[29]</sup> Graphite powder (5.0 g) was stirred in the presence of sodium nitrate (2.5 g) and concentrated sulfuric acid (115 ml) in a 1000 ml round-bottom flask placed in an ice bath. Then, potassium permanganate (15 g) was slowly added to the mixture and stirred for 2 h. The mixture solution was transferred to a water bath (35 °C) and stirred for 30 min. Afterwards, deionized water (230 ml) was added to the solution slowly and the solution temperature was monitored at about 98 °C and stirred for

15 min. Then deionized water (700 ml) and  $H_2O_2$  (50 ml, 30%) were each added to the solution. The obtained suspension was filtered and washed with diluted HCl (5%) and deionized water several times to eliminate excess acid and dried for 12 h at 60 °C under vacuum. The graphite oxide was dispersed in distilled water to get a concentration of 0.5 mg ml<sup>-1</sup> and exfoliated by ultrasound to afford GO nanosheets.

## 2.2.2 | Synthesis of 3-chloropropyltrimethoxysilane-functionalized GO (GO@CPTMS)

GO (1 g) was dispersed in 250 ml of dry toluene using an ultrasonic probe. Subsequently, 3.0 ml of 3chloropropyltrimethoxysilane (CPTMS) was diluted in 20 ml of dry toluene followed by dropwise addition to the GO dispersion. The reaction vessel was heated to reflux with continuous stirring for 48 h under nitrogen atmosphere. After completion of the reaction, the functionalized GO nanosheets were washed with toluene four times to remove excess/non-reacted CPTMS and then ethanol was used for the final washing. The CPTMS-coated GO nanosheets were dried in an oven at 70 °C.<sup>[30,31]</sup>

## 2.2.3 | Preparation of azide-functionalized GO (GO@PTMS-N<sub>3</sub>)

In a 1000 ml round-bottom flask, 1.0 g of GO@CPTMS was added into deionized water (150 ml), followed by sonication (35 W) for 5 min. Then, 2 g of NaN<sub>3</sub> and 0.2 g of KI were added into the round-bottom flask, and heated at 60 °C for 48 h. After this step, the resulting product was washed with water several times and dried at 50 °C in vacuum.

### 2.2.4 | Huisgen 1,3-dipolar cycloaddition between GO@PTMS-N<sub>3</sub> and tripropargylamine

GO@PTMS-N<sub>3</sub> was coupled to alkyne groups by a copper-catalysed azide–alkyne click reaction (Scheme 1). GO@PTMS-N<sub>3</sub> (1 g) was dispersed in 250 ml of deionized water using an ultrasonic probe. Subsequently, tripropargylamine (0.6 g) and copper catalyst based on CuSO<sub>4</sub> and sodium ascorbate (0.05 and 0.1 equiv., respectively) were added. The reaction was performed for 48 h at room temperature. The resulting product was washed with water several times and eventually dried under vacuum overnight.

# 2.2.5 | Preparation of copper complex catalyst immobilized on GO (GO@PTA-Cu)

1,2,3-Triazole-functionalized GO (1 g) was dispersed in 250 ml of dry acetonitrile using an ultrasonic probe. In the



SCHEME 1 Preparation of GO@PTA-Cu organocatalyst

subsequent step, CuI (0.26 mmol, 0.05 g) was added to the stirring mixture. The resulting mixture was refluxed for 24 h. After completion of the reaction, the immobilized catalyst was filtered and washed with  $CH_3CN$  and dried under vacuum overnight.

# 2.3 | General procedure for preparation of β-Hydroxy-1,2,3-triazoles catalysed by GO@PTA-Cu under thermal conditions

In a 25 ml round-bottom flask equipped with a magnetic stir bar and condenser, a mixture of NaN<sub>3</sub> (72 mg, 1.1 mmol), epoxide (1 mmol), alkyne (1 mmol) and GO@PTA-Cu (10 mg, 0.017 mol%) was heated at 60 °C in water (5 ml) for a suitable time period. The progress of the reaction was monitored using TLC.

After the end of reaction, in order to separate the catalyst, the product was dissolved in hot methanol and the mixture was filtered under reduced pressure using a vacuum pump over sintered glass. The solution was recovered via evaporation using a rotary evaporator. The crude solid product was recrystallized from ethanol to afford the  $\beta$ -hydroxy-1,2,3-triazoles as pure product. All products were confirmed using spectral data and physical data and compared and verified with authentic samples.

