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FULL PAPER

Functionalized graphene oxide supported copper (I) complex as effective and recyclable nanocatalyst for one-pot three component synthesis of 1,2,3-triazoles

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Efficient, one pot three-component reaction of alkyl halides, sodium azide with terminal alkynes can be catalyzed by functionalized graphene oxide with copper(I) under thermal conditions. A series of 1,4-disubstituted 1,2,3-triazoles were obtained by this one-pot strategy. The catalyst was prepared and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX). The catalyst can be reused at least five times without significant deactivation.

KEYWORDS

1,2,3-triazole, graphene oxide, heterogeneous catalyst, one pot, three component

1 | INTRODUCTION

1,2,3-Triazoles are typical five-membered nitrogen heterocyclic compounds. They have a wide range of biological activities such as anti-HIV activity,[1] anti-microbial activity against gram positive bacteria,[2] anti-allergic,[3] anticancer,[4–6] β-lactamase inhibitory,[7] selective β_3 adrenergic receptor agonism.[8] Additionally, 1,2,3-triazoles have a range of important applications in industries such as dyes, corrosion inhibition, photostabilizers, photographic materials, and agrochemicals.[9] Several synthetic methods for producing 1,2,3-triazoles have been developed recently. The most popular method for the synthesis of 1,2,3-triazoles is the Huisgen 1,3-dipolar cycloaddition reaction of azides with alkynes.[10,11] The Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC),[12–15] one of the most reliable "click reactions",[16,17] has enabled the practical and efficient preparation of 1,4-disubstituted 1,2,3-triazoles. The required copper(I) catalysts are usually prepared by in situ reduction of copper(II) salts with ascorbate,[18,19] or by comproportionation of copper(0) and copper(II).[20,21] Recently, graphene and graphene oxide have attracted tremendous attention in the development of composite materials and catalysts,[22–32] due to their remarkable physical, chemical and electrical characteristics, including a very high specific surface area.[33–35]

In continuation of ongoing to our work toward click reaction,[36,37] here we wish to report an efficient and safe one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from in situ generated azides and terminal alkynes which were recyclably catalyzed by heterogeneous copper(I) functionalized graphene oxide under thermal condition at 70°C.

2 | EXPERIMENTAL

2.1 | Materials

The chemical and materials used in this research were purchased from Merck, Fluka, and Aldrich Chemical Companies. Alkyl halides and solvents were purified by use of standard procedures.

2.2 | Apparatus

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer or an Impact 400 Nicolet FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. X-ray diffraction patterns of samples were taken on a Philips Xpert X-ray powder diffraction diffractometer (CuK, radiation, k = 0.154056 nm). FE-SEM and elemental analysis were carried out using a Jeol SEM instrument (model- VESCAN) combined with an INCA instrument for energy dispersive X-ray scanning electron microscopy (EDX–SEM), Field emission scanning electron microscopy (FE-SEM) images were obtained by HITACHI S-4160. Melting points were obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

2.3 | Synthesis of graphene oxide (GO)

Graphene oxide was prepared using a modification of Hummers and Offeman's method.[38] Briefly in a typical reaction, 2 g graphite, 1 g $NaNO_3$, and 46 mL H_2SO_4 were stirred together in an ice bath. $KMnO_4$ (6 g) was slowly added while stirring, and the rate of addition was controlled to prevent the mixture temperature from exceeding 5°C. The mixture was then transferred to a 35°C water bath and stirred for about 30 min, forming a thick paste. Subsequently, 100 mL deionized water was added gradually and the temperature was raised to 98°C. The mixture was further treated with 500 mL deionized water and 15 mL 30% H_2O_2 solution. The warm solution was then filtered and dried at 65°C under vacuum. Finally, the precipitate was dispersed in water by sonication.

