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Synthesis Of Copper Graphene Nanocomposite By Amino Functionalization And Their Catalytic Applications

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Abstract

A heterogeneous catalyst containing copper nanoparticle covalently immobilized on the surface of amino functionalized graphene oxide i.e., (CuAMSGO complex) for studying the catalytic activity of Suzuki cross coupling of substituted aryl halides with phenylboronic acids. The yield of the product was 93% analyzed using GC. Under the optimized conditions, the catalyst was able to retain its activity upto 4 regenerative cycles with a metal leaching of 1.34% determined using ICP-AES analysis. The high activity of catalyst is ascribed to good synergistic effects of copper nanoparticle and the amino functionalized graphene oxide. High yield, environmentally benign, easy work-up procedure and easy separation of catalyst are some of the important features of this protocol.

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Keywords: Graphene oxide; Copper nanoparticles; heterogeneous catalyst; phenylboronic acids.

1. Introduction

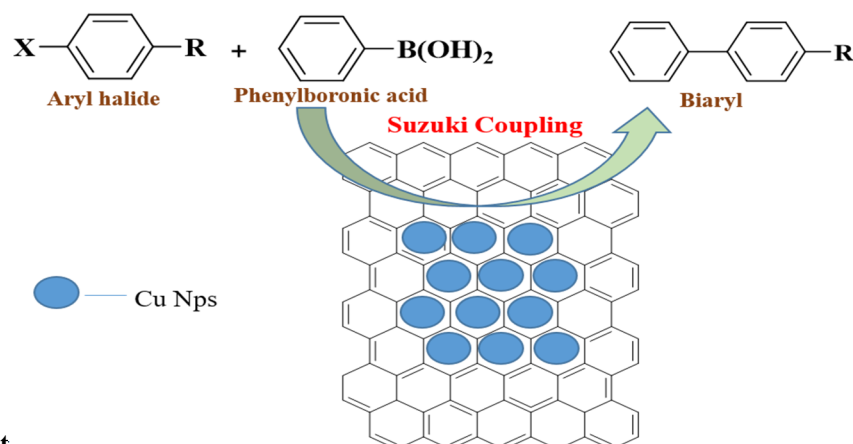
Metal nanoparticles (nps), which are supported on high surface area solid material, known to be heterogeneous catalysts among the wide range of synthetic organic reactions such as reductions (1-3), oxidations (4-6), and couplings (7-9). The key problem prevailing in this field is how to control the size of nanoparticles when exhibited to a chemical reaction, and the various crystallographic planes may vary in their specificity in catalysis field (10). Apart from the various types of high surface area materials which were termed as supports, a novel and interesting material among the carbon nanomaterial i.e., Graphene oxide (GO) gained interest in different catalytic fields such as photochemistry, electrochemistry and organic catalysis (11-15).

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Graphene and its substituents material possess unique properties such as high surface area, large water dispersity, intrinsic low mass, simple surface modification and various oxygen functionalities making it as a promising candidates for catalysis or supporting material(16-18). Graphene which comprises of sp^2 carbons in hexagonal arrangement having a one atom thick layer constitutes as 2D materials, in which most of the atoms gets accessible in order to interact with substrates as well as reagents (19).

Among the different techniques, graphite vigorous oxidation method is highly versatile and easily scalable methodology to synthesize Graphene oxide. GO owes magnificent hydrophilic property due to the abundance of a cluster of oxygen functionalities on its basal planes and edges (20). The functional groups and defects in GO making them to be easily functionalized with various surfactants, organic polymer, cyclodextrin, transition metal complexes and metal nanoparticles which are highly favorable for the catalytic application, by making these materials as good supports (21-24). However, these functionalized graphene with organometallic compounds or metal nanoparticles are valuable material for the recyclability of the catalysts.