# 2-Phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol (3a)

Pale yellow solid; m.p. 125.0–127.0 °C lit.<sup>[9]</sup> 125.5–127.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 690, 758, 1047, 1080, 1241, 1438, 1463, 1493, 1593, 2928, 3065, 3089, 3140, 3345. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): Applied Organometallic <u>3 of 11</u> Chemistry

7.80–7.79 (m, 3H), 7.70 (s, 1H), 7.42–7.38 (m, 6H) 7.33 (s, 1H), 5.69 (dd,  ${}^{3}J$ (H–H) = 8 Hz,  ${}^{3}J$  = 3.9 Hz, 1H), 4.67–4.60 (dd, 1H,  ${}^{3}J$ (H–H) = 12.4 Hz,  ${}^{3}J$ (H–H) = 7.6), 4.27–4.22 (dd, 1H,  ${}^{3}J$ (H–H) = 14.4 Hz,  ${}^{3}J$ (H–H) = 3.6), 3.21 (t, *J*(H, H) = 6.8 Hz; 1H, OH).

# 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)-2-p-tolylethanol (3b)

Yellow solid; m.p. 125.0–127.0 °C (lit.<sup>[32]</sup> 124.0–126.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 697, 726, 757, 1047, 1075, 1008, 1185, 1221, 1380, 1457, 1497, 2927, 3028, 3092, 3417. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.69–7.65 (m, 3H), 7.39 (m, 3H), 7.27–7.20 (m, 3H), 5.68–5.65 (dd, <sup>3</sup>*J*(H, H) = 8 Hz, <sup>3</sup> *J* = 3.2 Hz, 1H), 4.65–4.61 (dd, 1H, <sup>3</sup>*J*(H–H) = 12.6 Hz, <sup>3</sup>*J*(H–H) = 8.4), 4.25–4.20 (dd, 1H, <sup>3</sup>*J*(H–H) = 9 Hz, <sup>3</sup> *J*(H–H) = 3.6), 2.38 (s, 3H), 2.37 (t, *J*(H, H) = 2.8 Hz; 1H).

#### 1-(4-Phenyl-1H-1,2,3-triazol-1-yl)butan-2-ol (3c)

White solid; m.p. 110.0–112.0 °C (lit.<sup>[28]</sup> 110.0–111.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 697, 763, 981, 1079, 1136, 1228, 1456, 1617, 2926, 2962, 3138, 3254, 3419. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.87 (s, 1H), 7.80–7.79 (m, 2H), 7.43–7.40 (m, 2H), 7.34 (m, 1H), 4.55–4.50 (dd, 1H, <sup>3</sup>*J*(H–H) = 14 Hz),4.33–4.28 (dd, 1H, <sup>3</sup>*J*(H–H) = 13.8 Hz, <sup>2</sup> *J*(H–H) = 7.6), 2.66–2.65(d, <sup>3</sup>*J*(H–H) = 4.4, 1H), 1.66–1.53 (m, 2H), 1.09–1.05 (t, 3H).

# 1-Phenoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl) propan-2-ol (3d)

Pale yellow solid; m.p. 125.0–127.0 °C (lit.<sup>[33]</sup> 125.5–126.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 692, 756, 981, 1043, 1245, 1494, 1595, 2866, 2927, 3087, 3429. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.89 (s, 1H), 7.75–7.73 (m, 2H), 7.40–7.38 (m, 2H), 7.31–7.27 (m, 3H), 7.02–6.94 (m, 1H), 6.93–6.91(m, 2H), 4.75–4.73 (m, 1H), 4.56–4.54 (m, 2H), 4.22–4.04 (m, 2H), 3.94–3.76 (m, 1H).

## 1-Isopropoxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl) propan-2-ol (3e)

Yellow solid; m.p. 62.0–64.0 °C (lit.<sup>[28]</sup> 61.0–63.0). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 697, 765, 923, 975, 1078, 1127, 1228, 1373, 1466, 2867, 2973, 3062, 3137, 3425. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.91 (s, 1H), 7.79–7.78 (m, 2H), 7.42–7.37 (m, 2H), 7.34–7.31 (m, 1H), 4.60–4.57 (dd, 1H, <sup>3</sup>*J*(H–H) = 12 Hz, <sup>2</sup>*J*(H–H) = 2.8), 4.64–4.40 (dd, 1H, <sup>3</sup>*J*(H–H) = 14 Hz, <sup>2</sup>*J*(H–H) = 4), 4.21 (m, 1H), 3.64–3.57 (m, 1H), 3.53–3.51 (dd, 1H, <sup>3</sup>*J*(H–H) = 8 Hz, <sup>3</sup>*J*(H–H) = 4.4), 3.41–3.36 (dd, 1H, <sup>3</sup>*J*(H–H) = 10 Hz, <sup>3</sup>*J*(H–H) = 4), 1.15–1.17 (t, 6H).