2.4 | Synthesis of GO–COCl

In this step, GO (0.5 g) was suspended in $SOCl_2$ (10 mL) and 10 mL of DMF was added and refluxed at 70°C for 24 h. The resultant solution was filtered and washed with anhydrous tetrahydrofuran (THF) and dried under vacuum, the GO-COCl was obtained.

2.5 | Synthesis of amino-functionalized graphene oxide (GO-CONH$_2$)

In this step of catalyst preparation, GO–COCl (0.4 g) and 1,7-heptandiamine was added in 25 mL DMF and refluxed at 75°C for 18 h. The resultant solution was filtered and washed with ethanol to ensure that the excess diamine was completely removed. Finally, the products were dried at 80°C under vacuum.

2.6 | Synthesis of functionalized graphene oxide with Isotoic anhydride (GO-CONH-IA)

In continuation, GO-CONH$_2$ (0.36 g) and Isotoic anhydride (0.36 g) were added in 30 mL ethanol and refluxed at 60°C for 22 h. The resultant solution was filtered and washed with ethanol to ensure that the excess Isotoic anhydride was completely removed. Finally, the products were dried at 70°C under vacuum.

2.7 | Synthesis of functionalized graphene oxide with copper(I)(GO-CONH-IA-Cu(I))

In the final step of catalyst preparation, GO-CONH-IA (0.35 g) and copper iodide (0.35 g) was suspended in 30 mL acetonitrile and refluxed at 60°C for 18 h. The resultant solution was filtered and washed with acetonitrile to ensure that the excess copper iodide was completely removed. Finally, the products were dried at 80°C under vacuum, the pure complex was obtained.

2.8 | A typical procedure for the synthesis of 1, 2,3-triazoles

Alkyne (1 mmol), alkyl halide (1 mmol), NaN_3 (1.2 mmol) and Cu(I) functionalized graphene oxide (0.01 g)as a catalyst were added to a mixture of water and EtOH (1:1) (6 mL) and stirred at 70°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was isolated by filtration through celite and the product was extracted with EtOAc (3 × 10 mL). The products were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and melting pointsand were carefully identified by comparison of their spectral data with those of authentic samples.[39–44]

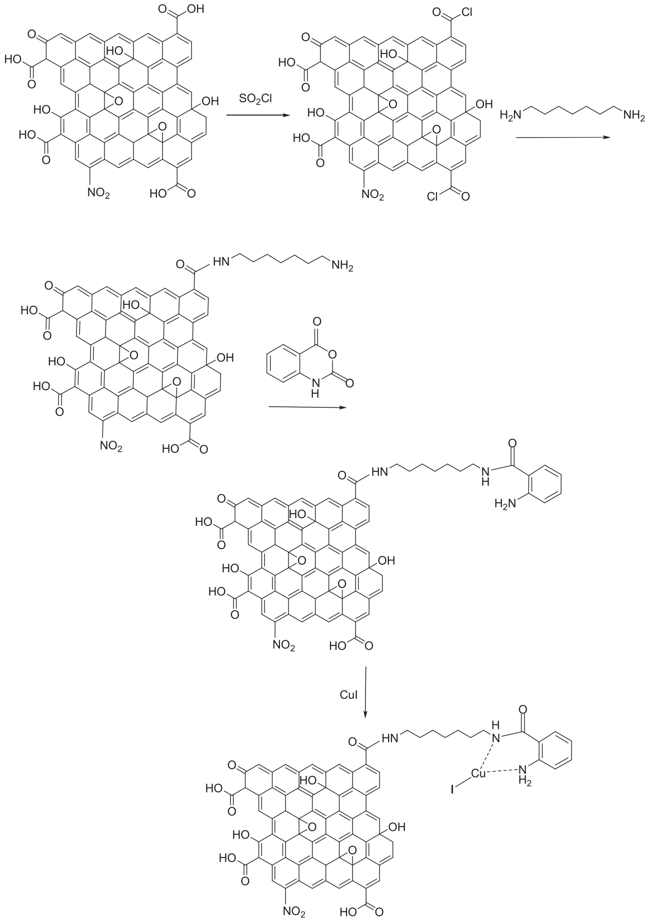
3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of the catalyst

