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ORIGINAL PAPER

An efficient Cu/functionalized graphene oxide catalyst for synthesis of 5-substituted 1H-tetrazoles

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Abstract
The copper nanoparticles (Cu NPs) and amide functionalized graphene oxide (Cu-Amd-RGO) catalyst were prepared. This prepared catalyst (Cu-Amd-RGO) used for the synthesis of tetrazole derivatives. The catalyst (Cu-Amd-RGO) was characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction analysis (XRD). The average particle size of Cu was found to be 7.6 nm. The Cu-Amd-RGO catalyst exhibited excellent catalytic activity and recyclability for synthesis of tetrazoles.

Keywords Aromatic nitrile · C–N coupling · Tetrazoles · Functionalization of graphene oxide · Heterogeneous catalyst

Introduction

Compounds comprising a five membered ring with four nitrogen atoms and one carbon atom are known as Tetrazoles. Tetrazoles are widely applicable heterocyclic class of synthetic compounds and not found in nature. Tetrazoles are commonly used in pharmaceutical since they exhibits properties such as antifungal, antibacterial (Feinn et al. 2017), antiallergic (Nohara et al. 1977), anticancer (De Souza et al. 2005), antiviral, (Vieira et al. 2005) Moreover, these tetrazole derivatives have vast applications as a potential energetic material utilized in explosives and rocket propellants (Talawar et al. 2009), in agriculture as plant growth regulator. Presently, researchers are binding aryl thio-tetrazolyl acetanilides with HIV-1 reverse transcriptase by making use of tetrazole derivatives (Gagnon et al. 2009). The abovementioned properties of tetrazoles make them a potential candidate for biochemical and pharmaceutical applications, particularly in drugs as isosteric replacement of carboxylic acid moiety (Holland and Pereira 1967).

In past, various methods for preparation of tetrazole were reported in literature. Sharpless et al. reported [3 + 2]-cycloaddition reaction of nitrile group with sodium azide for synthesis of tetrazoles (Demko and Sharpless 2001). Also the tetrazole synthesis was carried out by using catalysts such as, Lewis acids (Kumar et al. 1996), zinc (II) salts, Cu_2O, ZnO (Kantam et al. 2005), clays, Zn/Al hydrotalcite, $CuFe_2O_4$ Dendron-functionalized Fe_3O_4 (Zarchi and Abadi 2019), nanoparticles (Sreedhar et al. 2011). These reported procedures have several drawbacks such as toxic metals, harsh reaction conditions, use of strong Lewis acids, water sensitivity, extended reaction time, difficulty in isolation and recovery of the catalysts.

Nowadays, inclination toward the heterogeneous catalysts has attracted much interest because of its recyclable and environmentally benign nature (Shendage et al. 2014). These catalysts are usually, eco-friendly, high reactive, economical, easy to handle and recoverable. Graphene oxide and reduced graphene oxide is the widest members of support materials that have been used as heterogeneous catalyst and support in numerous organic transformations (Lonkar et al. 2015). These materials have high surface area, unique electronic, thermal, easy surface modifications, high water dispersibility and mechanical properties. Furthermore, functionalized, graphene could serve as nanofiller in composite materials and prevents agglomeration of metal nanoparticles (Soltani et al. 2012). Graphene oxide shows an exceptional

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hydrophilic nature, due to the enhancement of oxygen transport functional groups on its edges.

These excellent properties of graphene oxide permit GO to be functionalized with various functional groups. Owing to above-mentioned properties functionalized graphene oxide could enhance catalytic activity and reusability. Recently, copper supported on different solid materials such as silica gel, alumina, charcoal and montmorillonite (Choi et al. 2010) were used as catalyst for different organic zeolites, reactions. Conversely, the important disadvantages are leaching of copper species from support surface, less activity, and difficulty in recovery are associated with these reported copper catalysts. These catalysts are merely synthesized by surface assimilation of copper species on surface of support material (Panahi et al. 2017).

Graphite sheet that consists of sp^2 carbon atoms covalently bonded in a honeycomb crystal lattice. The combination of highest electron mobility, high chemical, mechanical and thermal stability with low manufacturing cost and metal immobilization capacity offer many interesting applications in catalysis. The oxidized and exfoliated sheet of sp^2-hybridized graphene carries various oxygenated groups, such as epoxide, hydroxyl, carbonyl, and carboxyl. Among all the oxygenated groups, the carboxyl group of GO is the most suitable site for reacting with an aniline group to form an amide bond. In the reduced graphene oxide (RGO) lattice which prepared from GO by reduction reaction. In the copper amide functionlized graphene oxide (Cu-Amd-RGO) lattice, amide moiety and copper nanoparticles play vital role in transition state of cyclization mechanism to form tetrazoles. The surface of graphene not only minimizes processing issues like wrinkling, restacking, aggregation but also causes higher dispersibility in organic solvents than GO which enhance rate of reaction.

