Synthesis, Characterization and First Application of Graphene Oxide Functionalized Cu(II) Complex for the Synthesis of 1,2,3-Triazole Derivatives

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ABSTRACT
In this research, the functionalized graphene oxide (GO) catalyst was prepared by covalently immobilization of metformin copper complex on the surface of GO. The chemical and physical structures of catalyst were fully characterized by various analyses like XRD, ICP, FT-IR, TEM, EDX, BET and TGA. Then, the effects of nanosheet heterogeneous catalyst were investigated for the synthesis of 1,2,3-triazoles via azide-alkyne cycloaddition reaction. This is the first report for the synthesis of 1,2,3-triazoles derivatives catalyzed by heterogeneous GO copper complex and water as a green solvent.

HIGHLIGHTS
- First preparation and characterization of GO functionalized Copper Complex.
- Covalently and chemically immobilization of Cu(II) complex on the surface of GO.
- Synthesis of 1,2,3-triazoles via click reaction in water and room temperature.
- Reusable catalyst for at least for five times without any decreasing in catalytic activity.

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**Introduction**

Carbon has several allotropes which the significant and widely used allotrope of carbon is graphene that it is including a single layer of atoms in a 2D hexagonal structure with sp² and sp³ hybridization.¹ Graphene also has various applications with a nearly transparent structure and is able to conduct heat and electricity efficiently.²⁻⁴ It can chemically convert to the oxidized form named graphene oxide (GO) with simple oxidation processes.⁵⁻⁸ During the oxidation reaction, three different oxygen-bearing organic functional groups (carboxyl, hydroxyl, and epoxy) are created on the surface of GO, both on its basal plane and edges which can be used for organic ligand functionalization⁹,¹⁰ and thereupon design and synthesis of novel heterogeneous catalysts.¹¹⁻¹⁵

Functionalization of GO nanosheet materials with transition metal nanoparticles though attracting considerable interest in the area of basic research,¹⁶,¹⁷ it can be simultaneously attractive for heterogeneous transition metal catalysis.¹⁸⁻²² For example, Ghadamyari and coworkers reported the GO functionalized Co(II)-porphyrin for the Beckmann rearrangement. Their new heterogeneous catalytic systems demonstrated higher catalytic efficiency in the synthesis of amide derivatives compared to simple cobalt salts.²³ Ghaedi and colleagues immobilized the nickel complex on the surface of GO and then they used this catalyst in Suzuki-Miyaura cross-coupling reaction. Interestingly, their heterogeneous nickel complex like palladium catalysts could catalyze the C-C bond formation with the good yields.²⁴ In another report, different metal complexes like Co(II), Fe(III) or VO(II) have been immobilized on the surface of GO and their catalytic applications have been investigated in epoxidation reaction. The GO cobalt Schiff base complex had the best result on the styrene epoxidation.²⁵

The organic reaction between a dipole (alkyne) and a dipolarophile (azide) is known as a Huisgen 1,3-dipolar cycloaddition reaction.²⁶ This azide-alkyne reaction without catalyst generally forms both 1,2,3-triazoles isomers which is the most disadvantage of this reaction in order to organic synthesis. For overcoming this problem, Meldal and coworkers²⁷,²⁸ presented the copper azide-alkyne (CuAAC) cycloaddition reaction.²⁹ In recent years, this method is hugely routine for the synthesis of 1,2,3-triazoles derivatives with different kinds of copper catalysts.³⁰ In addition to traditional copper salts like Cu(OAc)₂,³¹ CuSO₄.5H₂O,³² CuCl₂.2H₂O,³³ CuI,³⁴ CuO³⁵ for the synthesis of triazole derivatives, many heterogeneous metal-based catalysts have been reported by the researchers.³⁶⁻⁴¹ But most of them have some drawbacks like long reaction times, low isolated yield, use of hazardous materials and solvents and uneasy workup procedures. Therefore, it is essential and recommended to present new catalytic systems based on heterogeneous nature. In this study, for the first time, a new copper complex was chemically and covalently immobilized on the surface of GO nanosheet material by the organic condensation reaction of copper metformin complex and carboxyl groups on the surface of GO (Scheme 1). Then, the chemical structure of the synthesized catalyst was completely detected by different analyses and eventually, the applications of this nano heterogeneous organometallic catalyst have been investigated in the synthesis of 1,2,3-triazoles derivatives (Scheme 2).

