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## Synthesis and Characterization of 1, 3-diamino-graphene as a Heterogeneous Ligand for CuI-catalyzed C-N Coupling Reaction †

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1, 3-diamino-graphene (NH<sub>2</sub>-G-NH<sub>2</sub>) materials were synthesized by a simple chemical method. The as-prepared materials were characterized by FT-IR, TG, XRD, XPS, and SEM measurements. The results revealed that 1, 3-diamino has been successfully grafted on the graphene and can immobilize CuI by coordination interaction. The NH<sub>2</sub>-G-NH<sub>2</sub> materials can be used as heterogeneous ligands for CuI catalyzed C-N coupling reactions, and the desired products were obtained with good yields. The reaction system is much smoother at lower temperature compared with other previous reports. Additionally, the new method can easily realize the purification of products and recyclability of catalysts.

### Introduction

Graphene, which has a two dimensional carbon plane with a thickness of one atom, attracted extensive attention in catalysis fields such as photochemistry, electrochemistry and organic catalysis for the past few years.<sup>1-5</sup> Graphene oxide (GO) is an oxidized form of graphene, which holds rich hydroxyl, epoxy, carbonyl and carboxyl groups on its basal planes and edges.<sup>6</sup> Hence, these defective structures are favourable for chemical adjustment of graphene. The obtained functionalized graphene materials commonly hold superior performance than unmodified graphene, including electrical conductivities, mechanical performance, thermal stability, and dispersibility. Many applications of functionalized graphene have been explored based on these properties, such as sensors<sup>7</sup>, carrier materials for drug<sup>8</sup> and catalysts<sup>9</sup>. Especially, amino-functionalized graphene materials as solid base catalysts<sup>10,11</sup> or supports<sup>12</sup> have potential values which can be very promising substitutes for heterogeneous catalysts. Amino can be grafted on graphene via amino-silanes<sup>12,13</sup> or n-BuLi followed by an electrophilic substitution with bromotriethylamine<sup>10</sup>. Diamine is usually used as effective ligand in metal catalysis. Especially, 1, 3-Diamine can be used as chelating ligand<sup>14,15</sup> or key reagent for forming di-schiff base<sup>16,17</sup>. However, to our best knowledge, few reports exist about synthesis of 1, 3-diamino-graphene. Although, Ahmad shaabani and Mojtaba Mahyari reported a protocol to prepare 1, 3-diamino functionalized graphene oxide: firstly, malononitrile functionalized graphene oxide was synthesized via GO and malononitrile, and then malononitrile functionalized graphene oxide was reduced by using CoCl<sub>2</sub>·6H<sub>2</sub>O and NaBH<sub>4</sub> in MeOH.<sup>18</sup> Co contamination is inevitable by this way, which will affect the application of 1, 3-diamino graphene,

especially in the field of catalysis. Consequently, we attempted to reduce the malononitrile functionalized graphene oxide by using LiAlH<sub>4</sub> instead of CoCl<sub>2</sub>·6H<sub>2</sub>O and NaBH<sub>4</sub>. In this way, a clean 1, 3-diamino-graphene can be obtained.

In the past few years, copper-assisted C-N coupling reactions were extensively explored by using diamine ligands<sup>19,20</sup> or amino acids<sup>21</sup>. In our previous reports, different  $\alpha$ -amino acids were covalently grafted to the graphene sheets successfully through a simple chemical reaction, and the obtained amino acids functionalized graphene immobilized copper catalyst can effectively catalyze *N*-arylation of imidazole with iodobenzene.<sup>9</sup> Copper(I) catalyst showed high activity towards the C-N coupling reactions.<sup>22</sup> Based on these researches, we intensively believed that the diamine functionalized graphene can promote the CuI-catalyzed C-N coupling reactions.