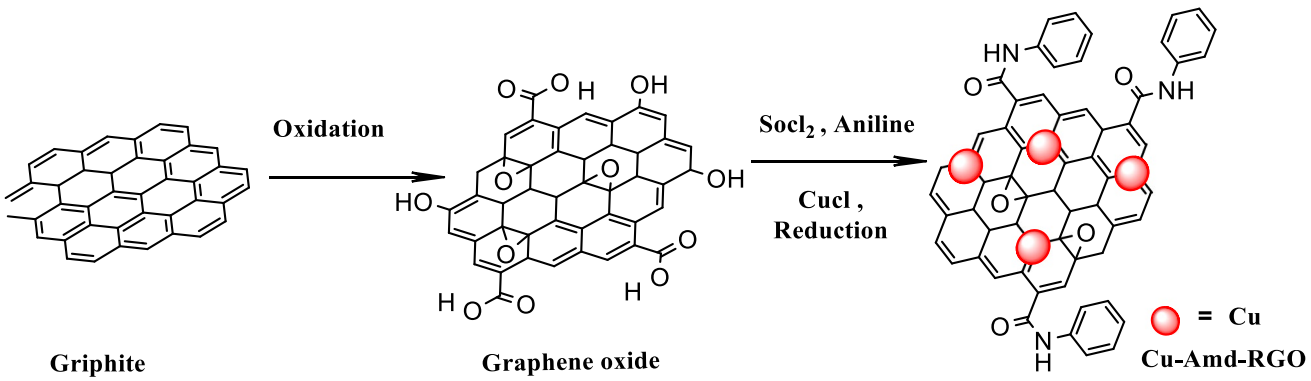
Here, in view of the simple surface modifications of GO and good synchronization ability of aniline, the performance of new approaches toward the grafting of copper amide functionalized graphene oxide (Cu-Amd-RGO) is reported in this paper (Scheme 1). The application of proposed catalyst (Cu-Amd-RGO) was studied for synthesis of tetrazole derivatives as a heterogeneous reusable nanocomposite catalyst.

Experimental

All chemicals and reagents were purchased from S D Fine chem limited and Merck used without purification. Reaction monitored on TLC (Merck silica gel 60). Isolated product confirmed by ^{1}H NMR spectra was recorded on a Bruker AC-400 (400 MHz) spectrometer C13 Bruker (100 MHz). Fourier transform infrared spectra were measured with range of 4000–400 cm^{-1} using Agilent Microlab spectrometer. X-ray powder diffraction (XRD) was collected using Rigaku Miniflex model by using CuKα = 1.54 Å. Field-emission scanning electron microscopy (SEM) on a single instrument FEI Quanta 200 ESEM FEG and Transmission electron microscopy (TEM) was measured using JEOL (JEM 2100F, 200 kV) sample dispersed in ethanol and Cu grid used.

Preparation of graphene oxide (GO)

Graphene oxide prepared as reported in the modified Hummers' method (Hummer and Offeman 1958); 2.5 g of graphite and 1.25 g of $NaNO_3$ were stirred with 50 mL H_2SO_4 and 7 mL H_3PO_4 in the ice bath for 15 min., and then 8 g of $KMnO_4$ was added slowly so at temperature 0 °C to 5 °C. The mixture was then maintained for 2 h in an ice bath and stirred for 1 h at 40 °C in water bath. Then, heated reaction mass at temperature 98 °C for 2 h, while water was added continuously. Pure water was added slowly to make the volume 500 ml, followed by adding 20 mL of H_2O_2. Then, reaction mass was centrifuged and washed with pure water and 10% HCl solution repeatedly. Obtained graphene oxide was dried at 80 °C.



Scheme 1 Synthetic route of Cu-Amd- RGO preparation

Preparation of catalyst (Cu-Amd -RGO)

In a 250-mL round-bottomed flask 2 gm GO and 20 ml DMF-stirred at 25–30 °C and 20 ml thionyl chloride was added slowly at 10 °C to 15 °C. Then, temperature of reaction mass is increased to 25 °C, and heated mixture for 5 h at 80 °C followed by cooling for 1 h at room temperature. This chlorinated graphene oxide centrifuged and washed with chloroform. Dried at 60 °C to 70 °C under vacuum for 8 h, and obtained material as chlorinated graphene oxide (**Cl-GO**).

In a 100-mL round-bottomed flask charged 2.5 gm chlorinated graphene oxide **(Cl-GO)** and 30 ml aniline heated to reflux for 6 h then cooled reaction mass. Then, it was centrifuged and followed by washing of ethanol. Dried at 150 °C under vacuum for 6 h and obtained material as amide functionalized graphene oxide (**Amd-GO**).

In a 250-mL round-bottomed flask amide functionalized graphene oxide (**Amd-GO**) 1.4 gm stirred with solution of $CuCl_2$ 0.4 gm in 100 ml water then 5 ml hydrazine hydrate added to above reaction mass at 25–30 °C. Then mixture was heated for 5 h at 80 °C, cooled and centrifuged catalyst with washing of ethanol. Dried at 140 °C for 6 to 8 h to get catalyst as Cu-Amd-RGO.

