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Green synthesis of stable Cu(0) nanoparticles onto reduced graphene oxide nanosheets: a reusable catalyst for the synthesis of symmetrical biaryls from arylboronic acids under base-free conditions[†]

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Highly stable Cu(0) nanoparticles were synthesized on reduced graphene oxide (rGO) sheets using a cost-effective and green method. The synthesized Cu(0)-nanoparticle-rGO composites exhibit excellent catalytic activity for the synthesis of symmetrical biaryls from arylboronic acids under microwave irradiation. The reaction proceeds smoothly in base-free conditions with easy recovery and reuse of the catalyst. The methodology is compatible with various functional groups and provides an attractive protocol for the synthesis of symmetrical biaryls with very good yields. HRTEM, XPS and XRD analyses showed the catalyst to be recyclable. The Cu(0) nanoparticles are stable in the rGO nanosheets, and the particle size distribution and oxidation state of the Cu(0) nanoparticle remain the same after performing the chemical reaction.

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1. Introduction

Metal nanoparticles (NPs) have received considerable attention during the last two decades because of their unique properties and applications in different research areas.¹⁻⁵ Cu(0) nanoparticles are attractive and have received much attention because they are inexpensive and abundantly available, and can thus replace other noble metal NPs such as Ag, Au and Pt NPs. Oxidation of Cu(0) nanoparticles, however, makes it challenging to synthesize them.^{6,7} Several methods have been developed for the synthesis of Cu(0) nanoparticles during the last two decades, and an inert atmosphere is used during the synthesis and storage in most of the cases.⁸⁻¹⁶ Just a few methods have been reported for the synthesis of stable Cu(0) nanoparticles using graphene as a supporting material; hydrazine hydrate or NaBH4 or the vapour deposition technique at high temperatures was used for their synthesis.^{17,18} The development of composites of metal NPs and graphene have drawn considerable attention of researchers in the area of catalysis, but only a limited study of the catalysis of graphene-based composite materials has been performed.¹⁹⁻²² Among the various catalysts, a ligand-free heterogeneous Cu(0) catalyst has received considerable attention due to it being safe to handle, environmentally benign and recyclable. Only a few research groups have reported the synthesis of Cu(0)nanoparticle-graphene composite materials and their applications in organic synthesis.^{17,18,22} For example, Fakri et al. reported the synthesis of Cu(0) nanoparticles supported with reduced graphene oxide (rGO) and the use of this composite as a heterogeneous catalyst for the synthesis of formamides and amination of arylboronic acids.¹⁸ Mondal et al. reported the N-arylation of N-heterocycles with arylboronic acids and the O-arylation of phenols with aryl halides using Cu(0) nanoparticle-rGO heterogeneous catalysts. They found that the developed heterogeneous catalyst is easily recoverable and could be reused several times.¹⁷ However, in all the cases, Cu(II) oxide was formed as an unavoidable mixture with Cu(0) nanoparticles. Moreover, both research groups used hydrazine hydride and NaBH₄, which are toxic, as reducing agents. Therefore, the selective synthesis of Cu(0) nanoparticles, although desirable, is a challenge. The synthesis of stable Cu(0) nanoparticles and their catalytic applications are limited. The notable examples are the synthesis of Cu(0) nanoparticles on modified montmorillonite along with their application for "click" reactions and the synthesis of pure Cu(0) nanoparticles for the reduction of aromatic nitro compounds.^{23,24} Although, these catalysts can be reused



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several times, some of the Cu(0) is converted to CuO during the catalysis process.²³

Biaryls are an important class of organic compounds for both synthetic and medicinal chemistry.^{25–29} In synthetic chemistry they are used as a ligand in asymmetric synthesis³⁰ and widely used as an intermediate for the synthesis of perfumes, dyes and polymers. In medicinal chemistry, they are used as a drug and drug intermediates; for example, α -DDB was used as a leading hepatoprotective agent³¹ and Crisamicin A was found to be active against Gram-positive bacteria^{32,33} (Fig. 1).