In continuation of these studies, 1,3-diamino-graphene (NH<sub>2</sub>-G-NH<sub>2</sub>) was prepared and used as heterogeneous ligand for copper-catalyzed C-N coupling reaction in this work. The experimental results showed that the new method can effectively overcome the hard separation of catalyst and purification of products. By using CuI as the catalyst and NH<sub>2</sub>-G-NH<sub>2</sub> materials as the promoters, the C-N cross-coupling of various aryl halides with *N*-heterocycles under very mild conditions gave the corresponding products in good yields.

### Experimental

#### Materials

Graphite powder was purchased from Shanghai Huayi Company (Shanghai, China). KMnO<sub>4</sub>, NaNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> (98%) and HCl (36%-38%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai China). Cuprous iodide (CuI) and malononitrile were purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu China). Iodobenzene, calcium hydride and lithium aluminium hydride were obtained from Aladdin Industrial Inc. America. GO was synthesized by the oxidation of graphite powder according to our previous

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report.<sup>9</sup> The deionized (DI) water used throughout all experiments was purified to 18.2 MXm with the Millipore system.

#### Synthesis of 1, 3-diamino-graphene (NH<sub>2</sub>-G-NH<sub>2</sub>)

40 mg GO was dispersed into 30 mL dry THF by sonication to obtain homogeneous suspension, and marked as A solution. Next, 70 mg CaH<sub>2</sub> and 200 mg malononitrile were mixed in 20 mL dry THF by continuously stirring at 0 °C, and labeled as B solution. Then, solution B was dropwise added into solution A by stirring at 60 °C for 24 h. After completion of the reaction, the solid was filtrated and washed by HCl, deionized water 3 times and ethanol 2 times to thoroughly remove the Ca<sup>2+</sup>.

30 mg malononitrile-functionalized graphene oxide (CN-GO) was dispersed into 20 mL anhydrous THF, and 150 mg LiAlH<sub>4</sub> was dissolved into 20 mL anhydrous THF. Next, the LiAlH<sub>4</sub> solution was added into the graphene derivatives suspension by continuously stirring at room temperature for 24 h. The obtained product was filtrated and washed by HCl, deionized water 3 times and ethanol 2 times to thoroughly remove the residual Li<sup>+</sup> and Al<sup>3+</sup>. Finally, the 1, 3-diamino-graphene (NH<sub>2</sub>-G-NH<sub>2</sub>) was dried under high vacuum.

#### General procedure for the catalytic C-N coupling reaction

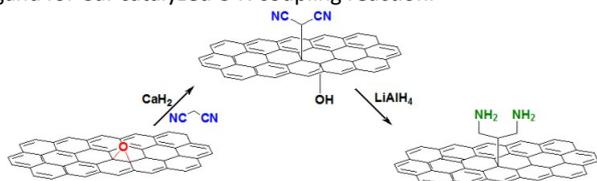
10 mg NH<sub>2</sub>-G-NH<sub>2</sub>, 1.2 mmol nitrogen heterocycles, 2.0 mmol base and 0.05 mmol CuI were added into a 10 mL reaction vessel fitted with a stir bar. Then 1.0 mmol aryl halide and 2 mL anhydrous DMSO was added into the vessel with the protection of nitrogen. The reaction mixture was stirred for a specified period of time at required temperature, and the progress of the reaction was monitored with thin layer chromatography. Next, the obtained product was diluted with 20 mL H<sub>2</sub>O and extracted with 3×15 mL ethyl acetate. The organic layers were combined together and dried overnight with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, the product was purified by flash chromatography using dichloromethane and methanol as the eluent, and the solvent was evaporated under vacuum.

#### Characterization

The samples were characterized by Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 6700, USA), Scanning Electron Microscopy equipped with an energy dispersive X-ray spectrometer (SEM, AJEOL JSM-6510LV, JAPAN), Thermogravimetric analyses (TGA, Netzsch STA 449F3, Germany), X-Ray Photoelectron Spectroscopy (XPS, Thermo ESCALAB 250XI, USA), and X-Ray Diffraction (XRD, D/MAX Ultima IV, JAPAN).