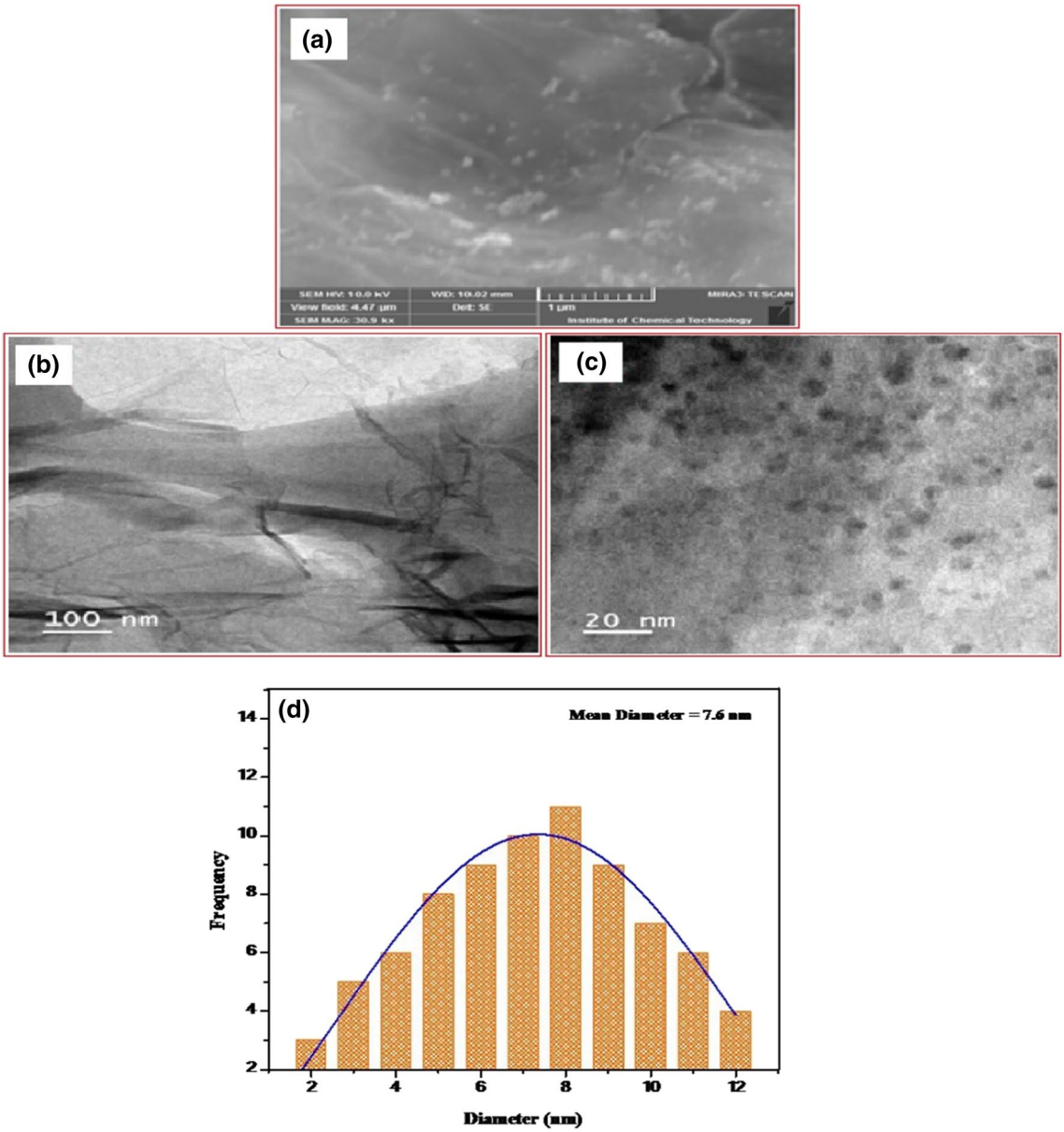


Fig. 1 (**a**) FEG-SEM image Cu-Amd-RGO (**b**) TEM image-Amd-RGO (**c**) TEM image Cu-Amd-RGO (**d**) particle size distribution curve for Cu nanoparticles