**Experimental**

**General**

All the materials and reagents were purchased from Sigma-Aldrich and Merck without any further purification. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet Avatar 370 FT-IR Therma spectrometer. NMR spectra were obtained with a Brucker AMX 100 and 400 MHz instruments in DMSO. Transmission electron microscopy (TEM) was performed with a Leo 912AB (120 kV) microscope (Zeiss, Germany). Inductively coupled plasma (ICP) analysis was carried out with a Varian VISTA-PRO, CCD (Australia). Energy-dispersive X-ray (EDX) analysis
was performed using a SAMX instrument. Melting points of products were recorded with an Electrothermal type 9100 melting point apparatus.

**Preparation of catalyst**

The GO and Functionalized GO (GO-M) have been synthesized according to the literature.\textsuperscript{42,43} For the preparation of final catalyst (GO-M-Cu), GO–M (1.0 g) was dispersed in DMF (10 mL) by sonication for 20 min and then and Cu(OAc)\textsubscript{2} (1.0 and 0.01 g) was added and refluxed for 6 h. Thereafter, the black mixture was permitted to cool to room temperature and separated by centrifuging at 8500 rpm for 20 min. Finally, the obtained nano heterogeneous catalyst was dried in vacuum oven at 80°C for 12 h to give the final catalyst (GO-M-Cu).

**General procedure for the synthesis of 1,2,3-triazole derivatives**

At first, the catalyst (30 mg, 2.0 mol%) was dispersed in H\textsubscript{2}O (10 mL) by sonication for 10 min and then sodium azide (1.2 mmole), phenyl acetylene (1.0 mmole) and benzylbromide (1.0 mmole) was added to the mixture and refluxed for the time mentioned in Table 2. The progress of the reaction was monitored by TLC and upon the completion of the reaction, the reaction mixture was diluted with EtOAc and the GO-M-Cu was separated by centrifuging at 8500 rpm for 20 min. The organic solution was dried by anhydrous sodium sulfate and the solvent evaporated. The obtained final product was purified by recrystallization from ethanol to give the purified 1,2,3-triazole derivatives. The structure of most synthesized products have been confirmed with \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR and FT-IR (See Supporting Information) and all the products were compared and approved with their melting points (Table 2).

**Results and discussion**

The nano heterogeneous catalyst was prepared by the route as depicted in Scheme 1. The bare GO and factionalized GO with organic ligand (GO-M) were synthesized according to the literature\textsuperscript{42,43} and the preparation of metal coordination to the metformin organic moiety of the
The catalyst (GO-M-Cu) was presented in the experimental section. The catalyst structure was successfully and completely characterized using various techniques including FT-IR, TEM, EDX, TGA, XRD, BET and ICP.

The FT-IR spectrum of all steps for the preparation of GO-M-Cu is compared and discussed in Figure 1. In the first FT-IR spectrum related to the GO (Figure 1a), the broad peak at 3368 cm\(^{-1}\) corresponds to stretching of O-H bonds (hydroxyl and carboxylic acid) on the surface of GO and two sharp peaks at 1728 and 1618 cm\(^{-1}\) are attributed to the carbonyl groups on the edges of the GO. The peaks at 1356, 1323 and 1051 cm\(^{-1}\) confirmed the presence of Carbon–Oxygen, Carbon–Oxygen–Carbon and C≡C bonds on the GO structure, respectively.\(^{44}\)

In the second FT-IR spectrum (Figure 1b) corresponds to the GO functionalized organic metalligand (GO-M), the broad peak and weak peak at about 3400 and 3200 cm\(^{-1}\) are assigned to the stretching vibration of N-H and C-H bonds and a sharp peak at 1595 cm\(^{-1}\) is assigned to the imine bond (C≡N) related to organic ligand.\(^{24,43}\) The last spectrum related to the final catalyst (Figure 1c) indicated the blue shift and the peak corresponds to C≡N group shifted from 1595 to 1589 cm\(^{-1}\) that approves the proper insertion of metal into the organic ligand.\(^{43}\) This analysis confirms the successful covalently grafting of M-Cu complex on the surface of GO.