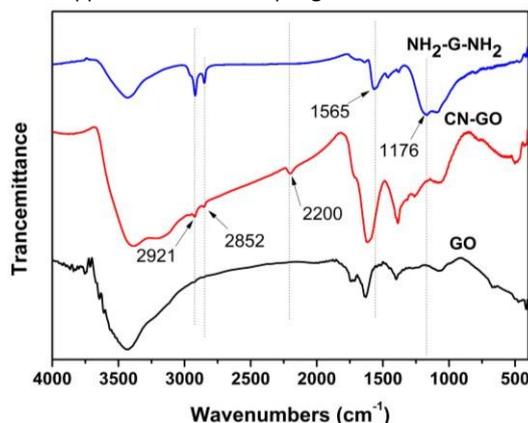
## Results and discussion

NH<sub>2</sub>-G-NH<sub>2</sub> materials were prepared according to the following procedure. Firstly, the reaction of malononitrile with GO was chosen and then the reduction of malononitrile functionalized graphene oxide was carried out by LiAlH<sub>4</sub> in THF (Scheme 1). The obtained materials were characterized and used as heterogeneous ligand for CuI-catalyzed C-N coupling reaction.



**Scheme 1** Illustration of the synthesis of NH<sub>2</sub>-G-NH<sub>2</sub> materials.

Firstly, FT-IR spectra of GO, CN-GO and NH<sub>2</sub>-G-NH<sub>2</sub> were shown in Fig. 1. Compared to the spectrum of GO, the CN-GO identified the presence of C-H ( $\nu_{\text{CH}}$  at 2921 and 2852 cm<sup>-1</sup>) and CN ( $\nu_{\text{CN}}$  at 2200 cm<sup>-1</sup>).<sup>18</sup> After reduction of CN-GO was completed by LiAlH<sub>4</sub>, the CN stretching frequency disappeared and NH<sub>2</sub> characteristic peaks at 1565 and 1176 cm<sup>-1</sup> were observed, which suggests that NH<sub>2</sub> has formed on the graphene. These amino groups are expected to coordinate copper for the C-N coupling reactions.



**Fig. 1** FT-IR analysis of GO, CN-GO and NH<sub>2</sub>-G-NH<sub>2</sub>.

Next, the thermal stability of GO and NH<sub>2</sub>-G-NH<sub>2</sub> were measured using TGA in Ar atmosphere and the results are shown in Fig. 2. The first weight loss was observed below 200 °C for GO materials, corresponding to the evaporation of water.<sup>18</sup> The second weight loss was observed between 200 and 500 °C, and the loss is due to the pyrolysis of COOH and carbonyl groups.<sup>23</sup> The weight loss above 500 °C may be caused by the decomposition of hydroxyl and epoxide groups.<sup>23, 24</sup> In contrast, the mass loss of NH<sub>2</sub>-G-NH<sub>2</sub> material is obviously lower than that of GO, which indicates that the NH<sub>2</sub>-G-NH<sub>2</sub> material is more stable. A significant weight loss was observed at 200 °C for NH<sub>2</sub>-G-NH<sub>2</sub> material. In order to study the functional groups on the NH<sub>2</sub>-G-NH<sub>2</sub> material around 200 °C, the sample after treating by TG in Ar atmosphere at 200 °C (NH<sub>2</sub>-G-NH<sub>2</sub>-200 °C) was measured by FT-IR (Fig.S1, ESI<sup>†</sup>). It can be seen that there is no obvious change between the FT-IR spectra of NH<sub>2</sub>-G-NH<sub>2</sub> and NH<sub>2</sub>-G-NH<sub>2</sub>-200 °C, but the relative intensity of  $\nu_{\text{OH}}$  at 3421 cm<sup>-1</sup> is weakened for NH<sub>2</sub>-G-NH<sub>2</sub>-200 °C sample, which may be caused by the evaporation of water. So the first weight loss below 200 °C for NH<sub>2</sub>-G-NH<sub>2</sub> material can be ascribed to the evaporation of water. The weight loss in the range of 200-500 °C can be attributed to the pyrolysis of a small amount of COOH and carbonyl groups which were unreduced by LiAlH<sub>4</sub>. The weight loss above 500 °C may be caused by the decomposition of 1, 3-diamino and hydroxyl groups.<sup>18, 24</sup>