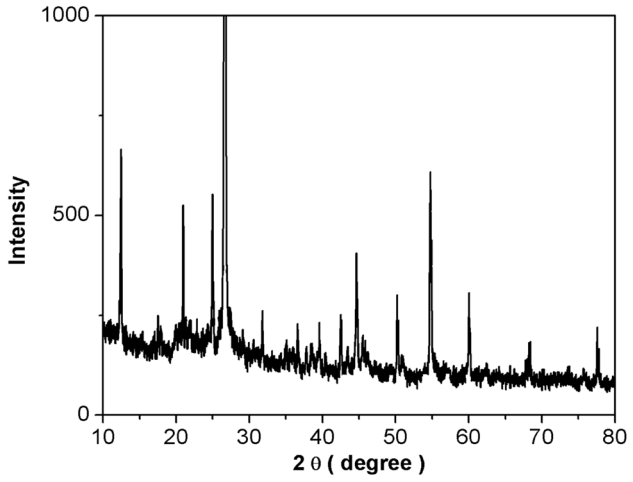


Fig. 2 XRD pattern of copper amide functionalized graphene oxide

General procedure for the synthesis of 5-substituted 1H-tetrazoles

Benzonitrile 0.1 g, and sodium azide 0.092 g, DMF (5 ml), and 5 mg catalyst were transferred in a 25-ml round-bottomed flask. The flask was mounted on mechanical stirrer and the reaction mass was stirred at 120 °C for 30 min. Then, mixture was cooled to room temperature. After the reaction is over the catalyst was regenerated by filtration and finally washed with 10 ml of ethyl acetate in order to remove the contamination from reaction. To the filtrate dilute HCl (15 ml) was added and stirred for 15 min. The organic phase was removed and the aqueous phase was further extracted with10ml of ethyl acetate. Final organic phase was obtained by combination of organic phases was washed with 10 ml H_2O, then it was dried over anhydrous sodium sulfate and concentrated to obtain the crude 5-phenyltetrazole. Finally, impurities from the products were removed by column chromatography. Final products were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (Supplementary Information).

Results and discussion

Fourier transform infrared spectroscopy (FT-IR)

The new (Cu-Amd-RGO) catalyst was prepared by amide functionalization of graphene oxide using aniline and Cu nanoparticles (Cu NPs). The synthesized catalyst (Cu-Amd-RGO) was characterized by Fourier transform infrared spectroscopy (FTIR) analysis. FTIR analysis (Supplementary Information figure S1) shows that aromatic C=O stretching vibrations in the GO materials was marked at 1746.16 cm^{-1}. The O–H deformation vibration at 3345.06 cm^{-1} and the C–O stretching at 1046.87 cm^{-1} (Gupta et al. 2018). Functionalization of graphene oxide was carried by chlorination and condensation of Aniline to form amide moiety. The FTIR spectra of Cu-Amd-RGO the O–H deformation vibration at 3345.06 cm^{-1} disappeared. The new peak at 2980.52 cm-^{1} represents (C–H) stretching vibrations of phenylic group (Joseph et al. 2015). Two peaks 1733.02 cm^{-1} corresponding to the amide carbonyl (C=O) stretch and the peak at about 1539.03 cm^{-1} (C–N) which may be due to copper oxide nanocomposite (Rani et al. 2014). The peak at 535.57 cm^{-1} corresponds to Cu–O stretching vibration characteristic of CuO nanoparticles (Gulati et al. 2018).

FTIR data show successful reduction in copper ions to copper nanoparticles on graphene oxide. Modification of graphene oxide sheet using aniline to form amide, which show change in stretching vibrations carbonyl moiety to amide carbonyl having less frequency value.

Table 1 Optimization of reaction conditions for synthesis of 5-substituted 1H-tetrazole

Entry	Catalyst (mg)	Solvent	NaN_3 (mmol))	Time (Min.)	Yield[b] %
1	2	DMF	1.4	120	81
2	3	DMF	1.4	110	88
3	4	DMF	1.4	60	94
4	5	DMF	1.4	30	96
5	5	Water	1.4	500	No reaction
6	5	EtOH	1.4	400	2
7	5	DMSO	1.4	60	86
8	5	Toluene	1.4	480	21
9	5	DMF	1.5	30	97
10	5	DMF	1.3	30	93
11	5	DMF	1.2	30	91

[a]Reaction conditions: benzonitrile (0.1 g), NaN_3 (1.4 mmol), (Cu-Amd-RGO) (5 mg), DMF (5 ml), temperature at 130 °C, [b]isolated yields