Transmission electron microscopy (TEM) is the best analysis for understanding and confirmation of functionalized nanocatalyst particularly the GO nanosheets. Thus, the images of GO functionalized copper complex (GO-M-Cu) are shown in Figure 2. As shown in this image, the catalyst has the uniform surface with sheet-like and transparent structures. Also this image shows some darker parts which attributed to copper complexes immobilized on the surface of GO.\(^{44}\) Moreover, the EDX technique was applied for studying the elemental analysis of the prepared final catalyst (Figure 3). The presence of all related elements (Cu, O, N and C) in the catalyst was approved by this technique as well.

In order to evaluate the thermal stability of Go-M-Cu, the TGA analysis was studied under air flow at temperature range between 0°C and 550°C (Figure 4). The TGA graph showed the three main weight losses from about 50–550°C. The first weight loss starts about 50°C and continues to 150°C is attributed to the evaporation of physical adsorbed water on the surface of GO and the second weigh loss begins from 200°C and stretches to 300°C is assigned to decomposition of functional groups on the surface GO and also decomposition of organic ligands that they adsorbed physically on the surface of GO. The last and significant weight loss between 300°C
and 550 °C is attributed to the decomposition of organic ligands and copper complexes that they covalently and chemically immobilized on the basal plane of GO.

The TGA analysis of final catalyst has been studied in order to evaluation crystal structure of catalyst (Figure 5). As shown in this figure the broad peak at $2\Theta = 24$ is assigned to the GO$^{45}$ and the sharp peaks at $2\Theta = 43.7$, 50.7 and 74.3 $\Theta$ are attributed to the copper nanoparticles.$^{46}$

On the best analyses for evaluation the amount of metals in structure of catalyst is inductively coupled plasma (ICP) technique. Therefore, for finding the amount of copper in the fresh and reused GO functionalized copper complex, the ICP technique has been applied. According to ICP
data, the weight percentage of copper in the fresh and reused catalyst was 4.316 and 4.201 wt%, respectively. These observations strongly confirmed that no leaching of metal was happened during the reaction and copper ion was successfully linked to the metformin moiety and also according to these data, the mol% and then TON and TOF of catalyst were calculated.

BET surface analysis is a very convenient analysis for evaluation of porosity and surface area of the prepared samples. On this basis, the reactive surface area and pore size distribution of the GO and functionalized GO with metformin-Cu complex (GO-M-Cu) have been analyzed by adsorption/desorption under the nitrogen gas and BET measurement. According to the adsorption/desorption isotherms, the total active specific surface area of GO and GO-M-Cu was 170 and 74 m² g⁻¹ (Figures S1 and S2, supplementary material) and the average pore sizes were 22.40 and 20.21 nm, respectively.⁴⁷ These outcomes are displayed in Table 1. The isotherm curve of GO and GO-M-Cu shows that they are in porous nature and the decrease in specific surface area confirms the successful immobilization of organic ligands and copper complex on the surface of GO.

| Entry | Samples      | BET surface area (m² g⁻¹) | Average pore size (nm) |
|-------|--------------|----------------------------|------------------------|
| 1     | GO           | 170 ± 3.2                  | 22.40                  |
| 2     | GO-M-Cu     | 74.0 ± 5.5                 | 20.21                  |

![Figure 4. TGA graph of catalyst (GO-M-Cu).](image)

![Figure 5. XRD pattern of catalyst (GO-M-Cu).](image)

Table 1. BET surface area and pore size of samples.
After confirmation of the nanocatalyst structure, the effects of catalyst for the synthesis of 1,2,3-triazoles via azide-alkyne reaction have been tested. For this purpose, the reaction of benzyl bromide, phenyl acetylene and sodium azide has been selected as a model reaction (Table 2). At first, the experiments showed that the reaction did not progress without catalyst (entry 1), but in the presence of heterogeneous GO copper catalyst (entries 2–5), the reaction carried out unbelievably and the highest amount of products was obtained in the presence of only 30 mg (2.0 mol%) of catalyst (entry 4). The next step was the investigation the effect of solvent and solvent-free conditions on the yield and time of the reaction. A wide variety of polar and nonpolar solvents have been tested in synthesis of compound 5a (entries 6–13), and the reaction was performed better in protic solvents like H2O, MeOH and EtOH and among them, H2O had highest yield of the products (entry 4). In second step, the synthesis of compound 5a was carried out at higher temperatures (entries 14,15). With increase the temperature to 50°C and reflux conditions, the yield of the reaction was not increased significantly. Next, this reaction was also studied in shorter time (entry 16). After reducing the time to 15 minutes, the yield of the reaction decreased to 71%. Besides, the model reaction has been carried out in the presence of low loading of Cu (0.01) on the 1.0 g of GO-M (entry 17). Interestingly, the 1,2,3-triazole product has been obtained in the moderate isolated yield and it was lower compared to high loading of Cu (1.0 g Cu on the 1.0 g GO-M). Eventually, the reaction has been tested in the presence of copper acetate (entry 18) as well. The yield of the reaction was approximately satisfying in this condition. These outcomes revealed that the Cu is necessary to move forward the reaction.