Synthesis strategy of functionalized graphene oxide is shown in the Scheme 1. At first, graphene oxide was prepared according to the modified Hummer's method. The obtained GO was treated with thionyl chloride in DMF at reflux temperature for 24 hours to generate GO–COCl and subsequently reacted 1,7-heptandiaminto yield amino-modified graphene oxide (GO-CONH$_2$). The obtained amino-modified graphene oxide were then treated with Isotoic anhydride in ethanol at reflux temperature for 24 hours to generate (GO-CONH-IA). Finally, the GO-CONH-IA was treated with CuI in acetonitrile at reflux temperature for 18 hours. The catalyst was characterized using various methods.

Figure 1 shows the FTIR spectra of GO, GO-COCl, GO-CONH$_2$, GO-CONH-IA. In the FTIR spectrum of GO, the peaks at 3349, 1719, 1580 and 1064 cm^{-1} correspond to the O–H, C = O, C = C and C–O stretching vibration. In the FTIR spectrum of GO–COCl (Figure 4b), the relative intensity of the C = O stretch of the –COOH at 1730 cm^{-1} has significantly decreased that confirmed the most carboxyl functionalities have been transformed into the acyl chloride.

Figure 2 shows XRD patterns of GO and GO-CONH-IA-Cu(I). The XRD pattern of GO (Figure 2a) shows an intense and sharp peak centered at 11.99° which corresponds to an interplanar distance of 0.78 nm. After the functionalization, in the XRD patterns of GO-CONH-IA-Cu(I), the peak at



SCHEME 1 Preparation routes of functionalized graphene oxide

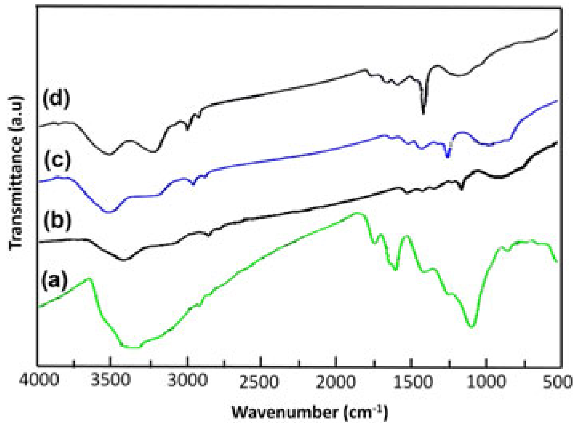


FIGURE 1 FT-IR spectra of a) GO, b) GO-COCl c) GO-CONH$_2$ d) GO-CONH-IA

about 2 = 23.7 ^{o} was broad peak. The reasons of this matter can be due to the covalent bond functionalization.

TGA thermograms were used to confirm the anchoring of organic groups on the surface of GO. As shown in Figure 3, the weight loss (9%) before 160°C is caused by the release of trapped water between GO nanosheets. Also, weight loss between 200 and 600°C is completely due to functional groups on the surface of graphene oxide nanosheets. As shown in Figure 3, the attached organic groups decomposed at 200°C, while the GO remained stable up to 600°C, at which temperature oxidation started. Accordingly, these results indicate that about 31 wt% can be ascribed to the covalency of organic groups. Results obtained by TGA showed good agreement with results of FT-IR spectroscopy.