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# 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)cyclohexanol (3f)

Yellow solid; m.p. 168.0–172.0 °C (lit.<sup>[9]</sup> 168.0–171.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 698, 768, 713, 1052, 1083, 1234, 1441, 2858, 2938, 3118, 3307. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.78 (s, 1H), 7.74–7.71 (m, 2H), 7.41–7.37 (m, 2H) 7.33–7.29 (s, 1H), 4.19–4.08 (m, 3H), 4.01–1.91 (m, 4H), 2.25–2.22 (m, 2H), 1.51–1.25 (m, 2H).

# 2-Hydroxy-3-(4-phenyl-1H-1,2,3-triazol-1-yl) propyl acrylate (3g)

Livid solid; m.p. 102.0–104.0 °C (lit.<sup>[28]</sup> 101.0–103.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 695, 756, 1044, 1245, 1494, 1596,



Wavenumbers (cm<sup>-1</sup>)





FIGURE 2 XRD patterns of (a) graphite, (b) GO and (c) GO@PTA-Cu

2925, 3087, 3426. <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>,  $\delta$ , ppm): 7.91 (s, 1H), 7.79–7.78 (m, 1H), 7.43–7.41 (m, 2H),7.35–7.30 (m, 2H), 7.02–6.98 (t, 1H), 6.92–6.91 (m, 2H), 4.22 (m, 1H), 3.64–3.57 (m, 1H), 4.08–3.98 (m, 1H), 3.38–3.37 (m, 1H).

# 1,3-Bis(4-phenyl-1H-1,2,3-triazol-1-yl)propan-2-ol (3h)

Green solid; m.p. 233.0–236.0 °C (lit.<sup>[34]</sup> 233.0–236.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 687, 724, 763, 1074, 1126, 1278, 1464, 1729, 2861, 2928, 2959. <sup>1</sup>H NMR (400 MHz, DMSO,  $\delta$ , ppm): 8.55 (s, 1H), 7.84 (m, 2H), 7.44–7.42 (m, 2H),



FIGURE 3 SEM images of (a) GO and (b) GO@PTA-Cu

7.32–7.30 (m, 1H), 5.81 (m, 1H), 4.61–4.56 (d, 1H), 4.40 (m, 2H). <sup>13</sup>C NMR (400 MHz, DMSO,  $\delta$ , ppm): 147.71, 132.42, 130.51, 129.68, 129.41, 127.11, 126.72, 124.12, 69.91, 54.84.

### 1-(4-Phenyl-1H-1,2,3-triazol)hexan-2-ol (3i)

Cream solid; m.p. 92.0–94.0 °C (lit.<sup>[32]</sup> 91.0–93.0 °C). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 693, 764, 1087, 1138, 1228, 1463, 2862, 2925, 2959, 3142, 3248, 3407. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.85 (s, 1H), 7.78–7.75 (m, 2H), 7.42–7.41 (m, 2H), 7.35–7.32 (m, 1H), 4.52–4.49 (m, 2H), 4.29–4.23 (m, 1H), 4.15–4.13 (m, 1H), 1.57–1.50 (m, 3H), 1.45–1.37 (m, 3H), 0.95–0.91 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 147.27, 130.33, 128.78, 128.06, 125.53, 121.16, 70.44, 56.34, 34.17, 30.77, 28.01, 22.59, 13.99.

# 2-Phenyl-2-(4-propyl-1H-1,2,3-triazol-1-yl)ethanol (3j)

Pale yellow solid; m.p. 62.0–64.0 °C. FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 697, 761, 1070, 1280, 1455, 1726, 2853, 2925, 3061, 3367. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.80 (s, 1H), 7.72 (m, 1H), 7.55–7.53 (m, 1H), 7.46–7.33 (m, 3H), 4.24–4.17 (m, 2H), 1.68–1.8 (t, 1H), 1.44–1.40 (m, 1H), 1.32–1.25 (m, 4H), 0.94 (m, 3H).