Scheme 2 Synthesis of tetrazole using Cu-Amd-RGO as heterogeneous catalyst

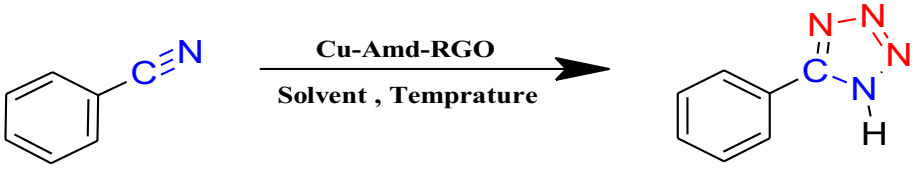
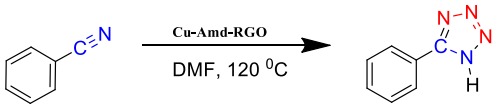
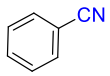
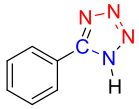
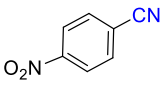
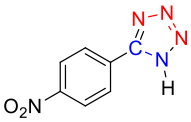
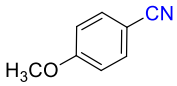
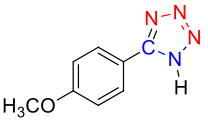
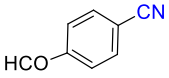
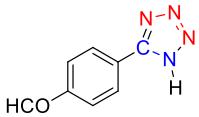
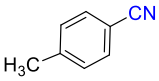
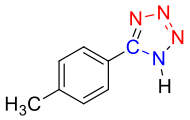
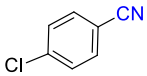
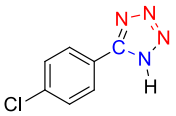
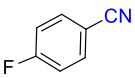
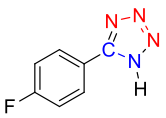
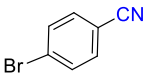
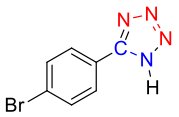
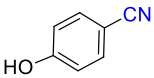
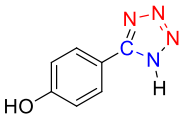
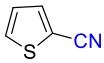
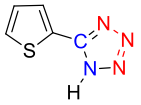
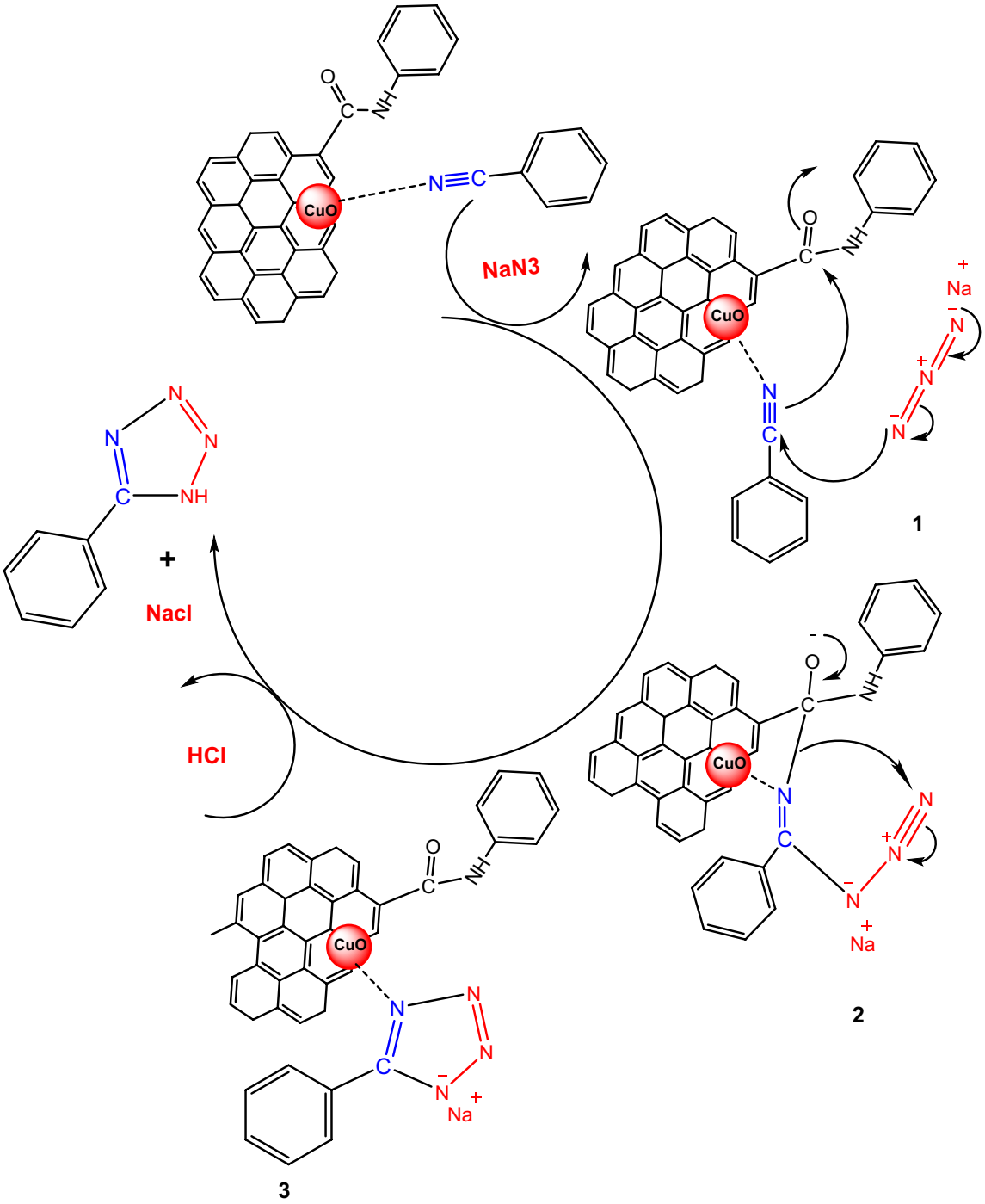


Table 2 Cu-Amd-RGO catalyzed synthesis of 5-substituted 1H-tetrazole[a] derivatives[a]



Entry	Reactant	Product	Yield[b] %	Time (min)
1.			96	30
2.			94	50
3.			83	280
4.			95	60
5.			92	78
6			97	60
7.			95	θ
8.			91	102
9.			92	98
10.			89	79

[a]Reaction conditions: Benzonitrile (0.1g), NaN3 (1.4 mmol), (Cu-Amd-RGO) (5mg), DMF (5 ml), [b]Isolated yields



Scheme 3 A plausible mechanism for the formation of Tetrazoles using Cu-Amd-RGO

SEM and TEM analysis

The morphology of prepared catalyst is characterized by SEM, TEM and XRD. In Figure 1a FEG-SEM image evidently shows that the Cu grain infuses between Amd-GO sheets, which demonstrates a good blending between Amd-GO sheet and Cu NPs (Fig. 1a).

The TEM images represent the surface morphology of the amide functionalized graphene oxide (Amd-G). Morphology of Amd-GO was observed to have flaky texture, and folded features of GO indicating its layered

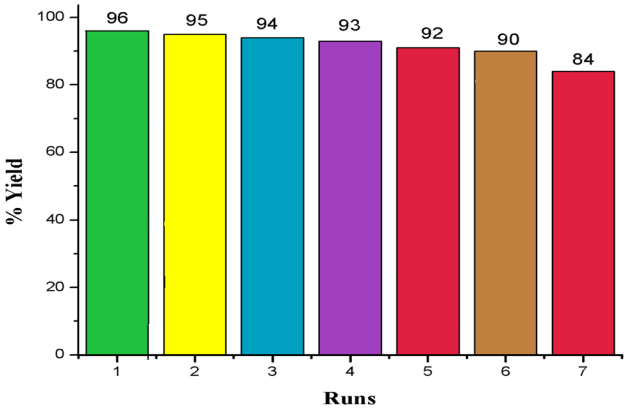


Fig. 3 Reusability of Cu-Amd-RGO catalyst[a]

microstructure (Fig. 1b). This clearly shows the surface modification of GO after functionalization.

TEM images revealed spherical shape of Cu NPs with diameters 7.6 nm (Fig. 1d). The particle size distribution is in the range of 2–12 nm (Fig. 1d). TEM image of Cu-Amd-RGO nanocomposite showed that the Cu NPs were homogeneously distributed on the graphene oxide sheets without aggregation.

XRD diffraction analysis

XRD patterns for Cu-Amd-RGO are shown in Fig. 2. RGO shows a diffraction peak at $2\theta = 26.6°$, which is the characteristic peak of the RGO (JCPDS File no. 03-0401).

The three other peaks at 44.7°, 50.1°, and 73.8° corresponding to (111), (200), and (220) planes (fcc) are the characteristic peaks of copper, matches with JCPDS file No. 04–0836 (Gupta et al. 2018). The peaks at 20.8°, 24.6° and 36.07° correspond to aniline (Rani et al. 2014). Doping of Cu nanoparticles and amide functionalization results change in interplanar spaces of RGO surface, which may be shifted slight higher than 2θ value as reported (Fig. 2).

In general, it is of great importance to investigate the use of a new material in the practical application. Therefore, the catalytic activity of the Cu-Amd-RGO composite for synthesis of 5-substituted 1H-tetrazole was evaluated. To optimize the reaction conditions, initially, the reaction of benzonitrile and sodium azide was selected as model reaction. Due to the harsh reaction conditions for the synthesis of tetrazole, the reaction parameters and media have large impact on the yield and time of reaction. The reaction was screened for various parameters such as temperature, solvent, amount of sodium azide and catalyst loading. To optimize the catalyst quantity, the model reaction was carried out in the presence of variable amounts of the catalyst.

The results showed that (Table 1, entries 1–4) 5 mg of the catalyst was the ideal amount of catalyst. The various solvents were examined by the model reaction (Table 1, entries 4–9). Among them, DMF was found to be the best solvent (Table 1, entry 3) in terms of the time and yield of desired product**.** Then, amount of sodium azide was also investigated in order to get maximum yield of the product. Results showed that 1.4 mmol of sodium azide gave maximum yield of the reaction product (Table 1, entry 4 and entries 9–11).

Subsequently, the optimized reaction parameters were explored for the synthesis of 5-substituted 1H-tetrazole derivatives (Scheme 2, Table 2 entries 1–10). As shown in Table 2, this protocol is general for various electron-rich as well as electron poor substituted benzonitrile (Table 2 entries 2–9). Thiophene-2 carbonitrile afforded 89% yield of the product in 79 min (Table 2 entry10). A plausible mechanism for the formation of Tetrazoles using Cu-Amd-RGO catalyst is shown in Scheme 3.