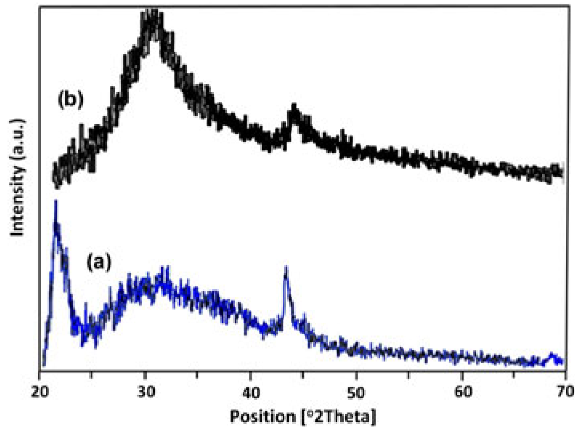


FIGURE 2 XRD patterns of (a) GO and (b) GO-CONH-IA-Cu(I)

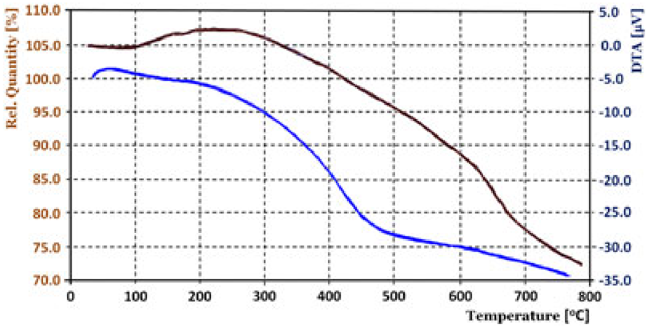


FIGURE 3 TGA and DTA graphs of the GO-NH-IA-Cu

The successful covalent grafting of NH-IA-Cu(I) onto the surface of graphene oxide was further confirmed by EDX analysis. EDX spectra of functionalized graphene oxide-Cu (I) is shown in Figure 4 and Table 1 that was confirmed the presence of copper, iodine and nitrogen elements in the complex structure (Table 1).

The FE-SEM images of GO and GO-CONH-IA-Cu(I) are shown in Figure 5. As can be clearly seen in this Figure, the GO has layered structures with sheets crumpled. Figure 5b is indicated the SEM image of GO-CONH-IA-Cu(I) revealing that the layered structure can be maintained in the functionalized graphene oxide after the treatments.

3.2 | Investigation of the catalyst activity

In order to optimization of the reaction conditions, the reaction of alkyne (1 mmol), alkyl halide (1 mmol) and NaN$_3$ (1.1 mmol) were studied as a simple model. The reaction was carried out in the presence of different quantities of the catalyst in water-ethanol solvent (Table 2). It was found that

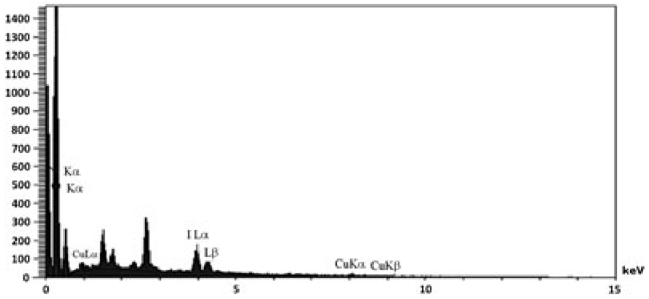


FIGURE 4 EDX spectra of GO-CONH-IA-Cu(I)

TABLE 1 Elemental analysis of GO-CONH-IA-Cu(I)