### **3** | **RESULTS AND DISCUSSION**

# **3.1** | Preparation and characterization of catalyst

Synthesis of the heterogeneous Cu(I) complex and the intermediate steps were examined and monitored using FT-IR spectroscopy, AFM, SEM, XRD, inductively coupled plasma (ICP) analysis and energy-dispersive X-ray (EDX) analysis.



#### FIGURE 4 TGA curve of GO@PTA-Cu

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GO is a notable support for the immobilization of organocatalysts as a result of its mechanical and thermal stability. These reasons prompted us to develop our work for the linking of an organocatalyst onto GO. The preparation





FIGURE 5 AFM images of (a) GO nanosheets and (b) GO@PTA-Cu

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of the GO-immobilized copper complex consists of the following steps, as shown in Scheme 1.

In the first step, GO was functionalized using CPTMS according to previously reported methods.<sup>[30,31]</sup> The chloro-functionalized GO was allowed to react with sodium azide to form GO@PTMS-N<sub>3</sub>. The azide-functionalized GO was then coupled to tripropargylamine to form 1,2,3-triazole-functionalized GO via a copper-catalysed azide–alkyne click reaction. 1,2,3-Triazole-functionalized GO formed a complex with CuI, affording the immobilized Cu complex catalyst (GO@PTA-Cu). The nitrogen-donating ligands of 1,2,3-triazole are particularly promising as they form stable Cu(I) complexes.

Figure 1 shows the FT-IR spectra of graphite, GO, GO@CPTMS, GO@PTMS-N<sub>3</sub> and GO@PTA. The FT-IR

spectrum of natural graphite powder exhibits peaks characteristic of C=C groups of which the peak related to C=C double bonds at 1573 cm<sup>-1</sup> is not sharp (Figure 1a). Figure 1(b) shows the FT-IR spectrum of GO powder. The stretching vibration at 3398 cm<sup>-1</sup> corresponds to the OH group. The absorption band at 1717 cm<sup>-1</sup> corresponds to C=O group. The absorption peaks at 1640 and 1056 cm<sup>-1</sup> are assigned to carbon–carbon double bonds and C–O, respectively. The various functional groups on the GO provide active sites for the bonding between GO sheets and silane.

Figure 1(c) shows the FT-IR spectrum of CPTES-coated GO. The absorption peak at 1045 cm<sup>-1</sup> corresponds to the Si–O–C bond. The vibrational bands at 2926 and 2854 cm<sup>-1</sup> are attributed to CH<sub>2</sub> and the peak at 695 cm<sup>-1</sup>



FIGURE 6 EDX patterns of (a) GO and (b) GO@PTA-Cu

representing the C–Cl bond indicates the successful coating of the CPTES onto GO through chemical bonding. After the reaction between sodium azide with GO@CPTMS, azide groups were attached to the surfaces of GO, which is evident from the appearance of the characteristic FT-IR absorption peak of azide groups at 2098 cm<sup>-1</sup> and disappearance of the peak at 695 cm<sup>-1</sup> corresponding to C–Cl bond (Figure 1d).

Figure 1(e) shows the FT-IR spectrum of 1,2,3-triazolefunctionalized GO. Disappearance of the peak at 2098 cm  $^{-1}$  indicates the successful azide–alkyne coupling reaction on the surface of GO. The N=N stretching absorption for triazole compounds appears at around 1457 cm<sup>-1</sup> which is assigned within the same absorption region of the C...C stretching for GO.

XRD patterns were analysed to determine the phase structure of GO. Figure 2 shows XRD patterns of graphite, GO and GO@PTA-Cu. The pattern of graphite powder shows a sharp peak at  $2\theta = 26^{\circ}$  (Figure 2a), corresponding to an interlayer spacing (d-spacing) of 0.335 nm. The exfoliated GO shows a broad peak at about  $2\theta = 26.5^{\circ}$  and a peak at  $2\theta = 12^{\circ}$  (*d*-spacing =0.78 nm) (Figure 2b). The enhancement in *d*-spacing is due to the intercalation of water molecules and the formation of oxygen-containing functional groups between the layers of the graphite. After the surface covalent functionalization of GO with CPTMS, click coupling process and finally production of the GO@PTA-Cu catalyst, the diffraction peak at  $2\theta = 12^{\circ}$  in the GO pattern disappears, indicating an increase the interlayer distances. Furthermore, because of the small amount of copper in GO@PTA-Cu, the signals pertaining to copper are not clearly detected in the XRD pattern (Figure 2c).