The scope of this experiment was studied in the synthesis of 1,2,3-triazole derivatives in two paths. In the first path, the reaction of various benzyl halides with phenyl acetylene and sodium azide was investigated in the presence of 30 mg (2.0 mol%) of GO functionalized copper complex (GO-M-Cu) in water and room temperature (Table 3). In the second path, the reaction of different terminal alkynes and various azides was also studied in the presence of 30 mg (2.0 mol%) of catalyst (GO-M-Cu) in water and room temperature. Generally, the first path had better yields of the reaction in shorter reaction time compared to second path. Also, in the first path, the benzyl halides possessing electron-withdrawing groups had better isolated yields compared to electron-
donating groups (entries 1–8), however, in the second path, the azides with electron-donating groups reacted better than azides with electron-withdrawing groups (entries 9–20) in terms of yield of the reaction and reaction time.

**Scheme 3.** The proposed mechanism for the synthesis of 1,2,3-triazoles in the presence of GO-M-Cu.

**Table 3.** Synthesis of 1,2,3-triazole derivatives using Go-M-Cu nanocatalyst.a

| Entry | R       | R₁-X     | R₂       | Productb | Time (min) | Yields (%)c | Mp °C         | Found         | Reported       |
|-------|---------|----------|----------|----------|------------|-------------|---------------|---------------|---------------|
| 1     | Ph      | PhCH₂Br  | –        | 5a       | 30         | 96          | 130–131       | 129–130⁶⁸     | 129–130⁶⁸     |
| 2     | Ph      | PhCH₂Cl  | –        | 5b       | 30         | 95          | 130–131       | 129–130⁶⁸     | 129–130⁶⁸     |
| 3     | Ph      | PhCH₃    | –        | 5c       | 20         | 98          | 130–131       | 129–130⁶⁸     | 129–130⁶⁸     |
| 4     | Ph      | 4-ClPhCH₂Cl | –    | 5d       | 15         | 98          | 142–144       | 143–144⁶⁹     | 143–144⁶⁹     |
| 5     | Ph      | 4-ClPhCH₂Br | –    | 5e       | 15         | 96          | 142–144       | 143–144⁶⁹     | 143–144⁶⁹     |
| 6     | Ph      | 4-NO₂PhCH₂Br | –   | 5f       | 20         | 95          | 156–157       | 156–157⁷⁹     | 156–157⁷⁹     |
| 7     | Ph      | 4-BrPhCH₂Cl | –    | 5g       | 30         | 94          | 150–152       | 152–153⁷⁹     | 152–153⁷⁹     |
| 8     | Ph      | 3-NO₂PhCH₂Br | –    | 5h       | 45         | 92          | 149–151       | 148–152⁵⁰     | 148–152⁵⁰     |
| 9     | Ph      | Ph        | –        | 6a       | 45         | 92          | 97–99         | 97–98¹²       | 97–98¹²       |
| 10    | Ph      | –         | 4-NO₂Ph | 6b       | 50         | 90          | 255–257       | 255–256¹²     | 255–256¹²     |
| 11    | Ph      | –         | 4-BrPh  | 6c       | 45         | 93          | 230–232       | 232–234¹²     | 232–234¹²     |
| 12    | Ph      | –         | 4-Ch₂Ph | 6d       | 35         | 95          | 168–171       | 173–174¹²     | 173–174¹²     |
| 13    | Ph      | –         | 4-ClPh  | 6e       | 60         | 88          | 226–228       | 227–229¹²     | 227–229¹²     |
| 14    | CH₂OH   | –         | Ph       | 6f       | 45         | 93          | 118–120       | 116–118⁵¹     | 116–118⁵¹     |
| 15    | CH₂OH   | –         | 4-NO₂Ph | 6g       | 60         | 89          | 201–202       | 201–202¹²     | 201–202¹²     |
| 16    | CH₂OH   | –         | 4-BrPh  | 6h       | 50         | 91          | 136–138       | 135–137⁵²     | 135–137⁵²     |
| 17    | CH₂OH   | –         | 4-Ch₂Ph | 6i       | 40         | 93          | 124–126       | 124–125⁵³     | 124–125⁵³     |
| 18    | CH₂OH   | –         | 4-ClPh  | 6j       | 60         | 86          | 145–147       | 144–145⁵⁴     | 144–145⁵⁴     |
| 19    | CH₂Br   | –         | Ph       | 6k       | 50         | 91          | 180–182       | 180–182⁵⁵     | 180–182⁵⁵     |
| 20    | CH₂Br   | –         | 4-NO₂Ph | 6l       | 60         | 87          | 150–151       | 152–154⁵⁵     | 152–154⁵⁵     |