Element	C	O	N	Cu
%W	54.21	17.67	17.37	0.73

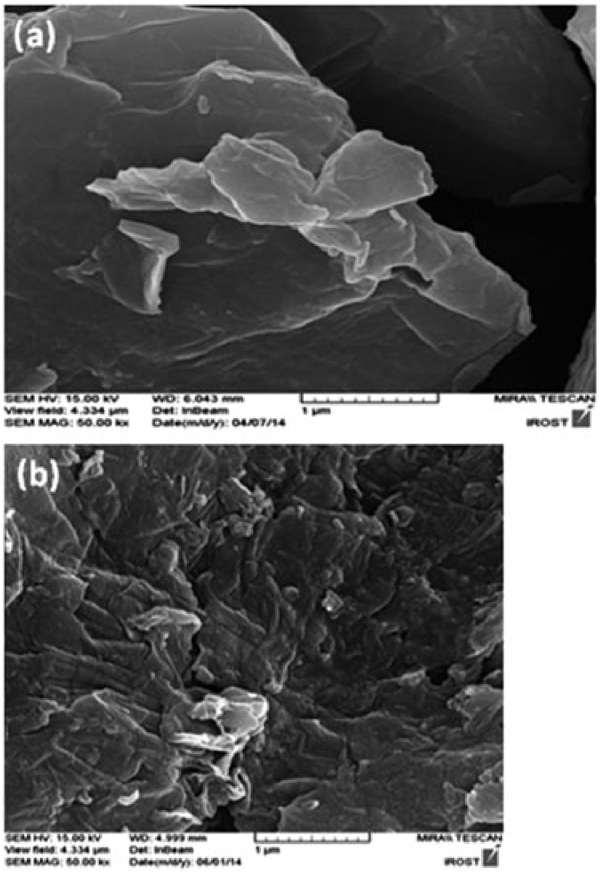


FIGURE 5 FE-SEM of (a) GO, (b) GO-CONH-IA-Cu(I)

the best result was obtained when the reaction was carried out in the presence of 0.01 g of catalyst (Table 2, entry 2).

In order to verify the effect of solvent, the model reaction was carried out in the presence of different solvents. The corresponding results are shown in Table 3. The best solvent was1:1 mixture of H_2O and EtOH, which was resulted in higher yield and shorter reaction time in compared to other solvents (Table 3, entry 4).

TABLE 2 Optimization of catalyst for synthesis of 1,2,3-triazole

Entry	Catalyst (g)	Time (h)	Yield (%)[a]
1	0.005	3	87
2	0.010	1	90
3	0.015	1	87
4	0.020	1	84

[a] Isolated yields

Reaction conditions: 1 mmol phenylacetylene, 1 mmol benzyl chloride, 1.1 mmol NaN_3, and selected solvent (6 mL) at 70°C temperature

TABLE 3 The preparation of triazols in the presence of various solvents

Entry	Solvent	Time (h)	Yield (%)[a]
1	CH_3CN	5	55
2	H_2O-CH_3CN(1:1)	4.5	62
3	H_2O-Acetone(1:1)	4	75
4	H_2O-EtOH(1:1)	1	90
5	EtOH	3	84
6	H_2O	3.5	68

[a] Isolated yields

Reaction conditions: 1 mmol phenylacetylene, 1 mmol benzyl chloride, 1.1 mmol NaN_3, and selected solvent (6 mL) at 70°C temperature.

To check the influence of temperature on the yield of the triazole product, we carried out model reaction at various temperatures in the range of 35°C to 80°C (Table 4), showing that at 70°C, the yield of the product was maximized to 90% (Table 4, entry 3). A further increase in temperature had no profound effect on the yield of the reaction (Table 4).

After optimization of the reaction conditions, the reaction was carried out according to the general experimental procedure shown in Scheme 2.

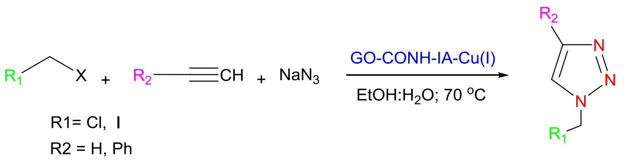
In order to development and limitations of the general method, we investigated the reaction, using a variety of benzyl and alkyl halides and alkynes as the substrates under the same conditions. The related results are summarized in Table 5.