**SCHEME 2** Synthesis of 2-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanol (**3a**)

 TABLE 1
 Solvent optimization for the synthesis of 3a in the model reaction<sup>a</sup>

Entry	Solvent	Time (min)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O	35	94
2	EtOH	35	60
3	PhCH <sub>3</sub>	75	35
4	$CH_2Cl_2$	60	20
5	<i>n</i> -hexane	60	15
6	DMF	40	55

 $^aReaction$  conditions: styrene oxide (1 mmol), phenylacetylene (1 mmol), NaN\_3 (1.1 mmol), GO@PTA-Cu (10 mg, 0.017 mol%), 60 °C.

<sup>b</sup>Isolated yield.

The SEM images of GO and GO@PTA-Cu are shown in Figure 3. Different morphologies are observed for GO nanosheets and the prepared catalyst. The images confirm that two-dimensional GO nanosheets can be produced via exfoliation of suspended graphite oxide.

TGA was used to verify the anchoring of organic groups on the surface of GO. As shown in Figure 4, there is a mass loss (42%) below 260 °C attributed to the removal of adsorbed water firstly and oxygen-containing functional groups on the GO surface. There is a decrease of weight (24%) when the temperature is between 260 and 610 °C that is attributed to the covalency of organic groups.

AFM was employed to observe the morphology of GO nanosheets and measure their thickness. The AFM images of GO and GO@PTA-Cu easily confirm the wrinkled twodimensional characteristic of the GO nanosheets. The images indicate that the thickness of GO is approximately 0.9 to 1.5 nm, corresponding to structures with one to two layers (Figure 5a). After surface functionalization, the thickness of sheets is increased to 4.3 nm (Figure 5b). The increase in thickness of functionalized GO nanosheets is perhaps caused by the organic compounds grafted on the GO sheets, indicating the successful functionalization of GO.

The Cu content for GO@PTA and GO@PTA-Cu catalyst was determined using ICP analysis. According to the

 TABLE 2
 Optimization of GO@PTA-Cu catalyst amount in the model reaction<sup>a</sup>

Entry	Catalyst (mg)	Cu (mmol)	Time (min)	Yield (%) <sup>b</sup>
1	0	_	120	_
2	2	0.00034	50	75
3	5	0.00086	35	90
4	10	0.0017	35	94
5	15	0.0026	40	90

<sup>a</sup>Reaction conditions: styrene oxide (1 mmol), phenylacetylene (1 mmol), NaN<sub>3</sub> (1.1 mmol), H<sub>2</sub>O, 60 °C, GO@PTA-Cu (0.017%).
<sup>b</sup>Isolated yield.

TABLE 3	Temperature optimization for synthesis of <b>3a</b> in the model	
reaction <sup>a</sup>		

Entry	Temperature (°C)	Time (min)	Yield (%) <sup>b</sup>
1	r.t.	120	_
2	40	60	_
3	50	120	30
4	60	35	94
5	80	35	94

<sup>a</sup>Reaction conditions: styrene oxide (1 mmol), phenylacetylene (1 mmol), NaN<sub>3</sub> (1.1 mmol), H<sub>2</sub>O, GO@PTA-Cu (10 mg, 0.017 mol%).

<sup>b</sup>Isolated yield

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#### TABLE 4 Synthesis of $\beta$ -hydroxytriazoles catalysed by GO@PTA-Cu<sup>a</sup>

