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An effective and environment-friendly system for Cu NPs@RGOcatalyzed C-C homocoupling of aryl halides or arylboronic acids in ionic liquids under microwave irradiation

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As an outstanding mesh catalyst support, reduced graphene oxide (RGO) has attracted enormous attention in recent years. Cu nanoparticles-RGO (Cu NPs@RGO) as a green catalyst was prepared through a green reduction method by ascorbic acid in N-methyl-2-pyrrolidone. The structure of prepared Cu NPs@RGO was characterized. The catalytic activity of Cu NPs@RGO was estimated. A green and efficient method for synthesizing symmetrical biaryl compounds was developed by Cu NPs@RGO-catalyzed Ullmann homocoupling of aryl halides or arylboronic acids in ionic liquids under microwave (MW) irradiation. The catalytic system could be recycled five times with slight loss of activity. Through this method, nine kinds of biaryls were prepared by homocoupling reaction of the corresponding aryl iodides, aryl bromides, aryl chlorides and aryl boronic acids in moderate to good yields.

Introduction

Reduced graphene oxide (RGO) is a kind of two-dimensional planar structure consisting of carbon atoms that using sp² hybrid orbitals.¹⁻³ Graphene as a novel nanocomposite has attracted a high concern in the field of catalysts due to powerful specific surface area. Recently, a large number of reported that graphene supported papers metals nanoparticles (NPs) has been used⁴⁻⁷ as catalysts. Cu NPs have received much attention because copper is cheap⁸ and abundantly available. Simultaneously, they can substitute other precious metal NPs such as Ag, Pd and Au. However, Cu NPs are easily oxidized to CuO in air.⁹⁻¹⁰ In recent reports,¹¹⁻¹³ it is found that the RGO can effectively avoid the oxidation of Cu(I) and Cu(0) NPs in air because of its high delocalized electron characteristic.Obviously, stable Cu NPs@RGO and Cu₂O NPs@RGO catalysts have great development prospects. The usual methods for preparing Cu NPs@RGO are to reduce Cu(II) by using hydrazine hydrate or NaBH_{4.}¹⁴⁻¹⁶ However, there are some problems with these methods that need to be improved such as long reaction time, environmental pollution and so on. It is necessary to develop a green and efficient method for preparing the catalyst.

Biphenyl compounds are important organic intermediates in the field of organic synthesis. Suzuki reaction and Ullman coupling are the main methods for the synthesis of this compounds.¹⁷⁻²²The reactions often need some expensive ligands²⁰ and harmful solvents for good yield. Heck and Sonogashira coupling reactions are also important methods for the synthesis of biaryls. Recently, the Pd NPs@RGO catalysts were applied to these reactions.²³⁻²⁵ However, Palladium as catalyst is relatively expensive. Therefore, it is necessary to develop an economical, green and efficient method for preparing these compounds, and to seek or prepare highly efficient and stable catalyst. Copper as a low-cost metal has a good performance in organic reactions. As a heterogeneous catalyst, copper nanocatalysts have good prospects. Some methods for the synthesis of biphenyl compounds were reported about reaction solvents and catalysts such as alloy nanoclusters and reduced graphene oxide supported metal nanoparticles. In recent years, ionic liquids as a green solvent were reported to be used in the reactions.²⁶⁻²⁸ Raghu Nath Dhital et al.²⁹ described the catalytic activity of Au/Pd alloy nanoclusters for Ullmann coupling of aryl chloride compounds at low temperature. Minoo Dabiri et al.30 reported the synthesis and application of Au/Fe₃O₄/s-G nanoparticles to prepare symmetrical biaryls in the water. Najrul Hussain et al.⁷ reported the synthesis of symmetrical biaryls from arylboronic acids using Cu NPs@RGO as catalysts under microwave conditions. However, these methods have certain degree of limitation and defect in the cost and environmental protection.