The regarding results were shown that in the presence of this new solid heterogeneous catalyst, the 1,2,3-triazole

TABLE 4 Effect of temperature on synthesis of 1,2,3-triazole

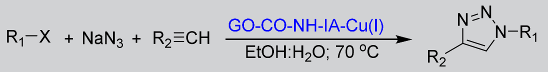
Entry	Temperature	Time (h)	Yield (%)[a]
1	35	3	86
2	50	2	87
3	70	1	90
4	80	1.5	88

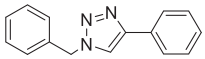
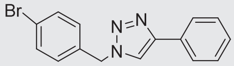
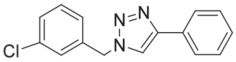
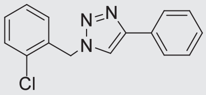
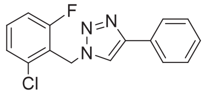
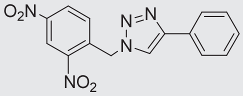
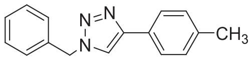
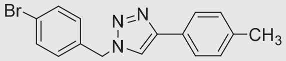
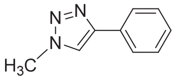
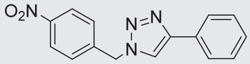
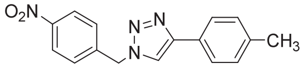
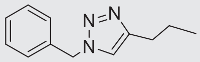
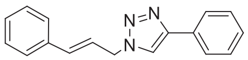
[a] Isolated yields



SCHEME 2 Synthesis of 1,4-disubstituted 1,2,3-triazoles

TABLE 5 Preparation of 1,2,3-triazoles from the reaction of alkyl halides, acetylenes, and sodium azide catalyzed by GO-NH-IA-Cu(I)



Entry	R_1	R_2	Product	Time (h)	Yield[a] (%)
1	Bn	Ph	 **a**	1	90
2	4-Br-Bn	Ph	 **b**	1.5	89
3	3-Cl-Bn	Ph	 **c**	2	87
4	2-Cl-Bn	Ph	 **d**	2.5	86
5	2-Cl-6-F-Bn	Ph	 **e**	3	83
6	2,4-$(NO_2)_2$-Bn	Ph	 **f**	3.5	82
7	Bn	*P*-CH_3-Ph	 **g**	3.5	92
8	4-Br-Bn	*P*-CH_3-Ph	 **h**	4	94
9	CH_3	Ph	 **i**	7	85
10	4-NO_2-Bn	Ph	 **j**	2	88
11	4-NO_2-Bn	*P*-CH_3-Ph	 **k**	4	89
12	Bn	CH_3-$(CH_2)_2$	 **l**	8	78
13	Cinamyl	Ph	 **m**	5	88

[a] Isolated yields

products were yielded in excellent within a very short reaction times. In order to show the merit of this study, we compared the obtained results with the recently reported works[45–52] in Table 6. The comparison was carried out on the basis of reaction conditions, reaction time, and yields of the products.

3.3 | The study of leaching and reusability of the catalyst

For catalyst leaching study, after completion of the reaction, the solid catalyst was separated by celite filter. The liquid phase was subjected as solvent to further reaction with the new three substrates of starting materials without using any catalyst and carried out under the modified reaction conditions. After the suitable time, the reaction was analyzed and was observed that there was no further conversion of moieties to triazole product when the catalyst was removed. The reaction cannot progress, and a negligible product was obtained (<2%) after 25 h reaction time. It is notable that the active catalyst did not leach from the GO as the solid supporter. Also, the final reaction media was analyzed by using atomic absorption spectroscopy and the resulted was observed that

TABLE 6 Comparison of triazole synthesis by using GO-CONH-IA-Cu (I) with literature reported methods