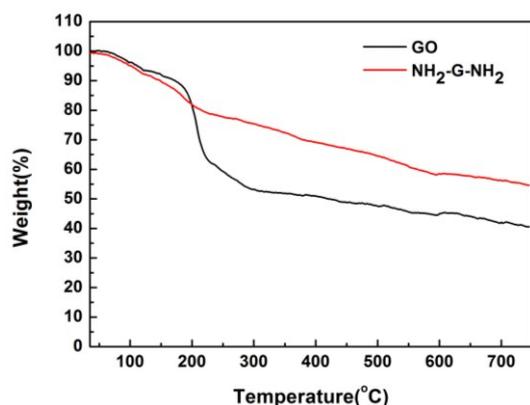


Fig. 2 TG analysis of GO and NH<sub>2</sub>-G-NH<sub>2</sub>.

To better understand the role of NH<sub>2</sub>-G-NH<sub>2</sub> in the C-N coupling reactions, we carried out a reaction between CuI (0.05 mmol) and 10 mg NH<sub>2</sub>-G-NH<sub>2</sub> in 2 mL of anhydrous DMSO in a sealed tube under stirring for 20 h at 90 °C. After reaction, solid material was obtained by filtering. The obtained material was denoted as CuI/NH<sub>2</sub>-G-NH<sub>2</sub>. Further characterizations were carried out by XRD, XPS, and SEM.

The X-ray diffraction patterns of GO, CN-GO, NH<sub>2</sub>-G-NH<sub>2</sub>, and CuI/NH<sub>2</sub>-G-NH<sub>2</sub> were shown in Fig. 3. The XRD peak of GO was observed at 2θ = 10.5, corresponding to an average interlayer spacing of ~ 0.84 nm due to the presence of oxygen-containing functional groups attached on both sides of the graphene sheets.<sup>25</sup> After grafting CN on the GO, the interlayer spacing of GO has no obvious change. However, the characteristic peak of NH<sub>2</sub>-G-NH<sub>2</sub> at 10.5° disappeared, which indicates that the reduction of CN-GO was accomplished successfully.<sup>26</sup> Next, the CuI/NH<sub>2</sub>-G-NH<sub>2</sub> catalyst was characterized. Obviously, the crystalline CuI can be observed, which indicates the NH<sub>2</sub>-G-NH<sub>2</sub> can well immobilize the CuI owing to the coordination interaction between amino groups and Cu ions.

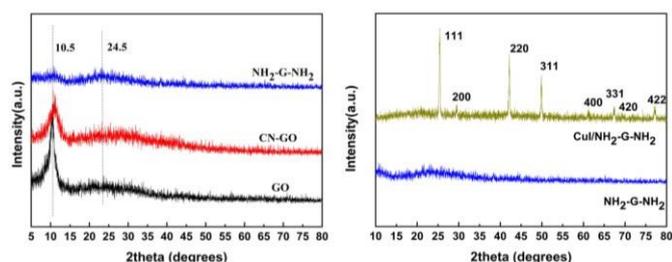


Fig. 3 XRD analysis of GO, CN-GO, NH<sub>2</sub>-G-NH<sub>2</sub>, and CuI/NH<sub>2</sub>-G-NH<sub>2</sub>.