		R <sub>1</sub> (1)	∆ <sub>+</sub> ===−R <sub>2 +</sub> NaN <sub>3</sub> <u>H</u> <sub>2</sub> O, 60° GO@PTA	$C \xrightarrow{R_2} N \xrightarrow{R_1} N \xrightarrow{R_1} N \xrightarrow{R_1} N \xrightarrow{R_2} N \xrightarrow{R_1} N \xrightarrow{R_1} N \xrightarrow{R_2} N \xrightarrow{R_1} N \xrightarrow{R_2} N \xrightarrow{R_1} N \xrightarrow{R_2} N$	(H) -OH		
Entry	Alkyne (R <sub>2</sub> )	Epoxide	Product	Time (min)	Yield (%) <sup>b</sup>	TON <sup>c</sup>	TOF $(h^{-1})^d$
1	Ph	(1a)	$\begin{array}{c} Ph_{N^{\mathrm{S}}N'} \\ N^{\mathrm{S}}N' \\ OH \end{array}$	35	94	543	936
2	Ph	(1b)	$Ph \xrightarrow{N=N'}OH$ (3b)	35	94	543	936
3	Ph	(1c)	$\bigvee_{N} \stackrel{OH}{\underset{N}{\overset{N_{\Xi}N}{\overset{N_{\Xi}N}{\overset{Ph}{\overset{(3c)}{\overset{(3c)}{}}}}}}$	65	90	520	481
4	Ph	Ph o O (1d)	Ph-OOHN_=N_ N_=NPh (3d)	70	92	531	454
5	Ph	(1e)	$\begin{array}{c} Ph & & \\ & & N {\sim} N {\longrightarrow} HO  O {\longrightarrow} O {\longleftarrow} (3e) \\ \end{array}$	85	90	520	366
6	Ph	(11)	$\begin{array}{c} Ph \\ N \geq_{N} \\ H \\ O \\ (3f) \end{array}$	60	90	520	520
7	Ph		$(3g) O \rightarrow N \rightarrow Ph$	150	82	473	189
8 <sup>e</sup>	Ph	TsO (1h)	$(Ph \underbrace{N}_{N=N} \underbrace{)_{2}}_{2} OH$ (3h)	55	85	491	534

(Continues)

#### TABLE 4 (Continued)

		R1 (1	△ + ====R <sub>2</sub> + NaN <sub>3</sub> <u>H</u> <sub>2</sub> O, 60 GO@PT/	$\begin{array}{c} \overset{\text{PC}}{\underset{A-Cu}{\overset{R_2}{\overset{N=N}{\overset{N=N}{\overset{N=N}{\overset{(H)R_1}{\overset{(3a-j)}}}}}}}$	₁(H) -OH		
Entry	Alkyne (R <sub>2</sub> )	Epoxide	Product	Time (min)	Yield (%) <sup>b</sup>	TON <sup>c</sup>	TOF $(h^{-1})^d$
9 <sup>e</sup>	Ph	CIO (11)	$(Ph \underbrace{N}_{N=N} \underbrace{N}_{2} OH$ (3h)	90	80	462	308
10	Ph	(1j)	Ph- N <sup>≠</sup> N OH (3i)	80	89	514	395
11	∕~CH₂	(1a)	$(3j) Ph \\ Ph \\ N=N \\ OH$	50	89	514	619

<sup>a</sup>General reaction conditions: **1** (1 mmol), **2** (1 mmol), NaN<sub>3</sub> (1.1 mmol), GO@PTA-Cu (0.017 mol%, 10 mg), H<sub>2</sub>O, 60 °C.

<sup>b</sup>Isolated yield.

<sup>c</sup>TON: moles of formed  $\beta$ -hydroxy-1,2,3-triazole per mole of catalyst.

<sup>d</sup>TOF: (mmol of product/mmol of active site of catalyst)/time of reaction (h).

<sup>e</sup>Reaction conducted with 1:2:2 mole ratio of epoxide, alkyne and NaN<sub>3</sub>, respectively.

obtained results from ICP analysis, the Cu content in the catalyst is 1.1%, while no Cu content was indicated in the GO@PTA species. Also, to support the mentioned observation, the catalyst was subjected to EDX analysis. The EDX analysis of GO and GO@PTA-Cu catalyst confirms the presence of organosilane and copper (Figure 6).

# 3.2 | Investigation of catalyst activity

Initially, the reaction parameters were optimized in the reaction of styrene oxide (1 mmol), phenylacetylene (1 mmol) and NaN<sub>3</sub> (1.1 mmol), in the presence of catalytic amounts of catalyst, as the model reaction (Scheme 2).

To choose the medium of the reaction, the model reaction was performed in various solvents: water, EtOH, PhCH<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, *n*-hexane and dimethylformamide (DMF). The results are summarized in Table 1. The reaction in water as solvent gave the best result (Table 1, entry 1). This is probably due to the high solubility of sodium azide in water. Furthermore, the reactions were clean in water compared to those in organic solvents. Therefore, in continuation of the process, water was chosen as the reaction medium.

The effect of the amount of GO@PTA-Cu as catalyst on the synthesis of 3a is presented in Table 2. The best result was observed with 10 mg (0.0017 mmol of Cu) of the catalyst and the catalyst afforded 94% yield of product **3a** in 35 min in water under reflux conditions. No product was formed in the absence of the catalyst.