Reusability of the catalyst[a]

The recyclability of the Cu-Amd-RGO catalyst was studied for the model reaction. The catalyst from the reaction mixture was recovered by centrifugation. Then, it was washed with ethyl acetate. Then, the reaction pot was charged with fresh reactants and used for next run. The Cu-Amd-RGO catalyst could be recycled over 6 runs without any major loss of its activity. This clearly specifies the practical importance of this catalyst (Fig. 3).

Table 3 Comparison of the Catalytic Performance for synthesis of 5-substituted1H tetrazole using different Catalysts[a]

Entry	Catalyst	Time	Yield[b] (%)	References
1	Cu-Amd-RGO	30 min	96	This work
2	Graphene oxide/ZnO	02 h	94	Thanaraj and Rama (2017)
3	Mesoporos ZnS nanosphers	36 h	96	Leiming et al. (2010)
4	Cu- immobilized on Fe_3O_4@ APTMS-DFX	01 h	98	Taghavi et al. (2017)
5	CoY Zeolite	14 h	92	Velladurai et al. (2011)
6	$FeCl_3$–SiO_2	12 h	79	Nasrollahzadeh et al. (2009)

[a]Reaction conditions: benzonitrile (0.1 g), NaN_3 (1.4 mmol), (Cu-Amd-RGO) (5 mg), DMF(5 ml), at 120°, [b]isolated yields

Comparison of activity of Cu-Amd-RGO catalyst with reported catalysts

The efficiency of Cu-Amd-RGO catalyst for the synthesis of 5-substituted 1H-tetrazoles is better explained by comparing experimental conditions and results obtained for the representative reaction with previously reported procedures. This comparison of the results demonstrates that catalyst Cu-Amd-RGO reported in this paper has better catalytic activity in the synthesis of 5-substituted 1H-tetrazoles (Table 3).

Conclusion

We have successfully grafted Cu NPs on amide functionalized graphene oxide (Cu-Amd-RGO) composite material. The morphology, dispersion, and loading of Cu NPs on amide functionalized graphene oxide are the key factors which increases the catalytic activity in synthesis 5-substituted 1H-tetrazoles.The structure of Amd-RGO can speed up Cu-aided C-N bond formation reaction. This could be due to good synergistic effect of copper nanoparticles and amide functionalized graphene oxide. This (Cu-Amd-RGO) catalyst is more efficient in terms of cost, non-toxicity, catalyst reusability, and stability and ease of handling.

Supplementary Information (SI)

Supporting information for this article is given via a link at the end of the document (characterization data, of the ^{1}H NMR and ^{13}CNMR spectra of final products.)

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11696-021-01506-0.

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References

Choi EY, Han TH, Hong J, Kim JE, Lee SH, Kima HW, Kim SO (2010) Noncovalent functionalization of graphene with end-functional polymers. J Mater Chem 20:1907–1912. https://doi.org/10.1039/b919074k

Demko ZP, Sharpless KB (2001) Preparation of 5-substituted 1H-tetrazoles from nitriles in water. J Org Chem 66:7945–7950. https://doi.org/10.1021/jo010635w

De Souza AO, Pedrosa MT, Alderete JB et al (2005) Cytotoxicity, antitumoral and antimycobacterial activity of tetrazole and oxadiazole derivatives. Pharmazie 60:396–397

Feinn L, Dudley J, CocaRoberts AEL (2017) Antimicrobial evaluation of 5-substituted aryl 1H-tetrazoles. Med Chem 13:359–364. https://doi.org/10.2174/1573406412666161220150028

Gagnon A, Landry S, Coulombe R et al (2009) Investigation on the role of the tetrazole in the binding of thiotetrazolylacetanilides with HIV-1 wild type and K103N/Y181C double mutant reverse transcriptases. Bioorg Med Chem Lett 19:1199–1205. https://doi.org/10.1016/j.bmcl.2008.12.074

Gupta A, Jamatia R, Patil RA, Yuan-Ron ma, Pal AK, (2018) Copper oxide/reduced graphene oxide nanocomposite-catalyzed synthesis of flavanones and flavanones with triazole hybrid molecules in one pot: a green and sustainable approach. ACS Omega 3:7288–7299. https://doi.org/10.1021/acsomega.8b00334

Gulati U, Chinna UR, Rawat U, Diwan S (2018) Reduced Graphene oxide supported copper oxide nanocomposites from a renewable copper mineral precursor: a green approach for decarboxylative C(sp3)–H activation of proline amino acid to afford value-added synthons. ACS Sustain Chem Eng. https://doi.org/10.1021/acssuschemeng.8b01376T2

Holland GF, Pereira JN (1967) Heterocyclic tetrazoles, a new class of lipolysis inhibitors. J Med Chem 10:149–154. https://doi.org/10.1021/jm00314a004

Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. J Am Chem Soc 80:1339. https://doi.org/10.1021/ja01539a017

Joseph A, Subramanian S, Ramamurthy PC, Srinivasan S, Kumar RV, Schwandt C (2015) Amine functionalized polyaniline grafted to exfoliated graphite oxide. Synthesis, characterization and multi-element sensor studies. J Electroanal Chem 757:137–143. https://doi.org/10.1016/j.jelechem.2015.09.015