Homocoupling of organoboron compounds is a potentially reliable method for the synthesis of symmetrical biaryls.³⁴⁻³⁶ Recently, many studies have been carried out on this topic, where palladium in the presence of a stoichiometric or excess amounts of base is used for this transformation, which precludes the use of base-sensitive compounds in the coupling process.³⁷⁻³⁹ Supported Au catalyst,⁴⁰⁻⁴² Mn(III),^{43,44} iodine,³⁵ Cu(II)- β -cyclodextrincomplex,⁴⁵ and other Cu(I) and Cu(II) salts⁴⁶⁻⁵⁰ are alternative catalysts/reagents for this transformation. Despite the potential utility of these catalysts/reagents, many of them are associated with several shortcomings such as long reaction time, harsh reaction conditions, low yields, occurrence of side products, and use of base and stoichiometric amount of metal salt, which produce an equivalent amount of waste. Therefore, the development of an efficient catalyst for the synthesis of symmetrical biaryls would be highly desirable.

In continuation of our research on the synthesis and catalytic applications of composites of metal NPs and rGO, herein, we report the green synthesis of stable Cu(0) nanoparticles on rGO nanosheets using ascorbic acid as an eco-friendly

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Crisamicin A α. Fig. 1 Examples of biologically active symmetrical biaryls.

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OH

C

reducing agent in aqueous medium, which could be used as reusable catalysts for the synthesis of symmetrical biaryls from arylboronic acids using the microwave irradiation technique. The use of a Cu(0)-nanoparticle-rGO composite as a catalyst for the synthesis of symmetrical biaryls has not, to the best of our knowledge, been previously reported.

2. Experimental

2.1. Materials and methods

Graphite powder (particle size <20 μ m, Sigma-Aldrich), sulfuric acid (AR grade, Qualigens, India), hydrochloric acid (AR grade, Qualigens, India), H₂O₂ (30%, Qualigens, India), potassium permanganate (>99%, E-Merck, India), ascorbic acid (99%, Fisher Scientific, India), Cu(CH₃COO)₂·H₂O (>99%, E-Merck, India) and all phenylboronic acids were supplied from Sigma-Aldrich, USA and used as received.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded with an IR Affinity-1, Shimadzu, Japan FTIR spectrophotometer from 4000-400 cm⁻¹. X-ray diffraction (XRD) analysis was performed with a scanning rate of 3 deg min⁻¹ and two theta values ranging from 5 to 100° using a Rigaku X-ray diffractometer (model: ULTIMA IV, Rigaku, Japan) with a Cu K α X-ray source (λ = 1.54056 Å) at a generator voltage of 40 kV and a generator current of 40 mA. Thermogravimetric analyses (TGA) of the samples were carried out using a TA-SDT (model: Q600DT, TA Instruments, USA) with the temperature raised at a rate of 5 °C per minute. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2011 electron microscope (Transmission Electron Microscope, Japan) operated at an accelerating voltage of 200 kV. All microwave (MW) reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor. Organic reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized first with ultraviolet light (254 nm) and then by immersion in solutions of *p*-anisaldehyde followed by heating. Flash column chromatography was performed with silica gel 60 (100-200 mesh). All NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer. Chemical shifts are



OMe

ÓМе

α-DDB

CO₂Me

CO₂Me

Scheme 1 Procedure for the synthesis of Cu(0) nanoparticles on rGO nanosheets.

reported on the δ scale (ppm) downfield from tetramethylsilane (δ = 0.0 ppm) using the residual solvent signal at δ = 7.26 ppm (1H) or δ = 77 ppm (¹³C) as an internal standard. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG Micro Tech ESCA 300° instrument at a pressure >1 × 10⁻⁹ Torr (pass energy: 50 eV, electron take off angle: 60° and the overall resolution: ~0.1 eV). Gas chromatography analyses were carried out by using a Chemito GC-8610, FID gas chromatograph fitted with a Porapak Q column (2 m × 1/8" O. D., SS), and data were analyzed using Winchrom GC data processing software.

2.2. Preparation of Cu(0)-nanoparticle-rGO composites





Fig. 2 Powder XRD diffractogram of Cu(0)-nanoparticle-rGO composites.



Fig. 3 FTIR spectra of GO and the Cu(0)-nanoparticle-rGO composite.

procedure. This procedure for GO is discussed in detail in our previous publication.⁵¹



Fig. 4 TGA curve of GO and the Cu(0)-nanoparticle-rGO composites.





Fig. 5 C1s XPS spectra of rGO nanosheets after deposition of Cu(0) nanoparticles (a); Cu 2p core level spectrum (b).

Cu(II) acetate monohydrate (0.8 g) was dissolved in water (10 mL) in a round-bottom flask. A GO-water suspension (20 mL of 0.0125 g mL⁻¹) was added to the above solution and stirred for 15 min. Finally, ascorbic acid (0.1 M, 10 mL)

was added dropwise to the reaction mixture, which was heated at 80 $^{\circ}$ C for 1 h. The color of the reaction mixture changed from brown to black due to simultaneous conversion of Cu(II) to Cu(0) and GO to rGO. The product was



Fig. 6 TEM images of Cu(0) nanoparticle on rGO nanosheets synthesized by ascorbic acid reduction process under thermal conditions: (a, b) HRTEM images with particle size distribution, (c-g) HRTEM images, (h) SAED image of the Cu(0) nanoparticle.

treated with H_2O_2 to remove excess ascorbic acid and finally the solid product was separated by centrifugation, washed with ethanol followed by water, and then dried in an air oven at 60 °C. The Cu(0)-nanoparticle-rGO composite catalyst was used for characterization and investigation of the catalysis.

2.3. Catalysis experiment

The Cu(0)-nanoparticle-rGO composites (50 mg) were dispersed in DMF (2 mL) in a reaction tube. Phenylboronic acid (1 mmol) was added and the resulting mixture was microwave irradiated at 360 W for 12–15 min. After completion of the reaction, the catalyst was recovered by simple filtration and the filtrate was poured into water. The organic product was extracted with ethyl acetate (3 × 10 mL). The combined organic fraction was dried over Na₂SO₄ and concentrated. The residue was purified by chromatography using silica gel (60–120 mesh) with hexane as eluent to afford the corresponding biaryls.

3. Results and discussion

The rGO-supported Cu(0) nanoparticles were synthesized using a simple one-pot method and ascorbic acid as an ecofriendly reducing agent at 80 °C in aqueous medium. The composite of Cu(0) nanoparticles and rGO was characterized by XRD, FTIR, XPS, TGA and HRTEM analyses. Previous work used toxic reducing agents such as NaBH₄ and hydrazine hydrate for the synthesis of this composite.^{17,18} In the current procedure, simultaneous reduction of both GO and Cu(II) salt takes place in the presence of ascorbic acid, finally yielding a powder form of the composite, which displays hydrophobic behavior in aqueous medium. The initial color of the homogeneous reaction mixture of GO and ascorbic acid was brown, and finally black precipitate was obtained after subjecting the mixture to a temperature of 80 °C for 1 h. The product is easily separable due to the hydrophobic nature of the heterogeneous catalyst. The hydrophobic nature of the Cu(0)nanoparticle-rGO composite indicates that the Cu(II) ions converted to Cu(0) and deposited on the rGO sheets, and simultaneously GO got reduced to graphene nanosheets. The procedure used to synthesize the composite is shown in Scheme 1.

3.1. Characterization of GO and Cu(0) nanoparticle-rGO composites

The complete characterization of the synthesized GO nanosheets from graphite powder was reported in one of our previous publications.⁵¹

The evidence for the formation of Cu(0) nanoparticles on rGO nanosheets was obtained by X-ray diffraction (XRD) analysis as shown in Fig. 2. The XRD pattern shows characteristic peaks at 2θ values of 43.30, 50.34, 74.01, 89.84 and 95.06° corresponding, respectively, to *d*-spacings value of 2.09, 1.81, 1.27, 1.09 and 1.04 Å, which in turn are assigned, respectively, to the (111), (200), (220), (311) and (222) indices of the

small face-centered cubic (fcc) lattice of the metallic Cu(0) nanoparticle. All the diffraction peak values along with the *d*-spacing values match those in JCPDS card no. 00-004-0836. The broad diffraction peak at a 2θ value of ~25.0° indicates the formation of the rGO nanosheets where the Cu(0) nanoparticles are deposited.^{52,53} Most importantly, there was no significant peak for Cu₂O and CuO in the composite of Cu(0) nanoparticles and rGO even after 2 months in the presence of air.¹⁸ The resistance of this composite to oxidation was investigated by exposing it to air under ambient conditions for more than two months, and then repeating the XRD experiment. The diffraction pattern obtained in this case was the same as that shown in Fig. 2, which was obtained on the first day. The rGO nanosheets play an important role in preventing the aerial oxidation of the Cu(0) nanoparticles.

The Cu(0) nanoparticles were also synthesized on the rGO nanosheets by an *ex situ* method. The rGO nanosheets were initially synthesized using ascorbic acid, and then the Cu(0) nanoparticles were incorporated on the rGO surfaces also using ascorbic acid. The XRD pattern (shown in Fig. S1 in ESI†) shows characteristic peaks at 2θ values of 43.40, 50.50, 74.14, 89.90 and 95.08, corresponding, respectively, to *d*-spacings of the Cu(0) nanoparticles at 2.08, 1.80, 1.28, 1.09 and 1.04 Å. This also indicates that the Cu(0) nanoparticles were deposited on the surfaces of the rGO nanosheets. It is clear from HRTEM images that the rGO nanosheets are folded and oriented in different directions, and it is assumed that Cu(0) nanoparticles are present inside the folded rGO sheets as well as along the basal planes and the edges of the sheets.

The FTIR spectra of GO and the Cu(0)-nanoparticle-rGO nanocomposite are shown in Fig. 3. The peaks at 1439 and 1224 cm⁻¹ of GO correspond to the vibration of carboxyl groups, and the prominent absorption bands observed at 3130, 1732, and 1052 cm⁻¹ are attributed to the stretching vibrations of O-H, C=O, and C-O-C of GO, respectively.⁵⁴ The FTIR bands found at 1585 cm⁻¹ and 1439 cm⁻¹ are due to stretching of the C=C bonds of the aromatic rings and the bending of phenolic C-O-H groups.⁵⁵ The band at 1224 cm⁻¹ is assigned to stretching of the C=O bond of the phenol. The

Table 1	Optimization	of reaction	conditions ^a

	•			
2 B(OH) ₂		Catalyst, Solvent MW, 360 W	→	
Entry	Solvent	Catalyst loading $mg mL^{-1}$	Time (min)	Yield ^b (%)
1	Water	28	14	42
2	DMSO	25	15	80
3	DMF	25	12	94
4	Toluene	30	14	54
5	Xylene	26	12	65
6	Dichloroethane	25	15	37
7	Ethanol	28	12	42
8	DMF	10	20	77
9	DMF	50	12	90

 a Reaction conditions: 1a (1.0 mmol), catalyst (10–50 mg mL $^{-1})$, solvent (2 mL), MW 360 W. b Isolated yield.

peak intensities of the oxygen-containing functional group in GO decrease after the formation of the Cu(0)-nanoparticlerGO composite materials. This observation suggests that the amounts of carbonyl, hydroxyl, epoxy and carboxyl groups in GO are substantially decreased after decoration with the Cu(0) nanoparticles.

Thermogravimetric analysis (TGA) shows that the conversion of GO to rGO and the formation of ${\rm Cu}(0)\text{-}nanoparticle-$

	1(a-m)	(OH) ₂ CuNPs-rGO, DMF MW, 360 W, 12 ⁻¹⁵ min	2(a-l)	
Entry	Boronic acid	Biphenyl	Time (min)	Yield ^b (%)
1	B(OH) ₂	\sim	12	94
2	$H_3C \longrightarrow B(OH)_2$		12	92
3	$H_3CO \longrightarrow B(OH)_2$		13	94
4	$Cl \longrightarrow B(OH)_2$		15	92
5	$Br \longrightarrow B(OH)_2$		15	92
6	OHC \longrightarrow B(OH) ₂	онс-С-сно	15	86
7	B(OH) ₂		12	94
8	$ \underbrace{ \sum_{i=1}^{NO_2} B(OH)_2 } $		15	94
9	Me ^S —B(OH) ₂	Me's - S' ^{Me}	12	94
10	B(OH) ₂		12	94
11			15	90
12	B(OH) ₂		12	94
13		21	15	90

^a Reaction conditions: 1a (1.0 mmol), CuNP-rGO (25 mg mL⁻¹), in DMF (2 mL), MW 360 W. ^b Isolated yield.

rGO composites occur simultaneously. The TGA curves of GO and of the composite are shown in Fig. 4. A major loss of weight of GO was observed at around 200 °C (37.72%), due to the pyrolysis of oxygen-containing functional groups. Upon deposition of Cu(0) nanoparticles onto rGO nanosheets, the weight loss in this region decreased from 37.72% to 13.97% due to the reduction of these oxygen-containing functional groups. In addition, the weight loss observed for the composite above 600 °C is due to the pyrolysis of the carbon skeleton of rGO nanosheets.⁵⁶

The X-ray photoelectron spectroscopy (XPS) technique was used to understand the chemical changes that occurred after deposition of the Cu(0) nanoparticles on the rGO nanosheets. The deconvoluted C1s XPS core level spectra of the composite of Cu(0) nanoparticles and rGO are shown in Fig. 5a. The XPS peaks at 284.29, 285.4, 286.5 and 287.5 eV are assigned to the C-C/C-H, C-C, C-O and C=O species, respectively. The total intensity of these peaks was decreased compared to that of the GO nanosheets. (Note that the C1s XPS core level spectrum of the GO was already reported in our previous publication.⁵³) This comparison indicates the removal of oxygen-containing functional groups after reduction with ascorbic acid. The appearance of the signals at 932.9 and 952.8 eV due to Cu 2P3/2 and Cu 2P5/2, respectively, indicates the formation of the Cu(0) nanoparticles on the rGO nanosheets (Fig. 5b).¹⁷ Moreover, there is a very weak signal at 934.35 eV, which is due to Cu(OH)2 from trace amounts of Cu(II) salt that ascorbic acid was not able to reduce. In our synthesis procedure, we did not take any precaution to prevent aerial oxidation of the Cu(0)-nanoparticlerGO composites. The synthesis of the Cu(0) nanoparticles on the rGO nanosheets was carried out in water, which is a universal solvent. Yet, we did not observe any major oxidation of the Cu(0) nanoparticles on the rGO nanosheets.

A high-resolution transmission electron microscope (HRTEM) was used to examine the morphology and structure of the Cu(0) nanoparticles deposited on the rGO nanosheets. Their HRTEM images and size distributions are shown in Fig. 6a-g and a selected area electron diffraction (SAED) image is shown in Fig. 6h. Fig. 6a-e shows that the Cu(0) nanoparticles are distributed on non-uniformly folded rGO sheets. The size distribution of the Cu(0) nanoparticles on the rGO nanosheets was analyzed by Image J software. The average size of the nanoparticles was found to be 12 ± 4.8 nm. Most of the Cu(0) nanoparticles are spherical and are well separated from each other. The average crystallite size of the Cu(0) nanoparticle was also determined by PDXL software and found to be 21 nm, which is close to the particle size indicated by the analysis of the TEM images. The crystal repeats of a single Cu(0) nanoparticle corresponding to the (111), (200) and (220) planes are clearly visible in the SAED image, which are also reflected in the XRD pattern. The presence of diffraction spots in the SAED image proves the crystalline nature of the Cu(0) nanoparticles on the rGO nanosheets (Fig. 6h). The fringe lattice of the Cu(0) nanoparticle corresponding to the (111) plane has a spacing of 0.21 nm, as shown in Fig. 6f (inset) and g.

Cu(0)-nanoparticle-rGO composite materials were also synthesized using hydrazine hydrate (details of the method used for this synthesis are provided in ESI[†]) and the morphology of this composite was analyzed using HRTEM (images shown in Fig. S2 in ESI[†]). These Cu(0) nanoparticles were observed to be agglomerated on the rGO nanosheets and the average size of the Cu(0) nanoparticle was found to be ~38-40 nm, which is bigger than the Cu(0) nanoparticle synthesized using ascorbic acid. Ascorbic acid is a weak reducing agent, which favors slow reduction and results in the formation of smaller particles and a more uniform distribution of Cu(0)nanoparticles on the rGO nanosheets compared to the Cu(0)nanoparticles synthesized using hydrazine hydrate. The role of ascorbic acid in our in situ method of synthesizing Cu(0) nanoparticles on rGO sheets is mainly to reduce the GO to rGO and Cu(II) to Cu(0) simultaneously.

3.2. Catalytic activity

Initially, we chose phenylboronic acid (1a) as the starting material to perform the optimization studies (Table 1). We examined the reaction with various solvents and catalyst loadings on the homocoupling reaction. Various organic solvents, including DMSO, DMF, toluene, and xylene, facilitated the coupling reaction with good yields. However, solvents such as ethanol and dichloroethane produced low yields. An excellent yield of the desired product was obtained in the presence of 25 mg mL⁻¹ of the catalyst when using 1 mmol of phenylboronic acid. The yield of product from the coupling reaction was low when the concentration of the catalyst was decreased from 25 to 10 mg mL⁻¹, but there was no remarkable change of the yield when increasing the concentration of catalyst from 25 to 50 mg mL⁻¹.

We investigated the scope of the base-free homocoupling reaction with respect to a variety of boronic acids. As shown in Table 2, these reactions, which took place under microwave irradiation, afforded excellent yields of the expected products regardless of the nature of boronic acid. The reaction conditions are notably compatible with a range of

Table 3 Comparative results for the synthesis of symmetrical biaryls			
Catalyst/copper salt	Reaction conditions	Yield (%)	
CuSO ₄ ·5H ₂ O	DMF/120 °C/12 h	28	
$Cu(OAc)_2 \cdot H_2O$	DMF/120 °C/12 h	58	
Cul	DMF/120 °C/12 h	62	
CuNPs-rGO	DMF/120 °C/12 h	92	
CuNPs-rGO	MW/360 W/12 min	94	



Scheme 2 Homocoupling of phenyl boronic acid under aerobic and anaerobic conditions.

functional groups such as methyl, aldehyde, ether, or nitro on the aryl ring. Remarkably, bromo and chloro groups remain intact, without forming other coupled products (Table 2,

94

2nd

Fig. 7 Recycling activity of the Cu(0)-nanoparticle-rGO composites.

Run

92

3rd

86

4th

94

Ist

100

80

60

20

0

% plai

entries 4 and 5). Interestingly, other popular boronic acid surrogates such as phenylboronic acid neopentylglycol ester



Catalytic cycle	Time (min)	Conversion of Ph-B(OH) ₂ ^{a} (%)	TOF^b , min ⁻¹
1st run	1	23.4	6.5
	4	34.7	2.4
	6	55	2.6
	10	56	1.5
	15	100	1.9
2nd run	1	19.89	5.5
	4	30	2.1
	6	64.5	2.9
	10	65.48	1.8
	15	100	1.9

^{*a*} Determined by GC. ^{*b*} TOF = (moles of phenylboronic acid consumed)/ (moles of Cu \times duration of the reaction). ^{*c*} Reaction condition is same as shown in Table 1.



Fig. 8 Characterization of the Cu(0)-nanoparticle-rGO catalyst after performing the reaction. (A) XRD pattern, (B) HRTEM images, (C, D) XPS analysis.

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Fig. 9 Rate of the original and re-used catalyst for homocoupling of phenylboronic acid.

(Table 2, entry 13) also proved to be a suitable substrate for the homocoupling reaction.

To compare the reaction conditions, homocoupling reactions of organoboron compounds were carried out by conventional heating using an oil bath at 120 °C. In addition, the catalytic performance of Cu(0)-nanoparticle-rGO was also compared with those of other Cu salts for the synthesis of symmetrical biaryls. The microwave heating using Cu(0)nanoparticle-rGO is effective with respect to time and yield. The results are summarized in Table 3.

At present, the exact mechanism of the homocoupling reaction is not known. However, two independent experiments have been done to investigate this mechanism. We carried out the homocoupling reaction of 1a independently in aerobic and anaerobic conditions in DMF (Scheme 2). To our surprise, the homocoupled product 2a was formed with a 75% yield under aerobic conditions whereas a trace amount of 2a was formed under anaerobic conditions. It appears that aerial oxygen plays some role in the coupling of arylboronic acid.

3.3. Reusability of the catalyst

The reusability and long lifetime of a catalyst are important parameters for the chemical industry. The reusability and activity of the prepared Cu(0)-nanoparticle-rGO catalyst was also investigated after the completion of the reaction. The catalyst was recovered by simple filtration and washed two or three times with water followed by acetone and finally dried in an air oven. The results shown in Fig. 7 indicate that the catalyst can be re-used three to four times without significant loss of its activity. The catalyst was again characterized by XRD, TEM and XPS after performing the homocoupling reaction of phenylboronic acids, as shown in Fig. 8. The XRD pattern (Fig. 8A) of the Cu(0) nanoparticle after performing the catalytic reaction clearly demonstrates that the Cu(0)nanoparticle remains in the same oxidation state without forming CuO or Cu₂O. We also observed from the HRTEM images (Fig. 8B) that, after performing the catalytic reaction, there is no change in the morphology and shape of the Cu(0)nanoparticles on the rGO nanosheets, and they remain well distributed on the rGO nanosheets. XPS analysis confirmed that the oxidation state of the Cu(0) nanoparticle on the rGO surface remains same after performing the catalyzing the reactions (Fig. 8C, D).

To understand the reusability of the catalyst, we investigated the rate of the phenylboronic acid homocoupling reaction in two consecutive operation cycles. The percentage conversion of phenylboronic acid to biphenyl at different time intervals is shown in Table 4. As shown in Fig. 9, the reaction rate (TOF) in the second run was slightly lower than that in the first run of the Cu(0)-nanoparticle-rGO catalyst at the start of the reaction (0 to 4 min). After 4 min, the rate of the reaction for the re-used catalyst (2nd run) slightly increased and these parameters stabilized after reaching at 15 min with 100% conversion.

4. Conclusion

In conclusion, we have reported the green synthesis of stable Cu(0) nanoparticles on rGO sheets and characterized them by IR, TGA, XRD, HRTEM and XPS analyses. The catalyst was successfully utilized for the homocoupling of various substituted arylboronic acids. The synthesized Cu(0) nanoparticles remain in the zero oxidation state even after performing the catalytic reaction. The catalyst is efficient, easily recoverable and reusable another three to four times without losing its activity. This work reveals a new procedure to synthesize symmetrical biaryls in a relatively inexpensive and environmentally friendly manner.

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