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Please cite this article as: R.M. Ansari, B. Ramachandra Bhat, Copper (II) Schiff base-graphene oxide composite as an efficient catalyst for Suzuki-Miyaura reaction, *Chemical Physics* (2018), doi: https://doi.org/10.1016/j.chemphys.2018.09.018

Copper (II) Schiff base-graphene oxide composite as an efficient catalyst for Suzuki-Miyaura reaction

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ABSTRACT

Transition metal copper (II) Schiff base composite (Cu-NH$_2$-GO) was synthesized using functionalized graphene oxide with (3-aminopropyl)methoxysilane (APTMS). X-ray diffraction, FTIR spectroscopy and thermogravimetric analyses ascertained the incorporation of the copper (II) Schiff base on the functionalized graphene oxide. Scanning electron microscopy and TEM evidences further confirmed the surface morphology of the composite. Catalytic activity study indicated that the synthesized Cu-NH$_2$-GO was active for cross-coupling of aryl halide with phenylboronic acid. Above 84 % (4-Iodobenzonitrile) biphenyl conversion could be achieved using Cu-NH$_2$-GO heterogeneous catalyst in the C-C coupling reaction. Recovery and reusability study suggests that the catalyst maintains very high conversion for biphenyl (~80 %, with 4-Bromobenzonitrile) even after being used for four cycles.

Key Words: Graphene oxide composite, Schiff base, Chemical grafting, Heterogenous Catalysis, Suzuki-Miyaura cross-coupling.

1. Introduction

The Suzuki-Miyaura C-C cross coupling reaction is one of the most important organic transformations and it has been broadly used to synthesize pharmaceutical compounds, natural products, fine chemicals, polymers, etc,. Complexes of palladium have been generally used as an active catalyst in the cross-coupling reactions [1, 2]. Palladium being more expensive needs to synthesize more cost-effective catalysts for Suzuki-Miyaura coupling reactions [3]. The simple and low cost transition metal complexes have been synthesized for Suzuki-Miyaura reaction to avoid the use of noble metal (Pd) [4]. Transition metal complexes play an outstanding role in the field of catalysis due to their structural diversity and binding protocols [5].

Copper complexes have achieved much attention recently for applications such as molecular recognition, storage, gas separation, magnetic material, optical material and catalysis [6-9]. The catalytic performances exhibited by some of the copper complexes are excellent and comparable to activity of the noble metal platinum catalyst, specifically in the C-C or C-N coupling reactions [10-12]. Schiff base complexes with N, O donor atom have been widely reported for their catalytic and biological properties [13] and their activity profile in both homogenous and heterogeneous catalysis are comprehensively documented [14, 15]. Graphene and its derivatives aptly suit as a solid substrate to immobilize the transition metal complexes owing to their large surface area. They find great application in the fields of composite materials, catalysis, drug delivery, sensors, and photovoltaics due to their distinguishable nanostructures and attractive properties [16-21]. Graphene oxide obtained from graphene exhibits various advantages in comparison with graphene majorly because of the additional functional groups. The sheet edges having carbonyl and carboxyl groups, whereas the basal planes richly decorated with hydroxyl and epoxide groups makes graphene oxide heavily oxygenated [22, 23]. These oxygenic groups present on the graphene oxide cause immobilization of metal complexes acting as active sites. Pd nanoparticles immobilized on graphene oxide was used for the Suzuki-Miyaura reactions. This composite exhibited high activity and low metal leaching [24]. The Schiff base oxo-vanadium complex grafted onto graphene oxide has reportedly been used for the oxidation of alcohols [25]. The catalytic activities reported for theses transition metal complexes have prompted the research of low-cost catalysts for the coupling reactions [26].

Here, we report the synthesis and characterization of copper (II) Schiff base composite grafted onto graphene oxide (Cu-NH$_2$-GO). The catalytic performance of Cu-NH$_2$-GO was

studied in the C-C cross coupling of aryl halides with phenylboronic acid. The catalyst showed high conversion, easy recovery and safer reuse.