For optimization of temperature of the reaction, an increase in temperature of the reaction (room temperature to 80 °C) led to decreased time of the reaction and increased yields of the desired product (Table 3). No significant increase in the yield of product was observed as the reaction temperature was raised from 60 to 80 °C. Therefore, 60 °C was chosen for this reaction.

After optimization of the reaction conditions, we used these conditions for the reaction of a series of different aryland alkyl-substituted oxiranes (**1a–j**) and terminal alkynes (**2a** and **2b**) to investigate the versatility of the protocols under GO@PTA-Cu catalysis. The results are summarized in Table 4. We first studied the reaction of aryl-substituted epoxides with phenylacetylene (Table 4, entries 1 and 2). The aryl-substituted epoxides **1a** and **1b** reacted rapidly, affording triazoles **3a** and **3b**, respectively, in high yield and short reaction time and with reverse regioselectivity to that displayed by the alkyl-substituted epoxides. Subsequently, we examined the reaction between aliphatic epoxides and phenylacetylene (Table 4, entries 3–10). In these cases, we observed a decrease in yield and increase in reaction time compared with the aryl-substituted epoxides. The formation of bis-triazole **3 h** from **1 h** and **1i** in this reaction can be due to the existence of good leaving groups (OTs, Cl) in the primary epoxides (Table 4, entries 8 and 9). Furthermore, the structures of these products were confirmed from <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra.

#### 3.3 | Proposed reaction mechanism

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The proposed mechanism for the formation of  $\beta$ -hydroxy-1,2,3-triazoles includes two routes,<sup>[28]</sup> in which GO@PTA-Cu has a two-fold catalytic effect as a bifunctional catalyst. which combines one-pot ring-opening and 1,3-dipolar cycloaddition. Firstly, GO@PTA-Cu catalyses the formation of organoazide (II) from epoxide and sodium azide (Scheme 3). Also, a  $\pi$ -complex is formed between phenylacetylene and GO@PTA-Cu to afford the copper(I) acetylide intermediate (III), the generation and disappearance of the organoazide intermediate being monitored by TLC. Coordination of the organoazide to the copper centre of the acetylide enhances the nucleophilicity of the triple bond and begins a sequence of steps which finally results in the formation of the new C-N bond between the nucleophilic \beta-carbon atom of the acetylide and the terminal electrophilic nitrogen atom of the azide.<sup>[35]</sup> Ultimately, after protonation of intermediate (IV),  $\beta$ -hydroxy-1,2,3-triazole is obtained in high yield and short reaction time.



SCHEME 3 Proposed mechanism for synthesis of  $\beta$ -hydroxy-1,2,3-triazoles



FIGURE 7 Reusability of GO@PTA-Cu catalyst in synthesis of 3a



FIGURE 8 SEM image of GO@PTA-Cu after recycling

#### **3.4** | Recycling the catalyst

The possibility of recycling the catalyst was examined through the reaction of styrene oxide, phenylacetylene and NaN<sub>3</sub> catalysed by GO@PTA-Cu under the optimized conditions. Upon completion of the reaction, the catalyst was separated by filtration, washed with methanol and dried at 80 °C in an oven for 8 h. The recycled catalyst could be reused five times without significant loss of its catalytic activity, with yields ranging from 94 to 85% (Figure 7). An SEM image of the catalyst after recycling from the reaction was obtained, which does not show any considerable change in the morphology (Figure 8). demonstrating the retention of the catalytic activity with recycling.

## 4 | CONCLUSIONS

We have established that GO@PTA-Cu is a robust, reusable and heterogeneous solid catalyst for the synthesis of  $\beta$ -hydroxy-1,2,3-triazoles in water under thermal conditions. We have reported the preparation of a tetradentate nitrogen ligand on the surface of functionalized GO support using click chemistry. This tetradentate nitrogen ligand not only stabilizes Cu(I) intermediates but also advances the catalytic process. Also, the prepared catalyst was characterized using some spectroscopic and microscopic techniques such as FT-IR spectroscopy, SEM, TGA, ICP analysis, EDX analysis, AFM and XRD. The spectroscopic and microscopic analyses confirmed that the functionalization of GO was successful. This method has several advantages, including high to excellent yields of products, green reaction solvent, reusability of catalyst and simple work-up process.

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#### SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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