Fig. 4 showed the X-ray photoelectron spectra (XPS) of GO, RGO, NH<sub>2</sub>-G-NH<sub>2</sub>, and CuI/NH<sub>2</sub>-G-NH<sub>2</sub>. The C1s XPS spectrum of GO is consisted of four types of carbon: the C-C/C=C (285.0), C-O (287.0), C=O (287.8), and COOH (288.8) (Fig.4a).<sup>27</sup> When GO was reduced by LiAlH<sub>4</sub> at room temperature, the RGO material could be obtained. In the C1s XPS spectrum of RGO, the peak intensities of C-O, C=O, and COOH obviously decrease, corresponding to the reduction of epoxy, carbonyl, and carboxyl groups by LiAlH<sub>4</sub> (Fig. 4b). The signals in the Fig. 4c can be associated with C1s, O1s, and N1s, confirming the presence of nitrogen in the amino functionalized graphene. According to previous reports<sup>28,29</sup> that binding energy of Al2p, Al2s, and Li1s are 74.5, 119.4, and 54.8 eV, respectively. But there is no

peak between 1-200 eV (Fig. 4c). Therefore, it can be concluded that a clean amino-graphene has been obtained. The C1s spectrum of NH<sub>2</sub>-G-NH<sub>2</sub> (Fig. 4d) was deconvoluted into five main peaks, which is attributed to C-C/C=C, C-N, C-O, C=O and COOH, respectively.<sup>9, 30</sup> Moreover, the N1s spectrum of NH<sub>2</sub>-G-NH<sub>2</sub> shows one peak at 399.8 eV, which can be ascribed to hydrogen-bonded amino groups.<sup>31,32</sup> But CuI addition will break the hydrogen bonding. The N1s spectrum could be divided into two peaks for CuI/NH<sub>2</sub>-G-NH<sub>2</sub> in Fig. 4e, one peak at 399.0 eV is ascribed to free terminal amines<sup>33</sup> and another peak at 400.1 eV is attributed to amino groups coordinated to Cu metallic center. Furthermore, the copper valence state on NH<sub>2</sub>-G-NH<sub>2</sub> surface was confirmed by the XPS analysis in Fig 4f. The Cu 2p<sub>3/2</sub> peak at 932.7 eV is assigned to Cu<sup>+</sup>,<sup>34</sup> whereas the peak at 934.5 eV is ascribed to Cu<sup>2+</sup>, which probably results from oxidation of Cu<sup>+</sup> exposure to air.