2. Experimental

2.1 Materials:

All the materials were used as procured. Copper acetate monohydrate, 6 % H_2O_2, H_2SO_4, H_3PO_4, potassium carbonate, salicylaldehyde, and sodium carbonate were procured from Merck India. (3-aminopropyl)trimethoxysilane (APTMS), acetonitrile (ACN), aryl halides, cesium carbonate, 1,4-dioxane, dimethylformamide (DMF), ethyl alcohol, graphite, phenylboronic acid, potassium tertiary butoxide, tetrahydrofuran (THF), toluene, and triethylamine were obtained from Sigma-Aldrich.

2.2 Characterization Methods:

FTIR spectra were obtained on a Bruker-Alpha FTIR spectrophotometer using KBr pellet method. Absorption spectra were obtained using Analytik Jena SPECORD S600 UV-Vis spectrophotometer. SEM analysis was carried out by JEOL-JSM-6360LV model to investigate morphology of the specimen. TEM analysis was carried out by JEM-2100Plus Transmission Electron Microscope. The metal content of the synthesized catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on Agilent 5100 Synchronous Vertical Dual View ICP-AES. XRD analysis was performed using Joel diffractometer with Cu-Kα (λ=1.542 Å) radiation. Thermogravimetric analysis (TGA) of GO and Cu-NH$_2$-GO were carried out on (EXSTAR-6000) (Carrier gas: N_2; flow rate: 50 mL/min) at 10 ˚C/min heating rate.

2.3 Synthesis:

GO was prepared using improved Hummers method [27]. (3-aminopropyl)trimethoxysilane was grafted on graphene oxide [28]. 0.1 g of GO was dispersed in 50 mL of toluene. To this dispersion, 2.0 mL of APTMS was added and refluxed at 110 ˚C for 24 hours in inert atmosphere. The obtained product was filtered, and washed with toluene and ethanol. The APTMS coated GO nanosheets (NH$_2$-GO) was dried overnight at 70 ˚C. 0.05 g of functionalized graphene oxide (NH$_2$-GO) was weighed and dissolved in ethanol (10 mL). To this 0.122 g of salicylaldehyde was added (Fig. 1). Then it was refluxed for about 8 hours. The obtained precipitate was filtered and dried overnight. The obtained product was named as GOSB. 0.1 g of GOSB was dispersed in 5 mL ethanol, to this 0.2 g of copper acetate was added and

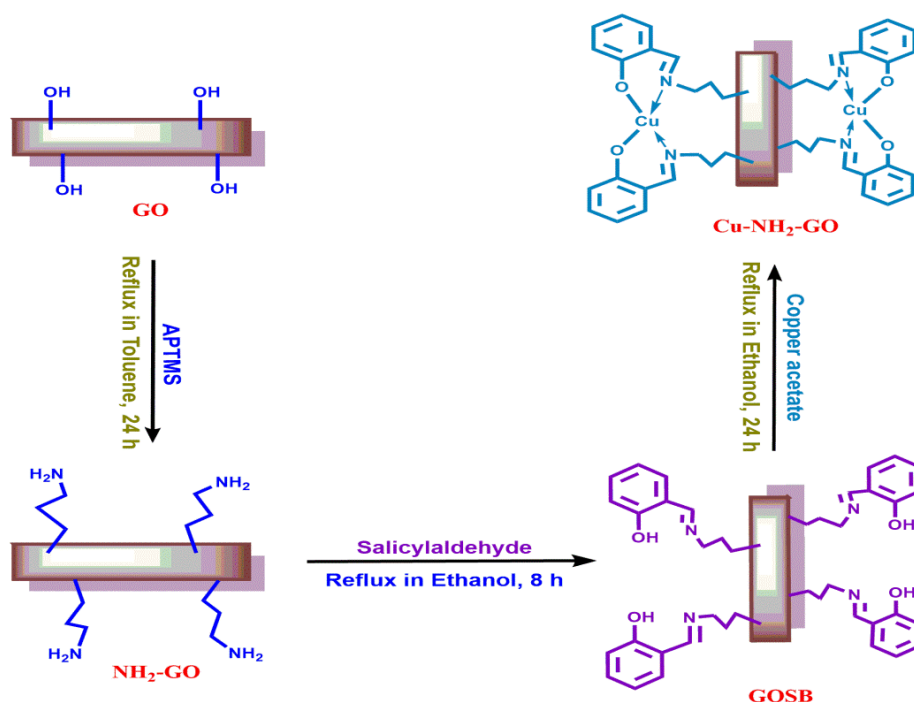refluxed for 24 hours (Fig. 1). The product was filtered and dried overnight. The obtained composite was named as Cu-NH$_2$-GO.

Figure 1 Stepwise synthesis of Cu-NH$_2$-GO

2.4 Suzuki coupling:

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), Cu-NH$_2$-GO (4.0 mg) and a base (2.0 mmol) was added in 3.0 mL of solvent and heated to 110 ˚C up to 12 hours. The organic layer was analyzed using gas chromatography (GC-2010, Shimadzu, Japan).

3. Results and discussion

The obtained GO, NH$_2$-GO, GOSB and Cu-NH$_2$-GO were examined by the FTIR spectroscopy (Fig. 2). In the spectrum of GO. the broad peak at 3425 cm^{-1} corresponds to stretching of O-H bonds and sharp peak at 1636 cm^{-1} ν(C=O) was due to the presence of carbonyl, hydroxyl, and carboxylic acid groups [29]. The peak at 1195 cm^{-1} and 1048 cm^{-1} are indicative of the C-OH and C-O- groups, respectively. NH$_2$-GO shows additional peaks at 3441 cm^{-1} (N-H stretching) and 1600 cm^{-1} (N-H bending) is due to presence of -NH$_2$ groups. The peaks within 2850-3050 cm^{-1} are due to presence of methylene and methyl groups [25]. Peaks at 1128 cm^{-1} and 1026 cm^{-1} are the evidence for the formation of Si-O-Si and Si-O-C bonds, respectively. This shows successful grafting of APTMS on GO. The FTIR spectrum of GOSB

shows a strong peak at 1616 cm^{-1} attributing to imine (C=N) stretching which is shifted to 1605 cm^{-1} in case of Cu-NH$_2$-GO sample. This confirms the formation of composite. The GO and Cu-NH$_2$-GO was analyzed by UV-Vis spectroscopy to investigate the chemical changes due to grafting of the complex on GO (supplementary Fig. S-1). GO shows absorption at ~220 nm due to sp^2 bonded carbon atoms [30]. The presence of n-π* (~259 nm) peak in Cu-NH$_2$-GO supports the grafting of the catalyst on GO.
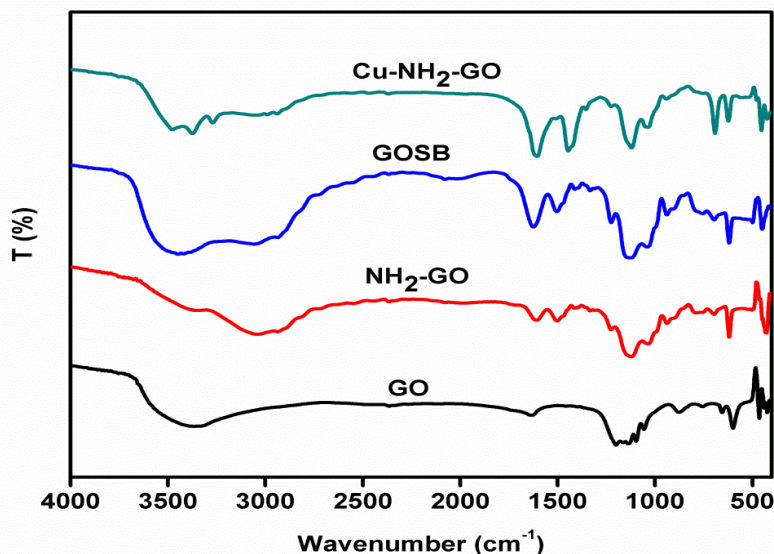
Figure 2 FTIR spectra of GO, NH$_2$-GO, GOSB and Cu-NH$_2$-GO