Till date, some of the investigations on literature about GO after physicochemical modification as a catalytic material for organic reactions was reported earlier (25-27). GO was chemically modified with oxovanadium Schiff base reported as a recyclable catalyst for the oxidation of numerous alcohols along with α -hydroxy substituted ketones to carbonyls compounds using tert-butyl hydroperoxide (TBHP) as oxidant (25). Pristine L-proline an amino acid which has been non-covalently deposited on to the GO sheet by a chemical methodology in aqueous solution is noted to be excellent catalyst for the aldol condensation (26). Wang et al (2013) described the N-heterocyclic carbene-palladium complex (NHC-Pd⁺) on the surface of GO as an effective catalyst for the Suzuki-coupling of aryl halides with arylboronic acids (27). Here, we synthesized GO immobilized Copper nps for the catalytic activity of C-C coupling reaction (Suzuki coupling).



Graphical Abstract

2. Experimental method

2.1. Chemicals required

Graphite, 3-aminopropyl trimethoxysilane, copper acetate. hexahydrate, phenylboronic acid and aryl halides were purchased from sigma-Aldrich. Ethanol, toluene, acetonitrile, DMSO, DMF, hydrogen peroxide, sulphuric acid, phosphoric acid are obtained from Finar chemicals limited. Caesium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium nitrate, sodium carbonate, potassium phosphate and potassium permanganate are obtained from lobo chemie limited.

2.2. Synthesis of GO

5g of graphite and 2.5g of NaNO₃ were mixed with 108ml of H₂SO₄ and 12ml of H₃PO₄ and kept stirring in an ice bath for 10 minutes. Later, 15g of KMnO₄ added slowly by maintaining temperature at 5 °C. Stirring the mixture for

2h at 0 °C and then it is increased to 40 °C for about 60 min in a water bath. Now the temperature of the mixture is adjusted to 98 °C for 60min. Further the deionized water is added to make the suspension upto 400ml. 15ml of H₂O₂ added to the above mixture after 5min. The obtained suspension centrifuged, filtered and washed with deionized water several times and 5% HCl solution repeatedly.

2.3. Synthesis of 3-aminopropyl trimethoxysilane functionalized graphene oxide (AMSGO)

1000mg of GO was dispersed in 50ml of dry toluene for 20 min was refluxed with 4ml of APTMS under the nitrogen atmosphere (25). After 24hrs, the black powdery sample was filtered off, later with toluene wash, and then final wash with EtOH to remove the unadsorbed APTMS on the surface of graphitic layers and further dried in vacuum oven at 70 °C for 6h.

2.4. Synthesis of Copper /Graphene oxide nanocomposites (CuAMSGO)

AMSGO (500mg) was dispersed in 50ml of EtOH under sonication for 5min. Later the copper acetate. hexahydrate (500mg) was dissolved in ethanol and added directly to the amino functionalized GO and the reactions were carried out in autoclave at 200 °C for 24h. After the reaction is done, the filtered product is washed several times with ethanol. The sample is dried at 200 °C for 12h in vacuum oven.

3. Results and Discussions

In this work, we reported the synthesis of CuAMSGO catalyst by the covalent interaction of copper nanoparticles with amino functionalized graphene oxide. The synthesized catalyst were characterized using physicochemical techniques such as FTIR, XRD, SEM, and ICP-AES to investigate the structural and surface composition as well as to improve catalyst stability. FTIR spectra recorded in KBr disks using Bruker-Alpha ECO-ATR FTIR within the range of 500-4000cm⁻¹. X-ray diffraction measurements were done using Cu Ka radiation on a Rigaku 600 diffractometer Miniflex equipped with Ni filtered Cu Ka radiation (operating at 40kV, 30mA, wavelength $\lambda = 1.54056\text{nm}$) within the range 2θ of 5°-80° at scanning speed of 2° per minute to determine the XRD planes in GO and Copper immobilized amino functionalized graphene oxide. Scanning electron microscopy were analyzed using SEM JEOL JSM-6380LA to analyze the surface topography as well as microscopic features. The products analyzed using the gas Chromatography (GC) (Shimadzu 2014, Japan), siloxane Restek capillary column (30m length and 0.25mm diameter) with a Flame Ionization Detector (FID).

3.1. FTIR:

For graphene oxide (GO), there is a strong band with a stretching frequency of 1725cm⁻¹ (C=O) indicates carboxylic acid and the bands around 1058, 1220 and 1621 cm⁻¹ as epoxy(C-O), phenol, carbon-carbon double bond groups 25. A broader band at 3394 cm⁻¹ resembled the stretching vibration of OH group, indicating various hydroxyl group situated on graphene oxide. FT-IR analysis of AMSGO have a band (doublet) at 2850 and 2917 cm⁻¹ which attributed to the presence of alkyl chains CH₂ i.e., both symmetric and asymmetric linkage. The peaks at 1121.5, 1034 and 1620 cm⁻¹ represented to be linkages of Si-O-Si, Si-O-C along with C-N vibrations which confirmed silylation process had taken place due to the chemical bonding of APTMS on to graphene oxide surface (29). The absorption bands around 3423.7 and 1573.2 cm⁻¹ attributed to the δ N-H vibrations which confirmed the presence of aminosilane chain on the GO nanosheets. FTIR result showed that the amino groups (APTMS) had been covalently functionalized on to the graphene nanosheets successfully through a simple chemical methodology. A new peak around 674 cm⁻¹ was attributed to the stretching of Cu-N bond confirms the coordination of Cu with N site of the CuAMSGO shown in figure 1 .

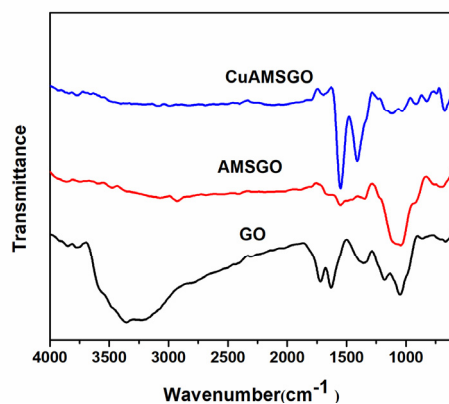


Figure 1. FTIR spectra of a) GO, b) AMSGO & c) CuAMSGO catalyst

3.2. XRD:

In graphene oxide GO, a broad peak at $2\theta = 10.91$ indicated the (001) reflection in graphite oxide, confirmed the formation of graphene oxide with various oxygen functionalities introduced into basal planes of graphene layers. A small peak of $2\theta = 10.9$ in the diffraction patterns of the GO-Cu catalyst confirmed the structure of graphene oxide not destroyed during the catalyst synthesis (30). A broad peak observed at $2\theta = 22.24$, near to reduced graphene at $2\theta = 22.24$ represented the various oxygen functionalities specifically hydroxyl groups had been successfully converted confirmed the presence of silane group on the GO surface. The diffraction peaks of GO, AMSGO and the CuAMSGO represented in the figure 2a-b. CuAMSGO catalyst diffraction peaks are 28.4, 36, and 74 represented the Cu_2O (200), Cu_2O (111) and Cu (220) respectively. The organized crystal structure of Cu nanoparticle highlighted its high intensive and sharp peaks (31) whereas amorphous nanoparticle represented weak due to broadened lines in XRD graph (32).

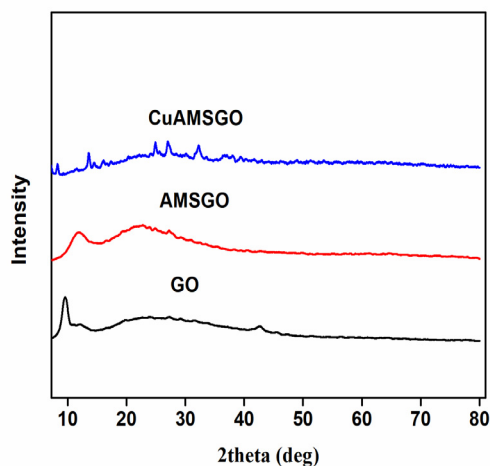


Figure 2. XRD spectra

3.3. SEM & EDX Analysis

The morphology and microscopic properties of the GO, CuAMSGO was further investigated using Scanning electron microscopy in Figure 3 (a-d). The 2D structure of GO Nanosheets and its composite are wrinkled with folded protrusions could be clearly observed (25). These sites acts as ideal templates which favor the reactant molecules to form target transformation of GO. Therefore, these stacking of GO-Cu hybrid is higher than that of GO, which significantly states that the amino functionalization on its periphery or basal planes of GO helpful for the formation of GO-Cu catalyst.

In EDX analysis, the atomic wt% of the GO, AMSGO and the CuAMSGO catalyst. In GO, it comprises of carbon and oxygen groups with different functional layers in the interplanar layers shown in supplementary information S1. In amino functionalized graphene oxide AMSGO, the different composition of elements include carbon, oxygen, silicon and nitrogen and it confirmed that APTMS has been successfully immobilized onto the GO shown in supplementary information S2. The synthesized catalyst CuAMSGO complex showed the various elements such as carbon, oxygen, nitrogen, silicon and copper with atomic wt% shown in figure. The copper nanoparticles immobilized onto graphene oxide confirmed by the EDX analysis of CuAMSGO catalyst. The elemental mapping illustrated that the homogeneous even distribution of Cu, N, Si, O on the heterogeneous support. The elemental mapping of CuAMSGO catalyst confirmed the EDX analysis is in equivalent representstion with the elemental proportion shown in Si, N and Cu elements.

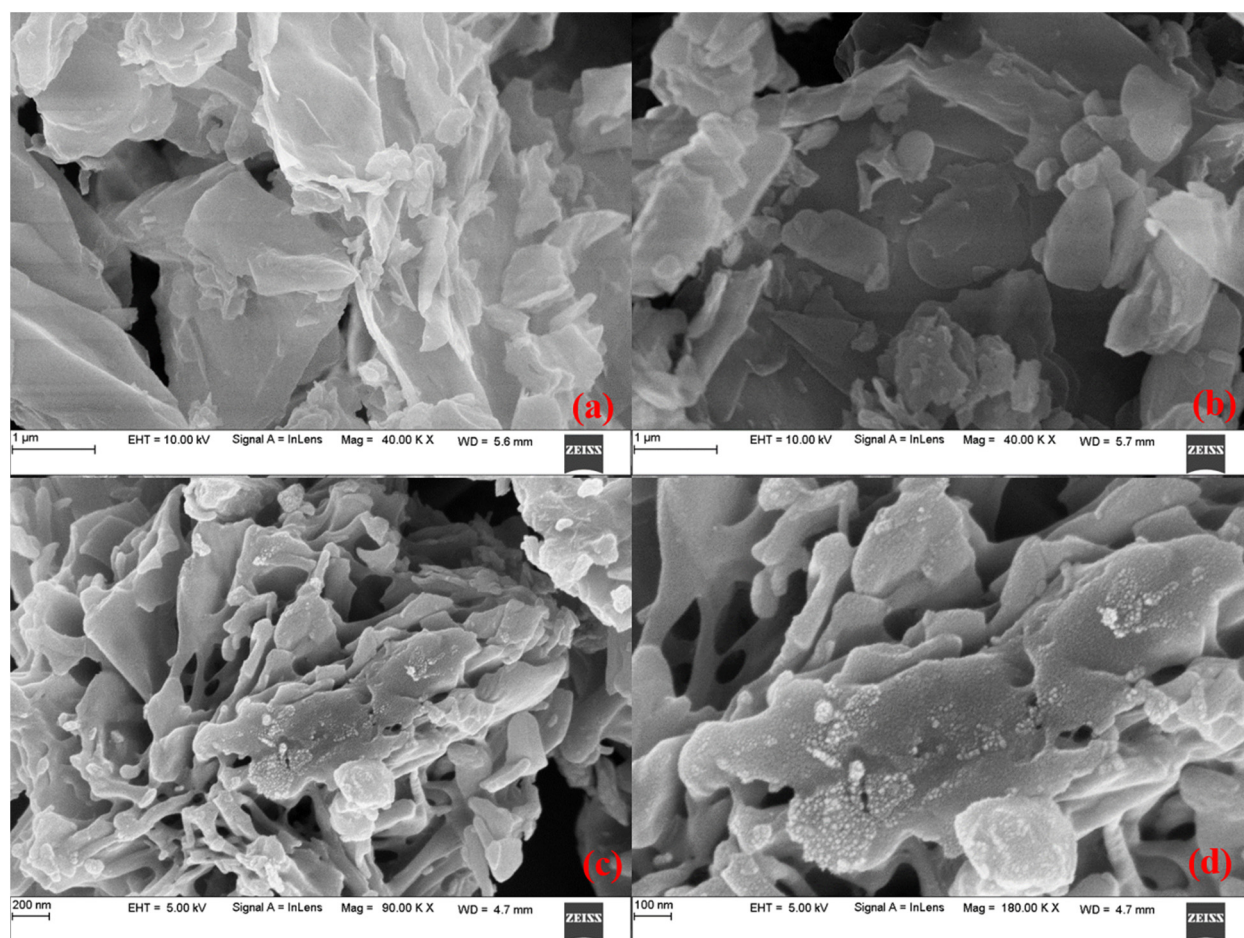


Figure 3. SEM images of (a) GO, (b) AMSGO, (c) & (d) CuAMSGO catalyst

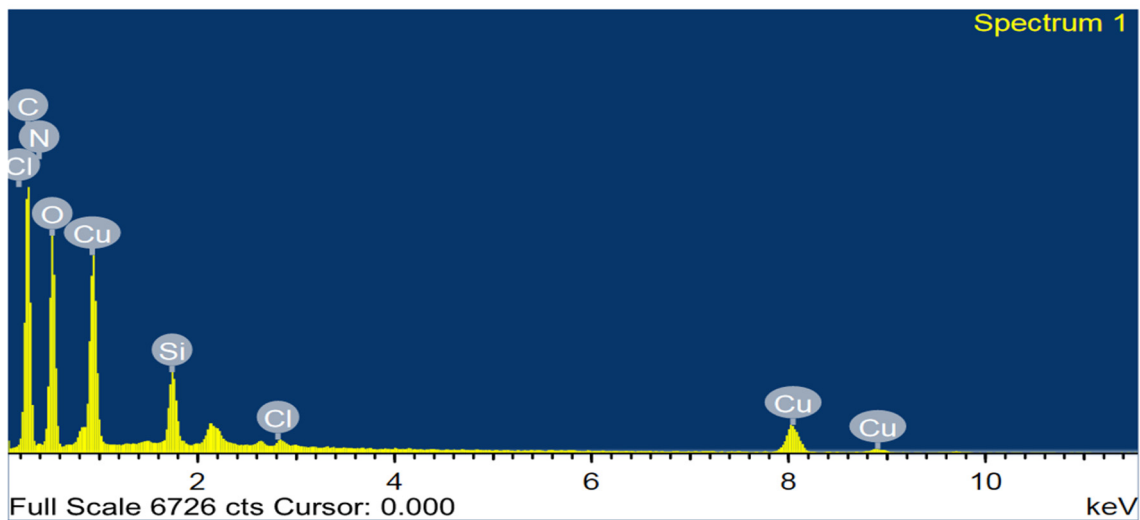


Figure 4. EDX of CuAMSGO

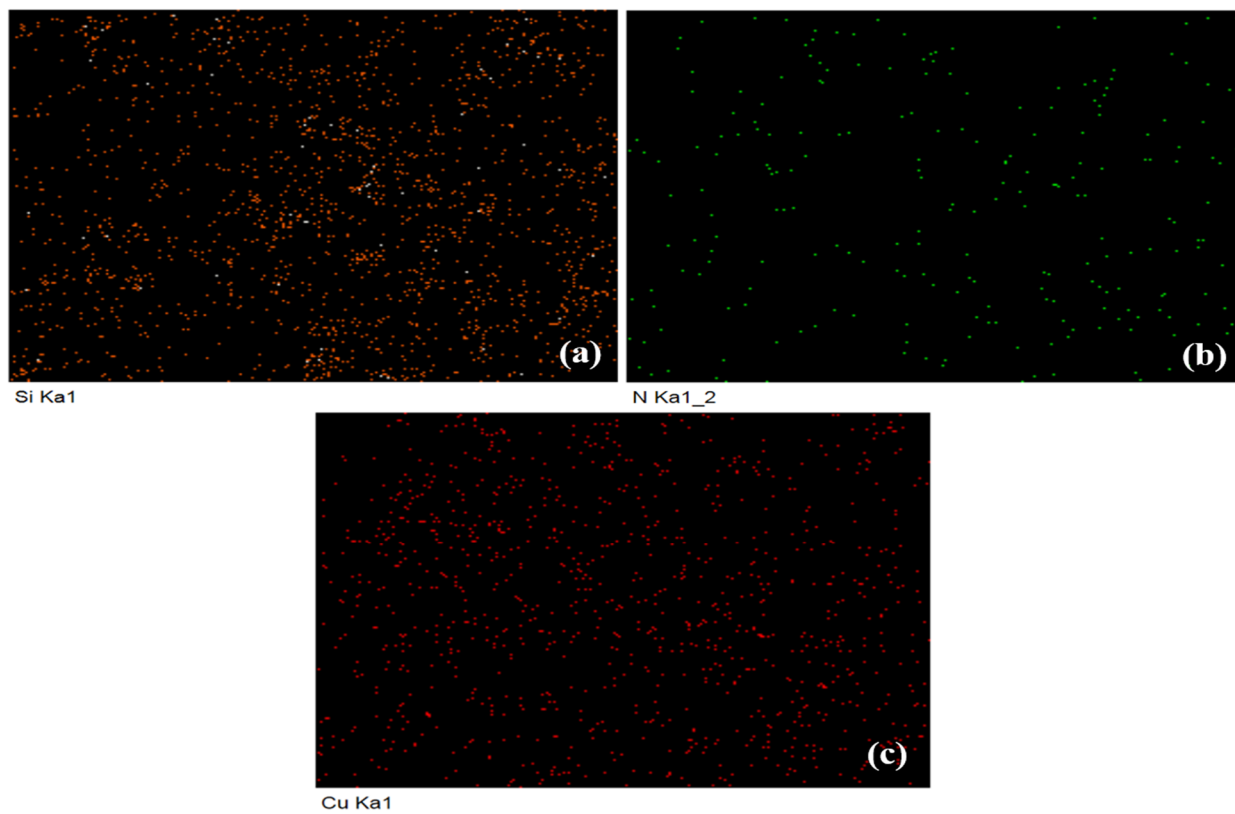


Figure 5. Elemental mapping of CuAMSGO catalyst

3.4. ICP-AES Analysis:

Atfirst, the CuAMSGO catalyst were digested in conc HNO₃ for 24hrs and then analyzed using ICP-AES. The molar mass of the fresh catalyst is 1.48 wt % and the molar mass after the 4th cycle is 1.34 wt % and futher the wt% is more than expected. The catalyst is stable upto 4 consecutive cycles with a minimum loss of CuAMSGO catalyst wt %.

3.5. Suzuki coupling:

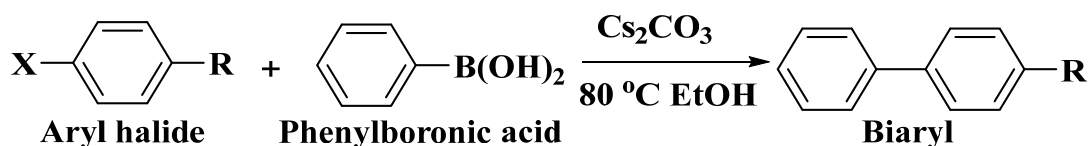
Aryl halide (1mmol) and phenyl boronic acid (1.5mmol) taken in a flask having the CuAMSGO catalyst (0.5 mol%) and Cs₂CO₃ (3mmol) in ethyl alcohol (5ml). The reaction flask was maintained in a parallel synthesizer Talboys at 80 °C with constant stirring under reflux conditions which is specified in Table 1b. The reaction is monitored with TLC (thin layer chromatography), the products were filtered and analyzed using Gas Chromatography (GC).

As a part of study, the Suzuki coupling was checked using CuAMSGO catalyzed C-C coupling reaction shown in scheme1 in supplementary information. The reaction between phenylboronic acid and aryl halides along with CuAMSGO catalyst resulted due to the formation of a carbon-carbon bond, a significant intermediate in most of the synthetic transformations. Here, the model reactions were performed between 1-bromobenzene and phenylboronic acid under variable conditions and the results were evaluated to find out the suitable conditions for the Suzuki coupling using GO-Cu catalysts.

To investigate appreciable reaction conditions, among the various solvents being tested, Ethanol found to be the best solvent media for the Suzuki coupling as shown in figure 1a. Of, all the bases examined from table1a, Cs₂CO₃ was selected as a superior base under the optimized conditions. Due to the varied temperature, the product formation has altered and the optimized temperature is 80 °C for the cross coupling of aryl halides with phenylboronic acids in presence of CuAMSGO catalyst.

The optimum amount of CuAMSGO complex was stabilized to 0.5mol%. The GC analysis of the reaction shows that the CuAMSGO catalyst is highly active for cross coupling under the optimized heterogeneous reaction medium. However, the time of the reaction under the optimized conditions is shown in figure 4a. After optimizing the reaction conditions for Suzuki coupling using CuAMSGO catalyst, various biaryl compounds were obtained using aryl halides with phenylboronic acid with a maximum yield up to 90%. (Table1b).

The represented products in table 1a explained that various aryl halides and phenylboronic acid has been applied to synthesize desired biaryl products using CuAMSGO catalytic moiety under the optimized conditions. Electron withdrawing groups possessing aryl halides resulted to form products with excellent yield compared to donating groups. The recyclability of CuAMSGO catalyst was investigated by the cross coupling of bromobenzene with phenylboronic acid under the optimized conditions and it is reusable up to 4 times without any further significant loss in its catalytic activity shown in figure 5a -c.



Scheme 1 is Suzuki coupling

Table 1a. Various Bases and solvents studies for Suzuki coupling

Entry	Base	Solvent	Temp (C)	Time(h)	Yield
1	K ₂ CO ₃	EtOH	80	16	65
2	Na ₂ CO ₃	EtOH	80	18	51
3	K ₂ CO ₃	Toluene	80	16	49
4	K ₂ CO ₃	DMSO	100	18	56
5	K ₂ CO ₃	DMF	120	18	45
6	K ₃ PO ₄	DMF	120	24	68
7	Cs₂CO₃	EtOH	80	12	90
8	Et ₃ N	EtOH	80	18	49
9	KOH	EtOH	80	24	64
10	K ₂ CO ₃	EtOH	60	18	54
11	K ₃ PO ₄	EtOH	80	24	59
12	K ₂ CO ₃	EtOH/H ₂ O	90	18	64
13	Cs ₂ CO ₃	EtOH/H ₂ O	80	24	90
14	Cs ₂ CO ₃	EtOH	RT	24	46
15	Cs ₂ CO ₃	EtOH	100	24	79
16	Na ₂ CO ₃	DMF	120	18	67
17	Cs ₂ CO ₃	DMF	120	24	70
18	Cs ₂ CO ₃	DMSO	120	24	54

Table 1b. The Suzuki coupling of different aryl halides

Entry	Aryl halide 'X'	Aryl halide 'R'	Time (h)	Yield (%)
1	I	H	12	90
2	Br	4-OCH ₃	16	75
3	Br	H	16	88
4	Br	4-CN	16	87
5	Br	4-NO ₂	14	89
6	Br	4-CH ₃	18	72
7	Br	4-OH	16	82
8	Br	4-CHO	16	80.5
9	Br	4-NHCOCH ₃	16	76
10	Br	2-OCH ₃	24	45
11	Cl	4-CH ₃	24	24
12	Cl	H	24	27

Therefore, for the CuAMSGO hybrid catalysts, the amino groups with silane moiety were immobilized on the graphene oxide nanosheets along with strong coordinating phenomena in between Cu²⁺ and its attachment sites on the amino functionalized graphene oxide which decreased reduction degree resulted in the formation of amorphous nanoparticles (33). In CuAMSGO hybrid material, the wormlike Cu nps explains the amino functionalized graphene oxide has N nitrogen sites along with π -conjugated system and these attachment sites further leads to the aggregation of Copper nanoparticles (34). Meanwhile, the amorphous copper nanoparticles gave comparative catalytic performance due to its crystalline nature in this catalytic reaction. Copper nanoparticles morphology can be tuned by grating of amino functionalization and further high of the catalyst can be gained due to the synergistic effect of APTMS silane moiety. Therefore, the effective synergistic mechanism plays a greater role in controlling the activity of copper nanoparticles.

Reusability of the catalyst

However, the repeated experiments were done for both Suzuki Coupling for obtaining the average catalytic data and later recycling experiments done to know its catalytic activity. After every reaction or run, the catalyst filtered by simple filtration and then through centrifugation and washed with acetonitrile (3*5ml) and several times with water, reused in sequential runs and dried in oven at 50 °C shown in figure 6.

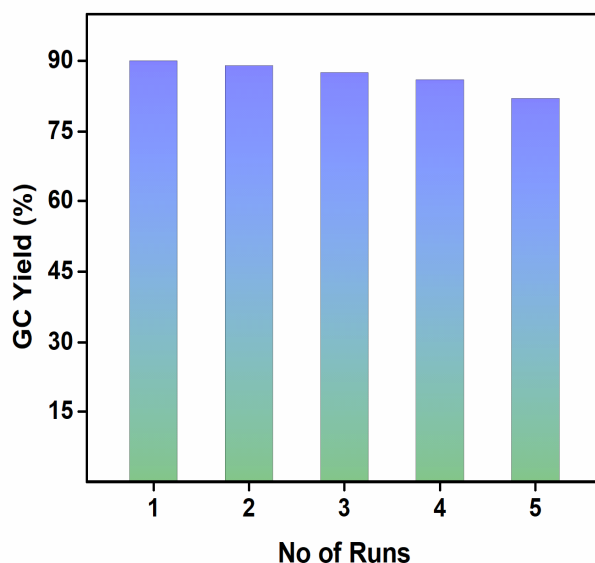


Figure 6. Reusability of the CuAMSGO catalyst

4. Conclusions

In summary, the development of a facile and efficient methodology to synthesize copper immobilized amino functionalized graphene oxide as a hybrid materials for the Suzuki coupling of aryl halides with phenylboronic acids to form biaryl compounds as products. The synthesized catalyst was monitored using different techniques like surface morphology as well as distribution and loading of copper nanoparticles and these nanoparticles size has been controlled by the immobilization on amino functionalized graphene oxide. The heterogeneous CuAMSGO catalytic system find its application in the formation of C-C coupling reaction under the mild and ecofriendly conditions. The catalytic system can be recycled for 4 times in consecutive cycles without any further decrease in its activity. The high catalytic activity of Suzuki coupling have been reported due to the good synergistic effect of Cu nanoparticles with amino functionalized GO. Here, the catalytic mechanism is quite unclear for this GO-Cu hybrid material catalyst and later investigation is in current need for these hybrid material catalyst. The strategy followed by us could pave way for the development of various metal amino functionalized Graphene based materials. From these results, these amino grafted Cu nanoparticles can be promising substitutes in heterogeneous catalysis.

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