Kumar A, Ramamurthi N, Harold S (1996) Rearrangement Reactions of (Hydroxyphenyl)carbenes. J Org Chem 61:4462–4465. https://doi.org/10.1021/jo952269k

Kantam ML, Kumar KBS, Sridhar C (2005) Nanocrystalline ZnO as an efficient heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazoles. Adv Synth Catal 347:1212–1214. https://doi.org/10.1002/adsc.200505011

Leiming L, Li B, Liu W, Li J, Zheng Xu, Gui Y (2010) Mesoporous ZnS nanospheres: a high activity heterogeneous catalyst for synthesis of 5-substituted 1H-tetrazoles from nitriles and sodium azide. Chem Commun 46:448–450. https://doi.org/10.1039/B912284B

Lonkar SP, Abdala AA, Deshmukh YS (2015) Recent advances in chemical modifications of grapheme. Nano Res 8:1039–1074. https://doi.org/10.1007/s12274-014-0622-9

Nohara A, Kuriki H, SaijoT SH, Kanno M, Sanno Y (1977) Studies on antianaphylactic agents. 5. Synthesis of 3-(1H-tetrazol-5-yl) chromones, a new series of antiallergic substances. J Med Chem 20:141–145. https://doi.org/10.1021/jm00211a030

Nasrollahzadeh M, Bayat Y, Moshaee S (2009) FeCl3–SiO2 as a reusable heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazoles via [2+3] cycloaddition of nitriles and sodium azide. Tetrahedron Lett 50:4435–4438. https://doi.org/10.1016/j.tetlet.2009.05.048

Panahi F, Dangolani SK, Fareghi AR, Golestanzadeh M, Khalafi NA (2017) Graphene grafted N-methyl-4-pyridinamine (G-NMPA): an efficient heterogeneous organocatalyst for acetylation of alcohols. ChemistrySelect 2:474–479. https://doi.org/10.1002/slct.201601578

Rani S, Kumar M, Kumar R, Kumar D, Sharma S, Singh G (2014) Characterization and dispersibility of improved thermally stable amide functionalized graphene oxide. Mater Res Bull 60:143–149. https://doi.org/10.1016/j.materresbull.2014.07.019

Sreedhar B, Kumar AS, Yadav D (2011) CuFe2O4 nanoparticles: a magnetically recoverable and reusable catalyst for the synthesis of 5-substituted 1H-tetrazoles. Tetrahedron Lett 52:3565–3569. https://doi.org/10.1016/j.tetlet.2011.04.094

Soltani RMN, Behrouz S, Doroodmand M, Movahedian A (2012) Copper-doped silica cuprous sulphate (CDSCS) as a highly efficient and new heterogeneous nano catalyst for [3+2] Huisgen cycloaddition. Tetrahedron 68:7812–7821. https://doi.org/10.1016/j.tet.2012.07.032

Shendage SS, Nagarkar JM, Singh AS (2014) Facile approach to the electrochemical synthesis of palladium-reduced graphene oxide and its application for Suzuki coupling reaction. Tetrahedron Lett 55:857–860. https://doi.org/10.1016/j.tetlet.2013.12.022

Talawar MB, Sivabalan R, Mukundan T et al (2009) Environmentally compatible next generation green energetic materials (GEMs). J Hazard Mater 161:589–607. https://doi.org/10.1016/j.jhazmat.2008.04.011

Taghavi F, Gholizadeh M, Saljooghi AS, Ramezani M (2017) Cu(ii) immobilized on Fe_3O_4@APTMS-DFX nanoparticles: an efficient catalyst for the synthesis of 5-substituted 1*H*-tetrazoles with cytotoxic activity. Medchemcomm 8:1953–1964. https://doi.org/10.1039/c7md00302a

Clarina T, Rama V (2017) [3 + 2] Cycloaddition promoted by zinc oxide nanoparticles anchored on reduced graphene oxide using green solvent. Synth Commun 48:1–13. https://doi.org/10.1080/00397911.2017.1393086

Vieira E, Huwyler J, Jolidon S, Knoflach F, Mutel V, Wichmann J (2005) 9H-Xanthene-9-carboxylic acid [1,2,4]oxadiazol-3-yl- and (2H-tetrazol-5-yl)-amides as potent, orally available mGlu1 receptor enhancers. Bioorg Med Chem Lett 15:4628–4631. https://doi.org/10.1016/j.bmcl.2005.05.135

Velladurai R, Kuppusamy K, Kasi P (2011) Syntheses of 5-substituted 1H-tetrazoles catalyzed by reusable CoY zeolite. J Org Chem 76:9090–9095. https://doi.org/10.1021/jo201261w

Zarchi MA-K, Abadi SSADM (2019) Dendron-functionalized Fe3O4 magnetic nanoparticles with palladium catalyzed CN insertion of arylhalide for the synthesis of tetrazoles and benzamide. J Organomet Chem 880:196–212. https://doi.org/10.1016/j.jorganchem.2018.11.006