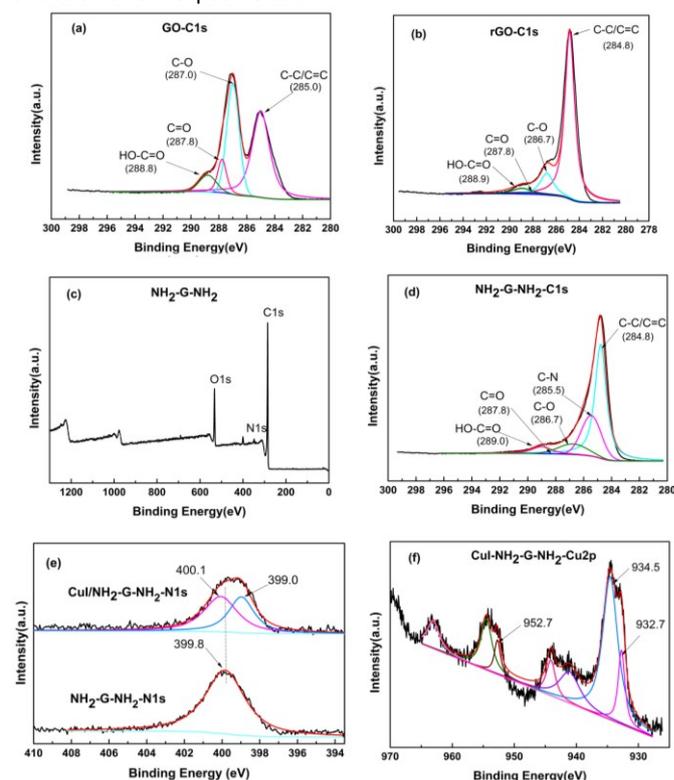


Fig. 4 XPS analysis of GO, RGO, NH<sub>2</sub>-G-NH<sub>2</sub>, and CuI/NH<sub>2</sub>-G-NH<sub>2</sub>. (a) C1s XPS spectrum of GO. (b) C1s XPS spectrum of RGO. (c) Full range XPS spectrum of NH<sub>2</sub>-G-NH<sub>2</sub>. (d) C1s XPS spectrum of NH<sub>2</sub>-G-NH<sub>2</sub>. (e) N1s XPS spectrum of NH<sub>2</sub>-G-NH<sub>2</sub> and CuI/NH<sub>2</sub>-G-NH<sub>2</sub>. (f) Cu2p XPS spectrum of CuI/NH<sub>2</sub>-G-NH<sub>2</sub>.

Finally, the morphology of the typical products was investigated by the SEM. From Fig. 5, it can be clearly seen that the NH<sub>2</sub>-G-NH<sub>2</sub> sheets exhibit a typical rippled and crumpled morphology and paper-like structure with single or very thin layers. However, the agglomeration of CuI/NH<sub>2</sub>-G-NH<sub>2</sub> catalyst is discovered after the CuI was supported. In order to identify the elementary composition of the agglomeration, four arbitrary little agglomerations were measured by energy dispersive X-ray spectrometer (EDS). The results of EDS images and analysis showed that these agglomerations are CuI/NH<sub>2</sub>-G-NH<sub>2</sub> catalysts (Fig. S2-S5, ESI†). So it may be reasonable that the coordination interaction between CuI

and amino on the graphene sheets caused the agglomeration of amino-graphene sheets.

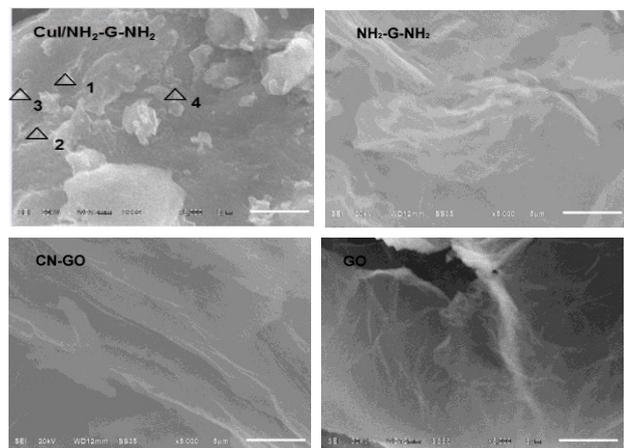


Fig. 5 SEM images of GO, CN-GO, NH<sub>2</sub>-G-NH<sub>2</sub>, and CuI/NH<sub>2</sub>-G-NH<sub>2</sub>.

Generally, it is of great significance to research utilization range of a novel material in the practical application like electrochemistry and catalysis areas. Hence, to evaluate the NH<sub>2</sub>-G-NH<sub>2</sub> materials in organic synthesis, C-N coupling reactions of imidazole with iodobenzene was investigated. A preliminary survey of reaction conditions was conducted including the effects of copper source, base, temperature and the amount of graphene. By using the NH<sub>2</sub>-G-NH<sub>2</sub> as the promoter, the results showed that the system containing 2 mmol KOH, 90 °C, 5 mol% of CuI and 10 mg NH<sub>2</sub>-G-NH<sub>2</sub> can drive the coupling reaction, obtaining 1-phenyl-1H-imidazole in 98% (Table 1, Entry 1). To better understand the role of the 1,3-diamino-graphene in the model reactions, we evaluated GO as the heterogenous ligand in place of NH<sub>2</sub>-G-NH<sub>2</sub>. As can be seen, the use of GO afforded 83% yield (Table 1, Entry 11). Meanwhile, in the absence of heterogeneous ligand, the yield of the desired product was 81% (Table 1, Entry 12). These results demonstrate that the 1,3-diamino-graphene is an effective additive for CuI-catalyzed C-N coupling reaction.