Fig. 3 demonstrates the XRD of GO and Cu-NH$_2$-GO. GO shows a diffraction peak at 12.86 ° which corresponds to (002) plane [31]. The broad peak around 22 ° is observed due to reduced graphene oxide in Cu-NH$_2$-GO catalyst. The XRD pattern for Cu-NH$_2$-GO showed that the synthesized catalytic composite is amorphous, which is disclosed by broad peak [32].
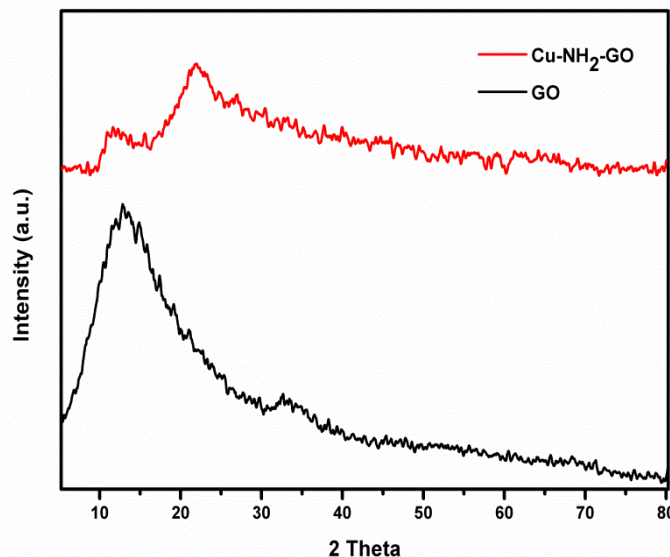
Figure 3 XRD patterns of GO and Cu-NH$_2$-GO

The SEM analysis was carried out to check the surface morphology of GO, NH$_2$-GO, GOSB and Cu-NH$_2$-GO (Fig. 4). It can be seen that SEM image of GO had sustained the sheet-like structure and it became wrinkled with the reaction of APTMS (NH$_2$-GO) [33]. SEM image of GOSB showed well defined arrangement of organic molecules onto sheets. Moreover, different distinctive shape of Cu- NH$_2$-GO was identified and the SEM image was quite different from that of GOSB. TEM image of the Cu- NH$_2$-GO is shown in Fig. 5. The black dots in TEM image could confirm the immobilization of copper Schiff base complex onto graphene oxide sheets. Also, ICP-AES analysis of Cu-NH$_2$-GO indicates the successful immobilization of the copper ions onto graphene oxide sheets.
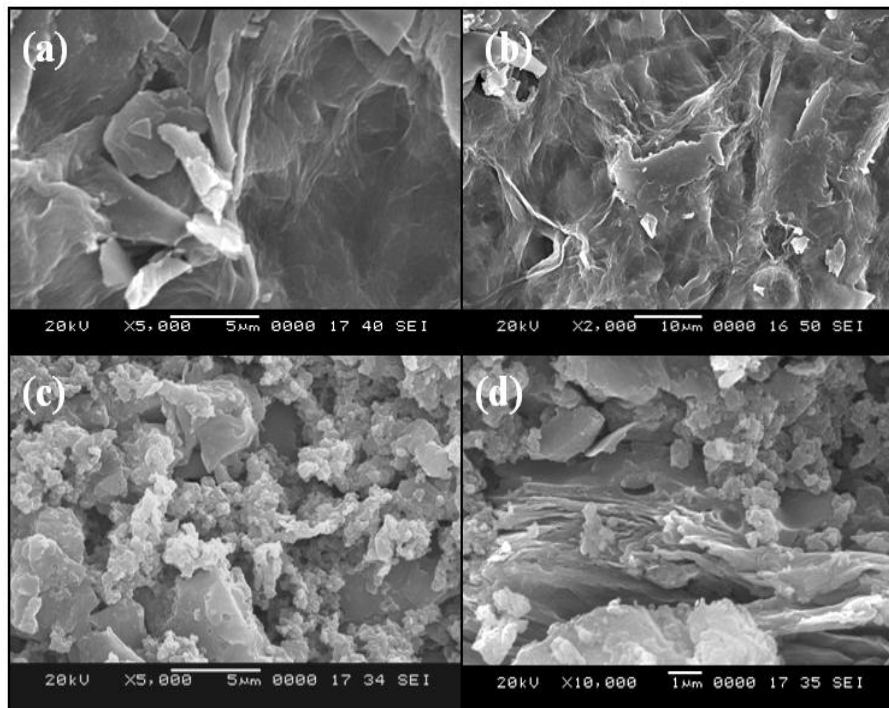
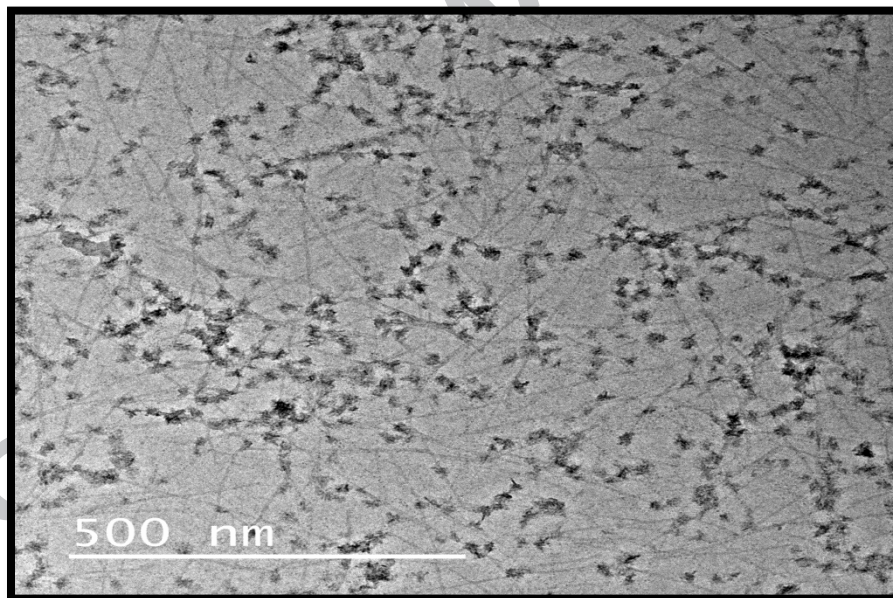**Figure 4** SEM images of (a) GO, (b) NH$_2$-GO, (c) GOSB and (d) Cu-NH$_2$-GO