Entry	Catalyst	Reaction conditions	Time /Yield [Lit.]
1	$[CuBr(PPh_3)_3]$	0.5 mol% cat., H_2O, r.t.	8 h/88% [45]
2	CuI/DIPEA/HOAc	2 mol % CuI, CH_2Cl_2, r.t.	2 h / 91% [46]
3	Copper(I) Isonitrile Complex	2 mol % cat., H_2O, r.t.	4 h / 92% [47]
4	1.5 equation $ZnEt_2$, 0.1 eq. *N*-methylimidazole, THF, r.t.		18 h / 76% [48]
5	$CuCl/Pd_2(dba)_3$	1 eq. CuCl, 2.5 mol% $Pd_2(dba)_3$, DMF, 70°C	2 h / 89% [49]
6	poly(imidazole-acrylamide):$CuSO_4$	0.25 mol % cat., *t*-BuOH, 50°C	2.5 h, 90% [50]
7	Cu-apatite	5 mol % cat., H_2O, 100°C	1.5 h / 85% [51]
8	$Cu(OAc)_2$/MCM-41	0.10 g cat., 100°C	2 h / 88% [52]
9 [a]	GO-CONH-IA-Cu(I)	0.01 g cat., H_2O-EtOH(1:1), 70°C	1 h / 90%

[a] Present study

leaching of the Cu metal from the GO, was less than 0.1% by weight of the initial copper metal.

The recyclability of functionalized graphene oxide-Cu(I) catalyst was tested in the cycloaddition of benzyl chloride, NaN_3 and phenylacetylene under the optimized reaction conditions. After the completion of reaction, the catalyst was separated by filtration and washed with acetone and water. After drying, the catalyst could be reused directly without further purification. Also, it could be recycled in six repetitive cycles without significant loss of activity (Figure 6). Moreover, the SEM image of recycled catalyst after fifth run was provided (Figure 7) in that indicated any changing in the structure of catalyst after the reactions.

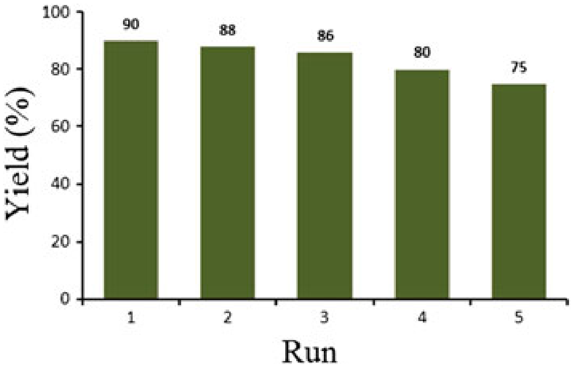


FIGURE 6 Recyclability of GO-NH-IA-Cu(I) catalyst in the synthesis of triazoles

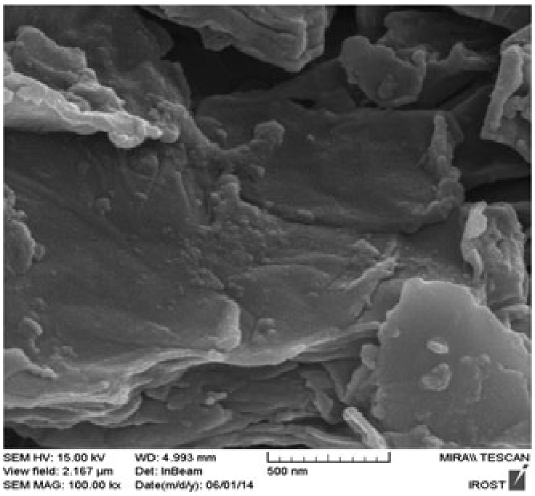


FIGURE 7 SEM image of the recycled catalyst after fifth run

4 | CONCLUSIONS

In this research, we have presented a new heterogeneous catalyst for the one-pot regiospecific synthesis of 1,4-disubstituted1,2,3-triazoles via Huisgen 1,3-dipolar cycloaddition reaction between terminal alkynes, halides and NaN_3 in the presence of GONH-IA-Cu(I). In addition, the catalyst could be readily recovered and reused for 5 cycles without significant loss of its activity.

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