In our past work, we found that ionic liquid²⁸ and Pd@PdO–NDG³¹ exhibited good catalytic activities for Suzuki

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cross-coupling of aryl bromides with arylboronic acid to form asymmetric biphenyl compounds. Here, the aim of our study is to synthesize an efficient catalyst using a low-cost copper and to catalyze coupling reaction in ionic liquids. Cu NPs@RGO nanocomposites were efficiently synthesized by using ascorbic acid as reducing agent in N-methyl-2-pyrrolidone and used as catalyst to synthesize symmetrical biphenyls by Ullmann homocoupling reaction of aryl halides and arylboronic acids in ionic liquid under microwave irradiation. Ionic liquids as green solvents not only meet the requirement of green chemistry, but also can effectively enhance the reaction yields. The catalytic system can be suitable for wide substrates including aryl halides and arylboronic acids. Furthermore the catalytic system has the advantages of high efficiency, economization, green environmental protection and recyclability and so on. Moreover, the catalyst is cheap, recyclable and easy to prepare.

Experimental section

General Information

lonic liquids including 1-Butyl-3-methylpyridinium bis(trifluormethylsulfonyl)imide ([BMPy][Tf₂N]), 1-Butyl-3-Methylpyridinium hexafluorophosphate ([BMPy][PF₆]) and 1-butyl-3methylimidazolium bis(trifluoromethyl)sulfonylimide ([BMIM] [Tf₂N]) were purchased from Nowe Wuhu Chemical Technology Co., Ltd. Graphite powder was purchased from Qingdao Tianyuan Company. All of the chemicals were purchased from Aladdin, Alfa, Kermel Chemical Company and used without purification.

The structure of catalyst was observed by high-resolution transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. X-ray diffraction (XRD) were characterized by D/MAX-III-B-40 KV X-ray power diffraction (Cu-K\alpha radiation, λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MK II with an Mg K\alpha (1253.6 eV) achromatic X-ray source. Infrared spectroscopy (IR) was measured by SP-100 Fourier transform infrared spectroscopy. Raman spectra were recorded using a Renishaw inVia spectrometer with an excitation laser of 532 nm in wave length. Melting points were measured on a digital melting point apparatus without correction.

Synthesis of the Cu NPs@RGO composites

Graphene oxide was synthesized from flake graphite through improved Hummer's method.³² Cu NPs@RGO hybrids with 10wt% Cu contents were prepared through a reduction method. A mixture of GO 100 mg and copper sulfate 25 mg in 75 mL of N-methyl-2-pyrrolidone was treated under sonication for 1 hour. The mixture's pH was adjusted to 10 by NaOH solution. After stirring for 30 minutes, ascorbic acid 120 mg was slowly added into the mixture and heated to 90 $^{\circ}$ C for 2 hours. Finally, the mixture became dark suspension and was filtered, and the obtained solids were washed with deionized water and absolute ethanol, and dried in a vacuum oven at 50 $^{\circ}$ C for 16 hours. According to percentage mass, different contents of copper catalysts (5wt%, 10wt%, 15wt%Cu NPs@RGO) were prepared. The weight content of copper metal element of the catalysts could be tested by EDXRF. The test results were consistent with the theoretical ratio.

Cu NPs@RGO catalyze the Ullmann homocoupling reaction

According to the experimental comparison, we found that Cu NPs@RGO have a good catalytic activity for Ullmann homocoupling reaction in ionic liquid. In a typical procedure, aryl halides or arylboronic acids (1 mmol) and Cu NPs@RGO (10% mmol Cu content) were dispersed in 3 mL of $[BMPy][Tf_2N]/H_2O(2:1)$ under sonication for 30 minutes. Then, the reaction system was irradiated under microwave at 70-90 W for 30 minutes. After adding 10 mL water into the reaction mixture, the mixture was extracted by ethyl acetate three times. The organic phase was dried over Na₂SO₄ and concentrated by a rotary evaporator. The crude products were purified by chromatography using silica gel with petroleum ether/ethyl acetate as the eluent to get the biphenyl compounds. In addition, after extraction residue mixture was distilled to remove 10 mL water, the residue mixture as the catalytic system was recycled.



X=I, Br, CI, B(OH)₂

Scheme 1 Synthesis of Cu NPs@RGO and catalytic process.