Figure 5 TEM image of Cu-NH$_2$-GO

The thermal behavior of the GO and Cu-NH$_2$-GO was examined by TGA. The first weight loss of GO in under 115 ˚C is due to the removal of trapped moisture. The second significant weight loss was noticed in the range of 250-330 ˚C, due to decomposition of oxygen moieties (Fig. 6) [34, 35]. The Cu-NH$_2$-GO catalyst shows three weight losses up to 600 ˚C. The slight reduction in weight within 150-200 ˚C corresponds to the removal of water. The weight

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loss around 360 ˚C is due to the decomposition of complex on GO. The subsequent reduction in weight above 450 ˚C is attributed to the decomposition of the residual by products which resulted from the decomposition of complex.
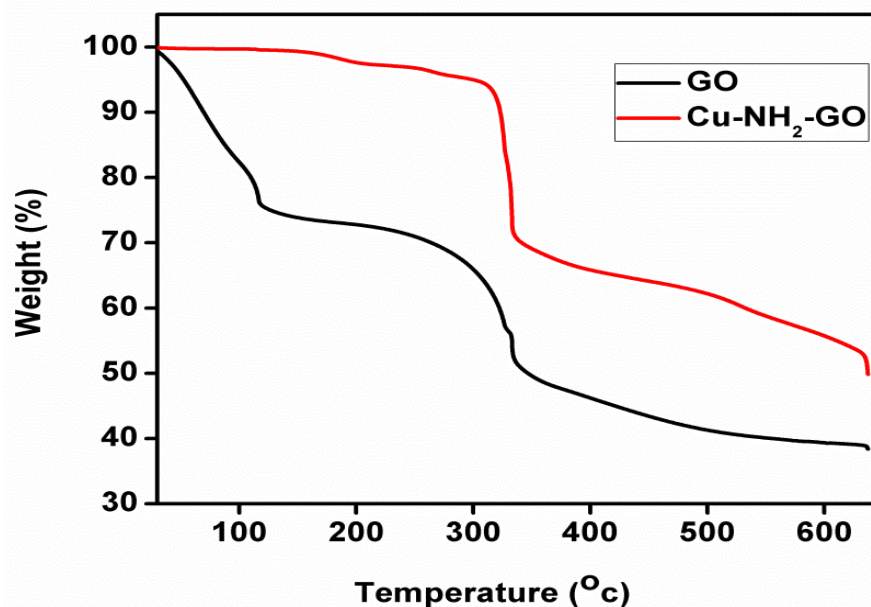