Table 1 Effect of different reaction conditions for the C-N coupling reactions of imidazole with iodobenzene

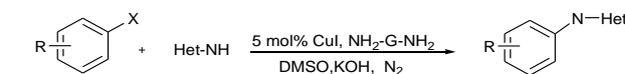
Entry	Cu source	Graphene	Base	Temp. (°C)	Yield (%) <sup>a</sup>
1	CuI	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	90	98
2	CuCl	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	90	77
3	CuCl <sub>2</sub>	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	90	82
4	CuSO <sub>4</sub>	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	90	96
5	Cu(OAc) <sub>2</sub>	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	90	76
6	CuI	NH <sub>2</sub> -G-NH <sub>2</sub>	NaOH	90	88
7	CuI	NH <sub>2</sub> -G-NH <sub>2</sub>	LiOH	90	86
8	CuI	NH <sub>2</sub> -G-NH <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	90	38
9	CuI	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	80	90, 70 <sup>b</sup> , 87 <sup>c</sup>
10	CuI	NH <sub>2</sub> -G-NH <sub>2</sub>	KOH	70	46
11	CuI	GO	KOH	90	83

12	CuI	-	KOH	90	81
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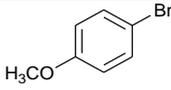
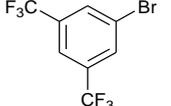
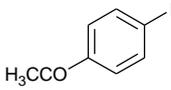
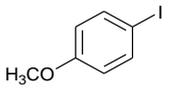
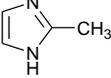
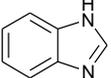
<sup>a</sup> Reaction conditions: iodobenzene (1 mmol), imidazole (1.2 mmol), Cu source (0.05 mmol), graphene (10 mg), base (2 mmol), DMSO (2 mL), t=20 h, GC yield. <sup>b</sup> 5 mg NH<sub>2</sub>-G-NH<sub>2</sub>. <sup>c</sup> 15 mg NH<sub>2</sub>-G-NH<sub>2</sub>.

After the optimization researches, we aimed to explore the scope and limitations of the developed methodology. Firstly, the coupling reactions of aryl halides with N-H heterocycles were carried out. As shown in Table 2, the reactivity of aryl iodides in the C-N coupling reaction is higher than the aryl bromides and chlorides. At the same time, the influence of electronic effect of substituent is obvious in these reaction systems. For the NH<sub>2</sub>-G-NH<sub>2</sub> catalytic system, aryl halides containing electron-withdrawing (EW) groups can be conducted smoothly to afford the corresponding products in good yields, while a moderate yields can be obtained for these aryl halides with electron-donating (ED) substituent. Interestingly, the steric hindrance of the substituent had a little effect for the reactions. When a nitro substituent was present in any position of the benzene ring of aryl halides, we obtained the desired compounds in 82%, 87%, and 90% yields for the NH<sub>2</sub>-G-NH<sub>2</sub> system (Table 2, Entries 4-6). In the next step, the cross-couplings between iodobenzene and various nitrogen heterocycles were tested in this work. It was found that relative good reactivity was obtained with different N-heterocycles (Table 2, Entries 12-16).

Table 2 C-N coupling reactions of different N-heterocycles with various aryl halides



Entry	Aryl halides	Het-NH	Yield <sup>a</sup> (%)
1			90
2			75
3			13
4			82
5			87
6			90
7			89

8			69
9			81
10			92
11			78
12			76
13			84
14			71
15			65
16			64

<sup>a</sup> Reaction conditions: aryl halides (1 mmol), *N*-heterocycles (1.2 mmol), KOH (2 mmol), CuI (0.05 mmol), NH<sub>2</sub>-G-NH<sub>2</sub> (10 mg), DMSO (2 mL), t=20 h, T=80 °C, isolated yield.

The recycling efficiency of the present catalysts was investigated in the C-N coupling reaction of iodobenzene with imidazole. The solid catalyst materials were isolated by filtration, and then washed thoroughly with DMSO. The used catalyst was reemployed in the next cycle under identical conditions. As seen from the Table 3, the catalyst could be separated and reused, which indicates that 1, 3-diamino-graphene as a heterogeneous ligand can immobilize CuI by coordination interaction, but to improve its stability is our next objective.

**Table 3** Recycling of the catalyst

Run	1	2	3
Yield <sup>a</sup> (%)	98	99	87

<sup>a</sup> Reaction conditions: iodobenzene (1 mmol), imidazole (1.2 mmol), KOH (2 mmol), CuI (0.05 mmol), NH<sub>2</sub>-G-NH<sub>2</sub> (10 mg), DMSO (2 mL), t=20 h, T=90 °C.

Finally, we compared the activity of NH<sub>2</sub>-G-NH<sub>2</sub> as a heterogeneous ligand in the C-N coupling reaction of imidazole and iodobenzene with the other previous reported ligands (heterogeneous or homogeneous) (Table 4). Compared with heterogeneous ligands such as Indion 770 and Meso-N-C-1, the NH<sub>2</sub>-G-NH<sub>2</sub> catalysis system exhibited higher yields under milder reaction conditions. (Table 4.

Entries 1, 2, and 8). Generally, the homogeneous catalysis has milder reaction conditions than heterogeneous catalysis. But, to our joy, the NH<sub>2</sub>-G-NH<sub>2</sub> catalysis system exhibited approximate activity compared with homogeneous ligand N,N'-dioxide (Table 4, Entries 3 and 7) and even higher activity compared with the other homogeneous ligands (Table 4, Entries 4-6, and 8).

**Table 4** Comparison of different heterogeneous or homogeneous ligand for CuI-catalyzed C-N coupling reaction of iodobenzene and imidazole

Entry	Ligand	Conditions	Yield (%)	Ref.
1	Indion 770	CuI: 10 mol%, K <sub>2</sub> CO <sub>3</sub> , DMSO, 125 °C	94	35
2	Meso-N-C-1	CuI: 15 mol%, KOH, DMSO, 125 °C	88	36
3	N,N'-dioxide	CuI: 10 mol%, Cs <sub>2</sub> CO <sub>3</sub> , DME, 80 °C	95	37
4	Metformin	CuI: 5 mol%, Cs <sub>2</sub> CO <sub>3</sub> , DMF, 110 °C	98	38
5	Tetrazole 1-acetic acid	CuI: 5 mol%, NaOH, DMSO, 110 °C	84	39
6	L-histidine	CuI: 10 mol%, K <sub>2</sub> CO <sub>3</sub> , DMSO, 100 °C	91	40
7	NH <sub>2</sub> -G-NH <sub>2</sub>	Cu: 5 mol%, KOH, DMSO, 80 °C	90	This study
8	NH <sub>2</sub> -G-NH <sub>2</sub>	Cu: 5 mol%, KOH, DMSO, 90 °C	98	This study

## Conclusions

In summary, 1, 3-diamino functionalized graphene material was synthesized by a simple chemical method. FT-IR, TG, XRD, XPS, and SEM measurements revealed that 1, 3-diamino has been successfully grafted on the graphene and can immobilize CuI by coordination interaction. Notably, the as-prepared amino functionalized graphene material can be used as heterogeneous ligand for CuI catalyzed C-N coupling reactions, and the desired products were obtained with good yields. Compared with other previous reports, the reaction system is much smoother at lower temperature. In addition, the new method can easily realize the recyclability of catalysts and purification of products. