# SYNTHESIS OF COPPER NANOPARTICLE DEPOSITED SULFONIC ACID MODIFIED GRAPHENE COMPOSITE: AN EFFICIENT CATALYST FOR N-ARYLATION REACTION

A

Dissertation

Submitted by

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# ACKNOWLEDGEMENT

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# CERTIFICATE

This is to certify that the dissertation entitled, **"Synthesis of copper nanoparticle deposited sulfonic acid modified graphene composite: An efficient catalyst for N-arylation reaction"** submitted by Arun Kumar Yelshetty for the award of Master of Science in Chemistry during the period of January 2013 - April 2015 in the Material Chemistry Laboratory, Department of Chemistry, National Institute of Technology, Rourkela, is a record of authentic work carried out by him under my supervision for training purpose. To the best of my knowledge, the matter embodied in this dissertation has not been previously submitted for any degree in this/any other institute.

Date:                                                                                    Dr. Sasmita Mohapatra

# CONTENTS

# ABSTRACT

A water soluble graphene based composite with surface-deposited copper nanoparticles ($SO_3H$-G-Cu) has been synthesized and used as catalyst for N-arylation of heterocycles with aryl halides. The structure and composition of the nanocomposite have been characterized by XRD, FESEM and EDAX. The catalytic activity of the $SO_3H$-G-Cu has been tested employing pyrrole and iodobenzene as model substrates. The synthesized catalyst is able to produce N-aryl heterocyles, under mild reaction conditions in a mixture of polar solvents (Ethylene glycol: water). The developed catalytic process is simple, efficient, economical, and environmentally safe.

# INTRODUCTION

Graphene has been considered as an excellent suitable catalytic support due to its high thermal conductivity[1], good mechanical strength[2], electrical conductivity[3], and large specific surface area.[4] Graphene based metal and metal oxide nanocomposite have been used in electrocatalysis, photocatalysis, bio and chemosensors and carbon-carbon bond formation.[5,6] Earlier it has been reported that graphene can enhance the catalytic activity of a catalyst by means of increasing the surface area, efficient capping, protection of catalyst materials, and efficiently storing and shuttling electrons through the $sp^2$ hybrid 2D carbon network.[7,8] However, developing homogeneous composites with a uniform distribution of catalyst and controlling the catalyst loading remains a major problem. This is a very challenging task due to the poor solubility of graphene and the weak interactions between graphene and catalyst. Chemically synthesized graphene from colloidal graphene oxide offers significant advantages in producing soluble graphene and graphene-based catalyst composites.[9] Metal and semiconductor nanoparticles have been loaded onto graphene by using chemical functional groups,[1,7] electrostatic interactions,[3] hydrophobic interactions and via functionalization of graphene.

However, these catalyst composites mainly focus on electrocatalysis that involves electron transfer reactions, and only limited studies have been performed on other types of catalysis.[8,9] Usually, N-arylated heterocyclic compounds are synthesized via nucleophilic aromatic substitution reactions with aryl halides bearing electron-withdrawing substituents or via Ullmann type couplings at high temperatures.[10,11] After the initial reports of Lam, the Cu-catalyzed cross coupling between N-heterocycles and aryl boronic acids has become an important synthetic method in modern organic synthesis.[12] Later, the discovery and development of the catalytic path for the N-arylation of heterocycles by Buchwald with bromo and iodoarenes using copper based complexes generated great interest in industry. C–N bond formation via transition metal based catalysis currently is a subject of great interest and intensive research is being carried out to achieve useful organic transformations.[13,14] Copper catalysed cross-coupling reactions, and arylation reactions have been recognised as a reliable pathway for carbon-nitrogen bond formation process as copper is cheap, nontoxic and ease of loading of catalytic support. Taillefer et al. reported oxime type, and Schiff base ligands[15], and Ma et al. reported α- and β-amino acids as ligands for the effective N-arylation of N-heterocycles with aryl halides.[16] In those catalytic reactions mostly Cu(I) and Cu(II)

based complexes were used as homogeneous catalysts. Here, we have investigated the copper nanoparticle–graphene (G-Cu) composite as a heterogeneous catalyst for N- and O-arylation reactions. The work undertaken in this project work is mainly focused on the synthesis of copper nanoparticles ($Cu^0$) loaded graphene composite for cross-coupling reactions. Furthermore to make the whole system water-soluble, sulfonic groups have been introduced on the graphene sheet. The phase, surface structure as well as composition have been characterised using XRD, FESEM and EDAX. The catalytic activity of the developed catalyst has been explored towards N-arylation of pyrrole with iodobenzene.

# EXPERIMENTAL

**Material**

All chemicals are of reagent grade and used without further purification. Graphite powder was purchased from SD-Fine chemicals. Iodobenzene, pyrrole, sulfanilic acid were purchased from Spectrochem, India. Petroleum ether, ethyl acetate and other organic solvents were procured from Rankem, India.

**Characterization**

The phase formation and crystallographic state of the sample were studied by X-ray diffraction (XRD) analysis using Rikagu Japan/Ultima-IV) by Cu Kα radiation in 2θ ranging. The morphology of the catalyst was studied by scanning electron microscopy (HITACHI COM-S-4200). All NMR spectra were recorded on Bruker Avance III (400MHz for $^1$H NMR, 100MHz for $^{13}$C NMR) spectrometer; chemical shifts were expressed in ı units (ppm) relative to TMS signal as internal reference in CDCl$_3$ (7.28 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and bs (broad singlet).

**Synthesis of graphene oxide (GO):**

Graphene oxide was prepared from purified natural graphite powder according to the Hummer's method. In details, graphite powder (1.0 g), NaNO$_3$ (0.5 gm) and KMnO$_4$ (3.0 g), were slowly added to a concentrated H$_2$SO$_4$ solution (23 mL) within an ice bath. After removing the ice bath, the above mixture was intensely stirred at 35$^0$ C for 30 minutes. After the reaction was completed, deionised water ( 46 mL) was added to the above mixture while keeping the temperature at 98º C for 15 minutes, followed by reducing the temperature to 60º C with the addition of warm deionised water (140 mL) and H$_2$O$_2$ (30 % , 10 mL) while stirring continuously for further 2 hours. The obtained mixture was centrifuged to collect the solid product and washed with 4 wt % HCl solution 5 times and then with deionised water until the pH of the supernatant was neutral. Finally the material was dried to obtain a loose brown powder.

**Synthesis of Copper nanoparticle-reduced Graphene oxide (G-Cu) composite:**

About 120 mL of an aqueous graphene oxide (90 mg) solution was prepared having a graphene oxide concentration of 0.5-0.8 mg mL$^{-1}$. Next 10 mL of 0.006 (M) copper acetate (108 mg) were added under stirring condition. After one hour of stirring, 600 µL of hydrazine followed by the appearance of a black precipitate after 90 minutes. Heating was continued for 2 hours and then the precipitated Cu-G composite was washed with water, ethanol for several times and dried under vacuum for 3 h.
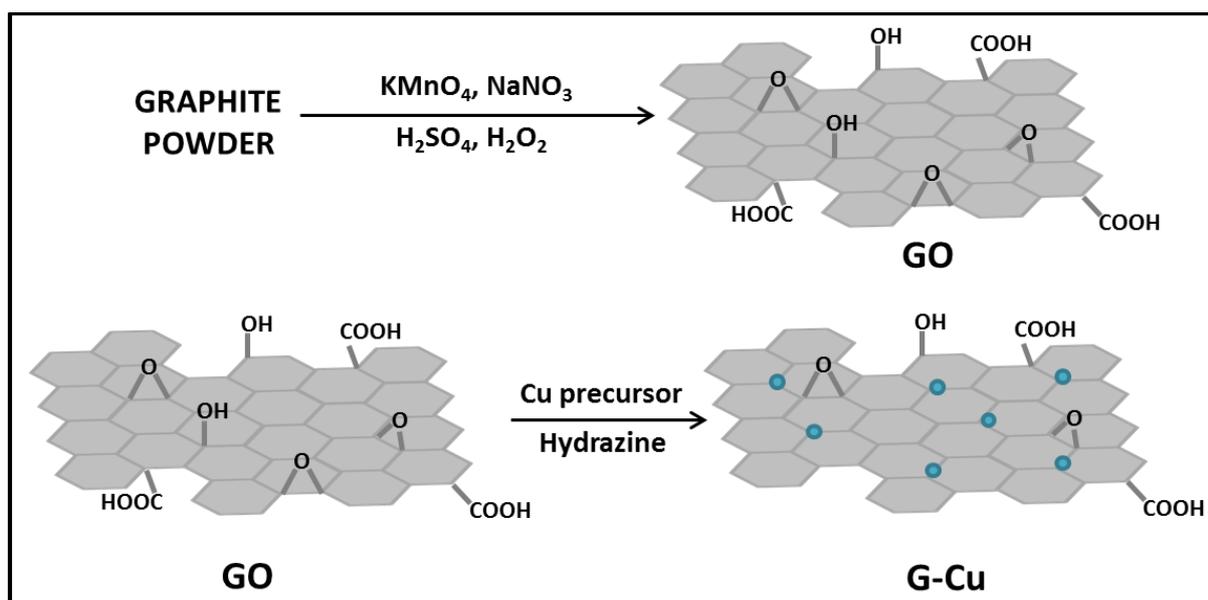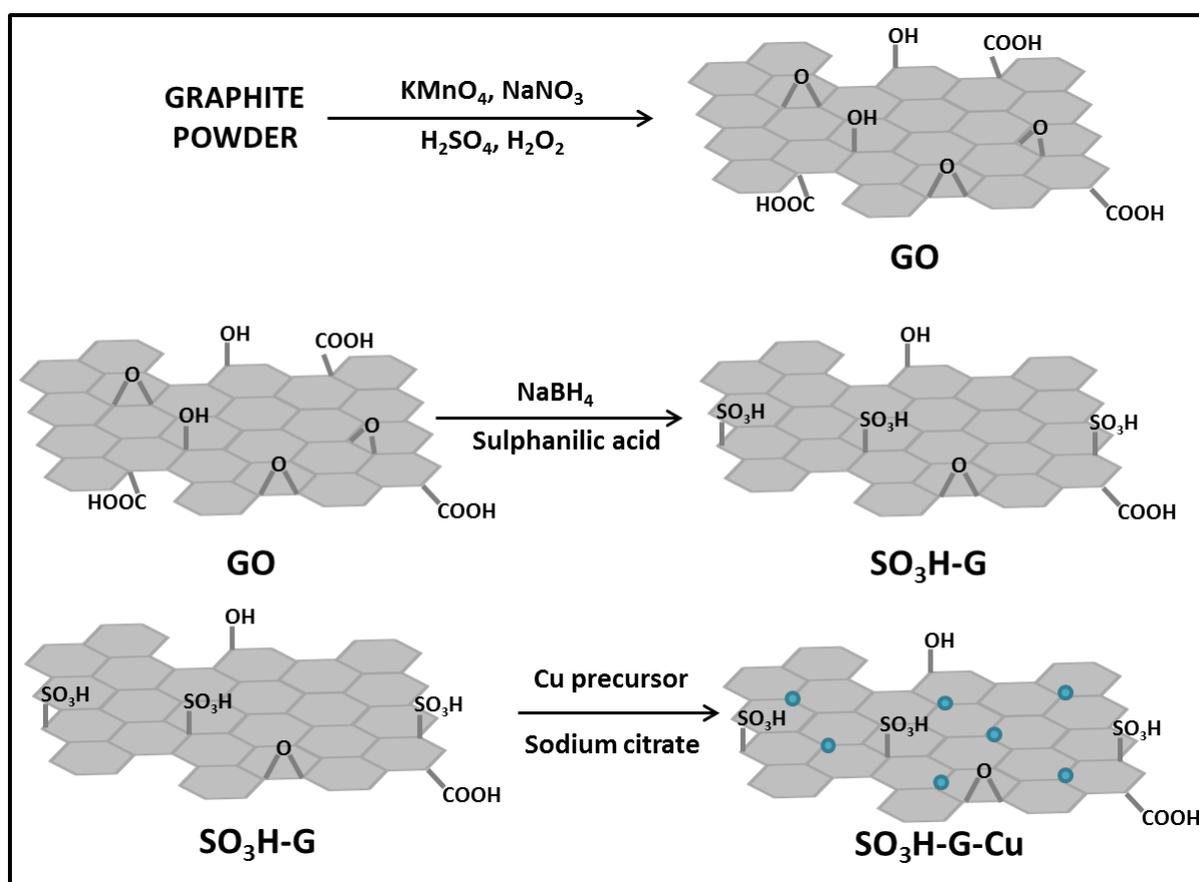


**Scheme 1. Preparation of Copper nanoparticles deposited reduced Graphene oxide**

**Synthesis of sulfonic groups decorated-reduced Graphene oxide (SO$_3$H-G):**

0.3 g graphene oxide in 600 mL water sonicated with an Electrosonic Scientific Probe Sonicator bath cleaner for 1 h, 3 g sodium borohydride in 50 mL water was added dropwise into the dispersion of graphene oxide after its pH was adjusted to 9-10 with 5 wt% sodium carbonate solution. The mixture was then kept at 80°C for 1h under constant stirring. After centrifuging and rinsing with water for several times, the partially reduced graphene oxide can be re-dispersed in 40mL water via mild sonication. The aryl diazonium salt used for sulfonation was prepared from the reaction of 210 mg sulfanilic acid and 90 mg sodium nitrite in 50 mL water and 2.4 g 1N HCl solution in an ice bath. The diazonium salt solution was added to the dispersion of partially reduced graphene oxide in an ice bath under stirring, and was kept in ice bath for 2 h. After centrifuging and rinsing with water for several times, sulfonated graphene oxide is re-dispersed in 800mL water.

**Synthesis of Copper nanoparticle deposited SO₃H-reduced Graphene oxide (SO₃H-G–Cu) composite:**

0.123 g copper (II) acetate was slowly added into the uniformly dispersed sulfonated graphene oxide in 800mL water, after stirring for 0.5 h, 2 g sodium citrate in 65 mL water was added under uniform sonication. The mixture was then kept at 95°C for 10 h under constant stirring. After centrifuging for 5 times and rinsing with water and ethanol for several times, the solid was further collected and dried at 50°C for 48 h.



**Scheme 2. Preparation of Copper nanoparticles deposited sulfonic acid decorated reduced Graphene oxide**

## CHARACTERIZATION

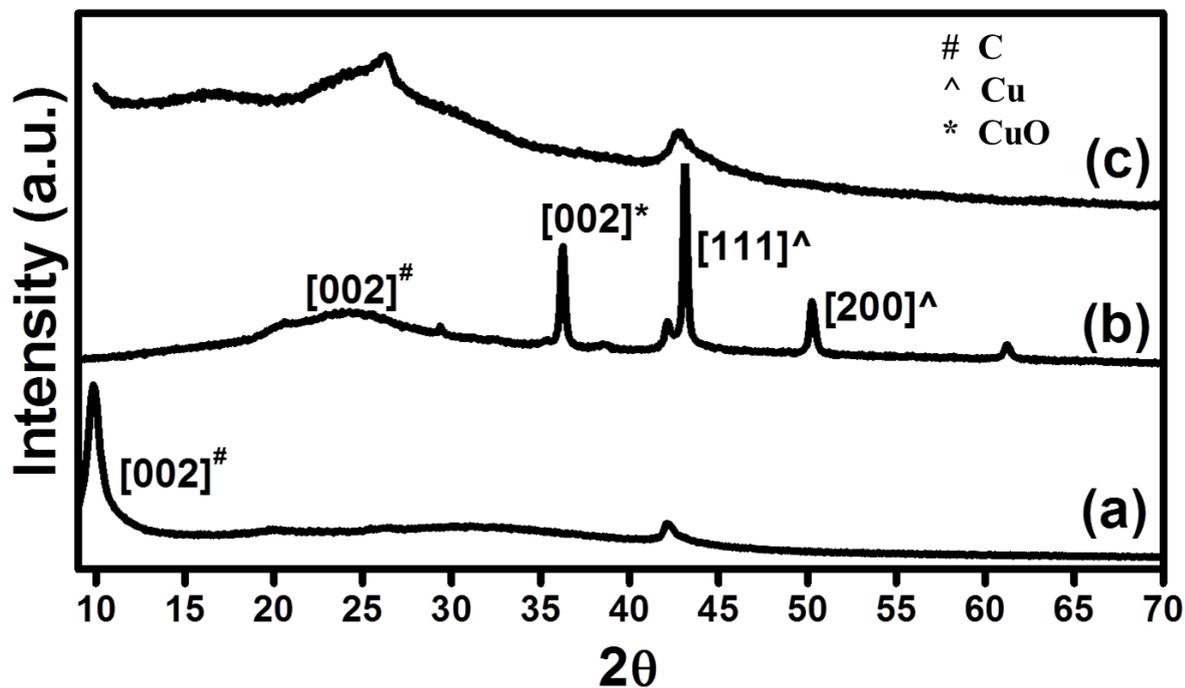**X-ray diffraction method (XRD):**



**Figure 1. XRD pattern of (a) GO, (b) G-Cu, (c) SO₃H-G–Cu.**

The phase composition diagram of the nanocomposite has been investigated from X-ray diffractometry. The mean size of the nanoparticles can be calculated from Scherer's equation

$$d = \frac{0.9\lambda}{\beta cos\theta}$$

The intense peaks of Cu-graphene nanocomposite had indicated that the copper nanoparticles have grown uniformly over graphene sheet. The XRD image is shown in figure 1. The interlayer distances of GO and G were confirmed using powder X-ray diffraction (XRD) patterns. The 2θ peak at 10.27° corresponds to the [002] plane of graphene oxide (GO), which indicates that the graphite was fully oxidized into GO. In contrast to the XRD pattern of the GO powder sample, the XRD pattern of the copper nanoparticles deposited reduced Graphene oxide (G-Cu) yielded only a new narrow peak at 24.36°, suggesting that the GO was reduced to graphene. The [111], [200] planes corresponding XRD pattern of the

deposited Cu nanoparticles can be indexed to the face-center cubic Cu (JCPDS 85-1326). The plane [002] in figure 2(b) shows the formation of copper oxide in case of Cu-G composite, whereas the absence of it in figure 2(c) confirms single phase deposition of copper nanoparticles in case of $SO_3H$-G–Cu composite.

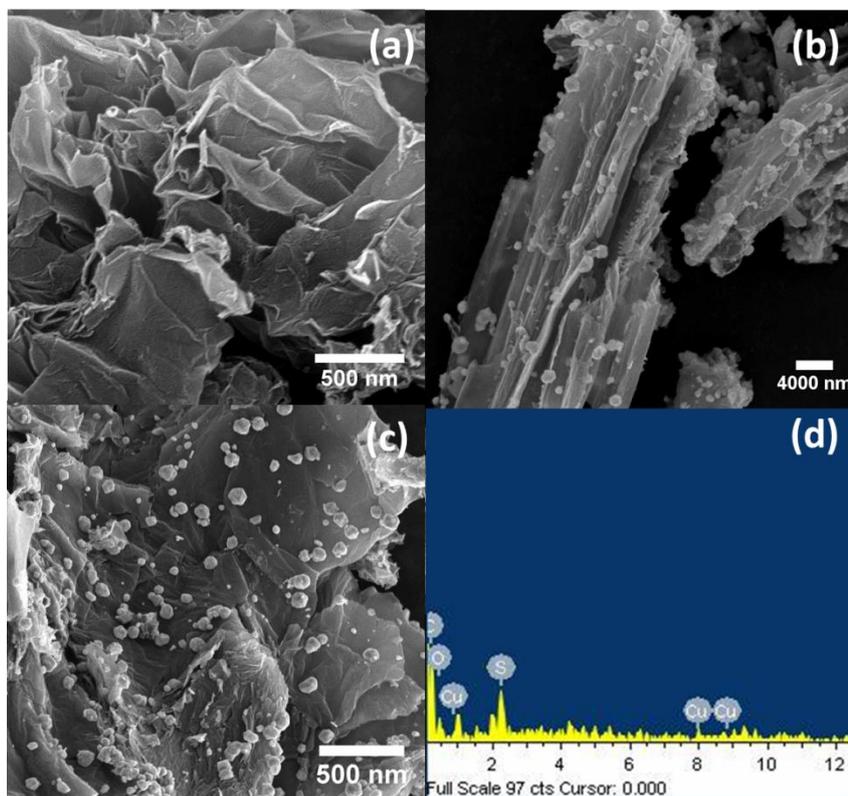**Field Emission Scanning electron microscopy (FESEM):**



**Figure 2. FESEM images of (a) GO, (b) $SO_3H$-G–Cu, (c) High resolution image of $SO_3H$-G –Cu (d) SEM-EDAX spectrum of $SO_3H$-G–Cu composite.**

The microstructure and the morphology of the nanocomposite has been showed in figure 2(b) and 2(c). From the FESEM images it could be clearly observed that the Cu nanoparticles were uniformly deposited over the graphene nanosheet. The sheet like morphology of graphene was also an advantage for catalytic activity which was clearly visible from the FESEM micrographs. The composition of the sample was determined from SEM-EDAX (Figure 2(d)). The elemental composition was found to be C, Cu, S and O which is in accordance with $SO_3H$-G–Cu.

# APPLICATION

N-arylation reaction is a useful method for the C–N bond formation between N–H heterocycles and aryl halides (Scheme 3). N-aryl heterocycles are very common in numerous natural products and in biologically active pharmaceuticals. The survey of the reaction conditions was conducted with iodobenzene and pyrrole as model arylating reactants.
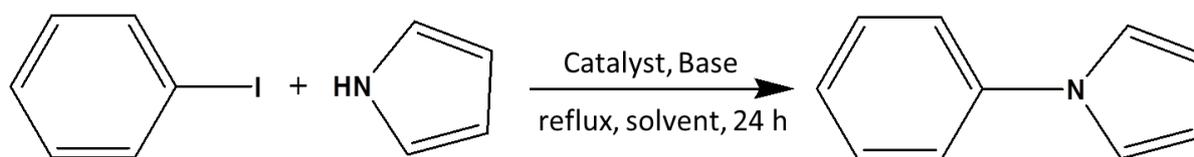


[Catalyst: G-Cu, SO$_3$H-G–Cu]

**Scheme 3. Cu–G composite catalyzed N-arylation of aryl iodide with pyrrole**

Among the various bases screened, $^t$BuOK resulted in product formation (Table 1 entries 1,5,8) while K$_2$CO$_3$, KOH and K$_3$PO$_4$ gave no product (Table 1 entries 2,3,6,7). It was earlier reported that N-arylation was more effective in polar organic solvents like DMF, NMP, acetonitrile etc. [17]

| Entry | Catalyst | Solvent | Base | Yield(%) |
|-------|----------|---------|------|----------|
| 1 | G-Cu | Dry DMF | $^t$BuOK | 81 |
| 2 | G-Cu | H$_2$O | K$_2$CO$_3$ | - |
| 3 | G-Cu | H$_2$O | KOH | - |
| 4 | G-Cu | H$_2$O | $^t$BuOK | - |
| 5 | G-Cu | EG:H$_2$O (1:1) | $^t$BuOK | 45 |
| 6 | G-Cu | EG | K$_3$PO$_4$ | - |
| 7 | SO$_3$H-G-Cu | EG:H$_2$O (1:1) | K$_2$CO$_3$ | - |
| 8 | SO$_3$H-G-Cu | EG:H$_2$O (1:1) | $^t$BuOK | 63 |

**Table 1.** [a]**Reaction conditions: Catalyst(G-Cu, SO$_3$H-G–Cu) (0.05 g), iodobenzene (1 mmol);pyrrole (1 mmol); Base (2 mmol); solvent (10 mL); 120°C, 24 h, N$_2$ atm.** [b]**Purification using column chromatography.** [c]**Product was identified by** [1]**H NMR spectral data with those reported in the literature.**

We thought of using $H_2O$ as a solvent as it is economic, green and easy to handle. However due to insolubility of organic reactants in water we used a mixture of ethylene glycol (EG) and water as solvent for the N-arylation. It was observed that ratio of 1:1 of EG: $H_2O$ solvent worked for G-Cu composite and $SO_3H$-G–Cu composite (Table 1 entries 5, 8). The reflux temperature was maintained at 120°C. This N-arylation was also found to be highly sensitive to the reaction temperature.

Development of an effective catalytic system for the coupling of pyrrole is satisfactory under the optimized conditions in this reaction. The results are summarized in Table 1. The N-arylation of pyrrole with aryl iodide proceeded smoothly to give the corresponding product in the polar solvent mixture (Table 1). No side products including hydrolysed products were obtained under these reaction conditions. In the hope of broadening the scope of the N-arylation protocol, we decided to check the efficiency of our catalyst system by using $SO_3H$-G–Cu composite instead of G-Cu composite (Table 1, entries 8).

## CONCLUSION

A water soluble graphene based composite with copper nanoparticles has been synthesized and used as catalyst for the N-arylation of pyrrole and iodobenzene. The composite shows excellent catalytic activity and selectivity in a mixture of polar solvents (Ethylene glycol: water).Comparison of the results obtained for our present catalytic system is provided in Table. This catalyst is air-stable, inexpensive and easy to prepare. Due to its well dispersion in aqueous medium the catalyst can be implied as a green approach towards the N-arylation reactions. Applications of this catalyst to other transformations are presently under study.

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