Figure 6 TGA of GO and Cu-NH$_2$-GO

The catalyst Cu-NH$_2$-GO was examined for C-C cross coupling of 4-bromobenzonitrile with phenylboronic acid. Optimum reaction condition was studied using different parameters like base, solvent, catalyst concentration and reaction time on product yield.

The catalytic activity of catalyst was carried out in Acetonitrile, 1,4-dioxane, toluene, THF and DMF solvent media at their reflux temperature (Table 1). Among different solvents chosen, highest catalytic activity was found in toluene, lightly lower yield by other solvents. Toluene was selected as solvent for further studies. The reaction was also examined for the effect of base on the yield of product. Among all the experimented bases, K$_2$CO$_3$ was found to be most active (Table 2). The effect of reaction time on the yield of product was established by examining the reaction mixture at different time intervals. The yield was observed to increase till 12 hours of reaction after which there was no further significant improvement (supplementary Fig. S-2). The catalyst concentration effect on the reaction was analyzed with different catalyst concentration for coupling. An expected increase in yield was observed with increase in concentration till 4.0 mg catalyst concentration before reaching the plateau (supplementary Fig.

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S-3). Further, different aryl halides were used to study the C-C coupling with phenylboronic acid. The yield obtained was different with various substituents. Presence of electron withdrawing group on the benzene ring facilitates the easy removal of halide group and thereby enhances the positivity on the para position favoring nucleophilic attack in the coupling reaction. The results are summarized in Table 3. Additionally, the catalyst was easily recovered and recycled without significant loss in its activity (supplementary Fig. S-4).

Table 1 Effect of solvents on Suzuki-Miyaura cross coupling reaction.

Entry	Solvents	Base	Yield[a]
1	Acetonitrile		76
2	Toluene		80
3	1,4-dioxane	K_2CO_3	75
4	THF		62
5	DMF		61

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), Cu-NH$_2$-GO (4.0 mg), solvent (3.0 mL), 12 h.

[a] Yield determined by GC.

Table 2 Effect of base on Suzuki-Miyaura cross coupling reaction.

Entry	Bases	Solvent	Yield[a]
1	Et_3N		72
2	K_2CO_3		80
3	Cs_2CO_3	Toluene	75
4	Na_2CO_3		69
5	KO^tBu		60

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), Cu-NH$_2$-GO (4.0 mg), solvent (3.0 mL), 12 h.
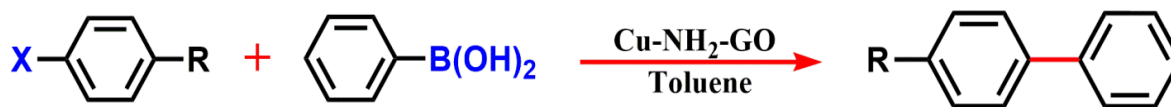
[a] Yield determined by GC.

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Table 3 Reaction yield for various aryl halides in Suzuki-Miyaura cross coupling reaction.

Scheme 1 Suzuki-Miyaura cross coupling reaction

Entry	R	X	Yield[a]
1	OCH$_3$		55
2	H		50
3	CN		80
4	COCH$_3$		78
5	NHCOCH$_3$	Br	75
6	OH		59
7	CH$_3$		44
8	F		52
9	OH		64
10	CN	I	84

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K$_2$CO$_3$ (2.0 mmol), Cu-NH$_2$-GO (4.0 mg), toluene (3.0 mL), 12 h.

[a] Yield determined by GC.