Results and discussion

Characterization of the Cu NPs@RGO catalyst

Cu NPs@RGO catalysts were characterized by fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

TEM images and XRD profile of Cu NPs@RGO catalyst were shown in Fig. 1. The characteristics of graphene fold could be clearly seen in Fig. 1a and copper nanoparticles were evenly dispersed on the surface of graphene (Fig. 1b). The particle size distribution of Cu NPs@RGO catalyst was counted (Fig. 1c). The average size of the copper particles was about 8 nm, which might be beneficial to enhance the catalyst activity because of the large specific surface area. The phase structure and purity of Cu NPs@RGO were characterized by XRD in the range of 15–80° (Fig. 1d). The diffraction peaks at 43.2°, 50.3°

and 74.1° of Cu NPs@RGO nanocomposites could be indexed to (111), (200) and (220) crystal planes of cubic Cu crystal(JCPDS 04-0836),^{8.33} respectively. Meanwhile appearance of a weak peak at around 25° indicated that GO were successfully reduced to RGO during the preparation of Cu NPs@RGO catalyst. In addition, we found that the catalyst could be stored in the air for at least one month.

The average size of Cu particles can be estimated by the Scherrer equation:

$d=0.9\lambda/\beta_{1/2}\cos\theta$

d is the average particle size (nm), λ is the wavelength of the X-ray used (0.15406 nm), $\beta_{1/2}$ is the width of the diffraction peak at half height in radians and θ is the angle at the position of the peak maximum.⁴ The calculated average particle size of copper supported on graphene is 18 nm, which is similar with the TEM results.



Fig. 1 (a,b) TEM images of the Cu nanoparticles on RGO nanosheets. (c) Particle size distribution of Cu NPs@RGO catalyst. (d) XRD profile of the Cu NPs@RGO catalyst.

XPS profile, FTIR and Raman spectra of the Cu NPs@RGO catalyst were shown in Fig. 2. The binding energies of Cu $2p_{1/2}$ at 952.7 eV and Cu $2p_{3/2}$ eV at 932.7 eV indicated the presence of Cu⁰ state, and confirmed that copper was supported on graphene sheet as the metallic phase^{11,12} in Fig. 2a. The existence of metallic Cu was also supported by XPS profile. The deconvoluted C1s XPS peaks at 284.6, 285.5, 286.5 and 287.6 eV corresponding to C–C/C–H, C–C, C–O and C=O species, respectively (Fig. 2b). This comparison indicated the reduction of GO nanosheets to RGO nanosheets.⁷

GO and Cu NPs@RGO were characterized by FTIR analysis as shown in Fig. 2c. In the spectrum of GO, the strong peaks around 3401 cm⁻¹ owing to O-H stretching vibrations of the absorbed water molecules.¹⁵ The C=C and C=O stretching vibrations were clear at near 1623 and 1738 cm⁻¹ in the GO materials. Moreover, the bands at 1206 and 1094 cm⁻¹ were associated with the O–H vibration in carboxyl acid and the deformation of the C–O band respectively. Compared with the spectrum of GO, the disappearance of C=O, C–OH and C–O in the spectrum of Cu NPs@RGO showed that the GO was reduced during preparing the catalyst.

The Raman spectra of Cu NPs@RGO and GO are shown in Fig. 2d. The D-bands and G-bands were clearly found in 1368 and 1600 cm⁻¹. The D band arised from edges, other structural defects in the hexagonal sp² carbon network or the finite particle-size effect, while the G band arised from E_{2g} phonon of sp² carbon pairs in both rings and chains.¹⁵ Compared to the spectrum of graphene oxide, the D to G peak intensity ratio (I_D/I_G) of Cu NPs@RGO was increased from 0.82 to 1.01.³⁴⁻³⁵ The relative changes of the I_D/I_G affirmed the reduction of graphene oxide.



Fig. 2 (a, b) XPS profile of the Cu NPs@RGO catalyst, (c) FTIR spectra of GO and the Cu NPs@RGO composite. (d) Raman spectra of Cu NPs@RGO and GO.

Optimization of the conditions of Cu NPs@RGO-catalyzed Ullmann homocoupling

The Ullmann reaction is a convenient method for the symmetrical biaryl compounds by C-C bond formation from aryl halides and arylboronic acids. Initially, iodobenzene was used as the starting material to optimize the reaction conditions of the Ullmann homocoupling by screening catalysts, solvents and reaction time. The results were summarized in Table 1. Firstly, the reaction solvents were screened. According to the experimental results, we found that the ionic liquids were better for the reaction. And then we found that the mass ratio 2:1 of [BMPy][Tf₂N]/H₂O as the solvent was able to improve the Ullmann homocoupling reaction to give a 97% yield by contrast with other solvent systems (Entries 1-9 in Table 1). Compared with the different reaction time, 30 minutes under the microwave irradiate was found to be the optimum reaction time (Entries 8 and 10-11 in Table 1). Meanwhile we found that the yield of 80% was obtained without microwave irradiation for 48 hours under 130 ^oC (Entry 8). Compared with the different molar ratio of

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catalyst, Cu NPs@RGO (10% mmol Cu content) under the microwave irradiate was found to be the optimum reaction catalyst dosage (Entries 8 and 12-13 in Table 1). Finally, compared with different catalysts, we found that Cu NPs@RGO catalyst exhibited high catalytic activity (Entries 8 and 14-16 in Table 1). In addition, Cu NPs@RGO was easier to separate than other catalysts.

corresponding symmetrical biaryls in excess 90% yields. Meanwhile, aryl bromides also got good yields in excess 76%. It was worth the excitement that aryl chlorides were obtained in approximate moderate yields.

Table 2 Substrate scope of Cu NPs@RGO-catalyzed Ullmann homocoupling^a

R Cu NPs@RGO [BMPy][Tf2N]/H2O MW R R

Table 1 Optimization of the reaction conditions^a

	x	Catalyst, Solvent MWV (70-90w)			Entry	R	X	Yield [°] (%)	Found; Reported ^b
Entry	X=I, B(OH) ₂ Catalyst (mmol%) ^b	Solvent (mass ratio)	Time(min)	Yield ^c (%)	1	н	I Br CI B(OH) ₂	97 87 48 94	68-71; 67-69 ¹⁷
1	Cu NPs@RGO (10)	Water	30	24/36	-		I	92	
2		DMSO	30	63/69	2	4-NO ₂	Br	86	
з		DME	30	68/73	-		Cl	54	235-238; 237-239 ¹⁸
5	CUNPS@RGO (10)		30	36/75			B(OH) ₂	93	
4	Cu NPs@RGO (10)	[BMPy][PF ₆]	30	/6//5	3	4-CHO	I	91	
5	Cu NPs@RGO (10)	[BMPy][Tf ₂ N]	30	84/89			Br	/8	148-150; 148-149 ⁷
6	Cu NPs@RGO (10)	[BMIM][Tf ₂ N]	30	79/76				37	
7	Cu NPs@RGO (10)	[BMPy][Tf ₂ N]/H ₂ O(3:1)	30	86/84			B(011)2	95	
8		[BMPv][Tf ₂ N]/H ₂ O(2·1)	30	97/94 80 ^d		4-OCH₃	Br	81	
0		[BMDy][Tf N]/H O(1:1)	20	27/21/00 77/00	4		Cl	45	172-174; 171-175 ⁷
9	Cu NPs@RGO (10)	[BIVIPY][112N]/H2O(1.1)	50	11/82			B(OH) ₂	94	
10	Cu NPs@RGO (10)	[BMPy][Tf ₂ N]/H ₂ O(2:1)	20	82/75		4-CH₃	I	90	
11	Cu NPs@RGO (10)	[BMPy][Tf ₂ N]/H ₂ O(2:1)	40	93/90	5		Br	79	-
12	Cu NPs@RGO (5)	[BMPy][Tf ₂ N]/H ₂ O(2:1)	30	80/72			Cl	36	123-124; 123-125 7
13		[BMPv][Tf ₂ N]/H ₂ O(2:1)	30	96/94			B(OH)₂	92	
14	Cu (10)	[PMDy][Tf N]/H O(2:1)	20	27/10	6	4-CN	l Dr	93	
14	Cu (10)		50	27/19			C	65 //1	234-236-234-237 18
15	Cul (10)	[BMPy][Tf ₂ N]/H ₂ O(2:1)	30	42/46			B(OH)₂	92	234 230, 234 237
16	CuSO ₄ (10)	[BMPy][Tf ₂ N]/H ₂ O(2:1)	30	16/9				96	
^a The reactions conditions: iodobenzene or phenylboronic acids					- 7	2 NO	Br	91	
(1mmol), 3 mL of solvent and catalyst under a microwave irradiation at						2-INU2	Cl	59	119-123; 120-122 ¹⁷
$70-90 \text{ W}^{\text{b}}$ The molar ratio of catalyst (Cu content) ^c loolated yields after							B(OH) ₂	95	
vo so w. The molar ratio of catalyst (ed content). Isolated yields after							I.	90	

(1mmol), 3 mL of solvent and catalyst under a microwave irradiation at 70-90 W. ^bThe molar ratio of catalyst (Cu content). ^cIsolated yields after silica gel column chromatography. The yield of the iodobenzene in front and the yield of the phenylboronic acid in the back. ^dThe yield without microwave irradiation under 130 ^oC for 48 hours.

According to the above experimental results, optimized homocoupling reaction conditions are aryl halides (1 mmol) as substrates, Cu NPs@RGO (10% mmol Cu content) as the catalyst, [BMPy][Tf₂N]/H₂O=2:1 as the solvent under MW irradiation at 70-90 W for 30 minutes. Meanwhile, the catalytic system can effectively catalyze Ullmann C-C homocoupling of arylboronic acids, and the reaction have a good yield. Interestingly, the reaction can smoothly proceed under the condition of base-free with easy recovery and reuse of the catalyst.

Catalytic activities of Cu NPs@RGO catalyzed system

Applying to above optimized reaction system, different arylboronic acids and aryl halides including aryl iodides, aryl bromides and aryl chlorides were used as the substrates to explore the Ullmann homocoupling reaction. The experimental results were summarized in Table 2. Aryl iodides and arylboronic acids were successfully able to give the ^aThe reactions were conducted in a microwave irradiated at 70-90 W for 30 minutes using aryl halides or arylboronic acids (1 mmol), 3 mL of $[BMPy][Tf_2N]/H_2O$ (2:1) and Cu NPs@RGO(10% mmol Cu content). ^bThe values reported in the literatures.^cIsolated yields after silica gel column chromatography

76

39

91

92 80

42

90

82-83; 82-83 21

131-132; 130-132 21

Recyclability of Cu NPs@RGO catalyzed system

Br

CI

Br

CI

B(OH)₂

B(OH)₂

4-CF₃

3,4-Dimethoxy

8

9

To study the recyclability of the catalytic system, the catalytic system of iodobenzene was monitored for five successive rounds. In the Fig. 3a, we found that the reaction activity was slightly decreased in successive. The catalysts after five rounds were analyzed by XRD and TEM. The XRD of the recovered catalyst could clearly show peaks corresponding to the metallic Cu NPs without turning into CuO or Cu₂O in the Fig. 3b. There

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was no obvious change in the morphology and aggregation of the Cu nanoparticles in the Fig. 3c and Fig. 3d. Thus, the recovered catalyst and ionic liquids could effectively catalyze

the Ullmann homocoupling and exhibit high catalytic activity. Fig.3 (a) the yields of catalytic system recycled. (b) XRD profile after 5round test. (c,d) TEM image of the catalyst and the size distribution of nanoparticles after 5-round.

Conclusions

In summary, Cu NPs@RGO as an efficient catalyst was prepared by a green reduction method to make copper nanoparticles support on the surface of graphene. The average size of the copper nanoparticles is about 8 nm. Cu NPs@RGO can effectively catalyze Ullmann C-C homocoupling of aryl halides and arylboronic acids under microwave irradiation in green solvent ionic liquid, and the catalytic system could be recycled five times with slight loss of activity. Through this method, not only aryl iodides and arylboronic acid were successfully catalyzed in good yields, but also aryl bromides and aryl chlorides were obtained in approximate moderate yields. Therefore, this research work provided a green and efficient catalytic method for synthesis of symmetrical biaryl compounds.

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An effective and environment-friendly system for Cu

NPs@RGO-catalyzed C-C homocoupling of aryl halides or

arylboronic acids in ionic liquids under microwave irradiation

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Cu NPs@RGO as an efficient catalyst was prepared by a green reduction method to make copper nanoparticles support on the surface of graphene. Cu NPs@RGO can effectively catalyze Ullmann C–C homocoupling of aryl halides and arylboronic acids under microwave irradiation in green solvent ionic liquid, and the catalytic system could be recycled five times with slight loss of activity. Through this method, not only aryl iodides and arylboronic acid were successfully catalyzed in good yields, but also aryl bromides and aryl chlorides were obtained in approximate moderate yields.