aReaction condition: For products (5a–h): phenylacetylene (1.0 mmol), benzyl halides (1.0 mmol), sodium azide (1.2 mmol), catalyst (30 mg, 2.0 mol%) and H₂O at room temperature; For products (6a–l): terminal alkynes (1.0 mmol), azides (1.1 mmol), catalyst (30 mg, 2.0 mol%) and H₂O at room temperature.

bSome of our products were characterized by ¹H-NMR, ¹³C-NMR and FT-IR and all of them were charachterized by melting points.

cIsolated Yields.
According to the literature, a plausible mechanism for the synthesis of 1,2,3-triazoles via azide-alkyne cycloaddition reaction in the presence of GO copper catalyst has been proposed in Scheme 3. In this reaction mechanism, firstly, a phenyl acetylene is coordinated to heterogeneous cooper complex and the Cu–alkylidine intermediate is produced. Then, the sodium azide as a nucleophile is attacked to beznyl halide as an electrophile and the benzyl azide is formed and promptly reacts with Cu–alkylidine intermediate and eventually, after intramolecular cyclization, the 1,2,3-triazole product is produced.

One of the best advantages of our catalyst is the ability to reuse. In order to approve of this claim, the effects and stability of the catalyst were investigated a couple of times in the model reaction. Thus, after the completion the reaction, the catalyst was removed from the reaction mixture using centrifuging (7500 rpm for 20 min) and washed properly with acetone and dried in vacuum oven at 80°C for 8 h and reused in other reactions. The results confirm that the structure of catalyst stays stable after five runs reusing and probably no leaching of copper complex occurs during the reactions, because the reused catalyst acted like a fresh catalyst without any significant decrease of yield (Figure 6).

Another experiment for investigation of catalyst stability is hot filtration test. To perform this test, the model reaction was carried out in the presence of catalyst under optimized reaction condition. So, a mixture of benzyl bromide (1.0 mmol), phenylacetylene (1.0 mmol), sodium azide (1.2 mmol) and GO-M-Cu (30 mg, 2.0 mol%) was stirred in water at room temperature for 15 min. After fifty % progress the reaction, the GO-M-Cu was removed from the reaction and afterward, the reaction was continued for further 15 min. The reaction did not move forward during this time which was monitored by thin layer chromatography (TLC). These observations truly confirm that the catalyst has strong stable structure and no leaching of Cu or Cu complex has happened during the reaction and they are in agreement with ICP observations.

In order to show the advantages of our method, the effect of our heterogeneous Cu catalyst has been compared with other homogeneous and heterogeneous copper catalysts in the synthesis of 1,2,3-triazoles 5a (benzyl bromide, phenyl acetylene and sodium azide) (Table 4). Based on the results, our new copper complex catalyst has better results compared to homogeneous copper
salts like CuCl$_2$, Cu(OAc)$_2$ and CuO (entries 1-3), and the heterogeneous supported copper catalysts (entries 4-8) in the term of time of the reaction.

**Conclusion**

In summary, a new and heterogeneous Go functionalized copper complex has been reported by covalent and chemical grafting of copper complex on the surface of GO. This report is the first synthesis of 1,2,3-triazole derivatives in the presence GO heterogeneous copper complex. This efficient catalyst can catalyze the synthesis of 1,2,3-triazoles in water and room temperature. TEM analysis also confirmed the proper immobilization of Cu complex on the basal plane of GO and EDX and ICP and other characterizations approved successful synthesis of catalyst and the existence of copper in the structure of catalyst.

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