4. Conclusions

This work reports the immobilization of different chemical moieties on the graphene oxide and presents opportunities for designing high activity, heterogeneous, and eco-friendly catalysts. The catalytic activity of synthesized composite was studied in Suzuki-Miyaura reaction. Aryl halides with electron withdrawing groups fared better as compared to those with electron donating groups w.r.t the yield of reaction. Among the various aryl halides, iodide was found to be a better leaving group. The grafted catalyst was easy to recover and recycle with consistent activity (~80 %, 4-bromobenzonitrile). Therefore, the developed GO based catalyst is viable heterogenous catalyst owing to its ease of synthesis and stability for the Suzuki-Miyaura reaction.

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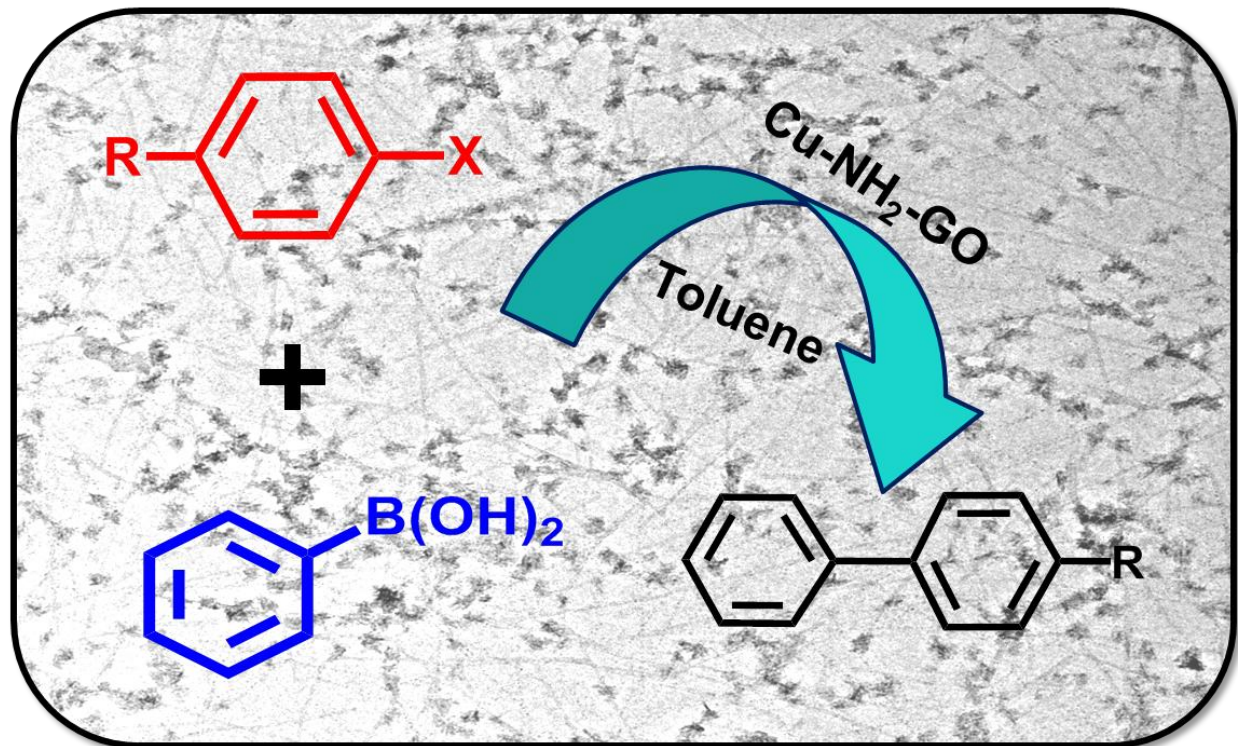
- Copper Schiff base complex (Cu-NH$_2$-GO) grafted on graphene oxide is synthesized and characterized with different characterization techniques.
- The catalytic activity of catalyst has been investigated for Suzuki-Miyaura cross coupling reaction using different aryl halides with phenylboronic acid in optimum condition.
- The synthesized catalyst maintains very high conversion for biphenyl (~80 %, with 4-bromobenzonitrile) even after being used for four cycles.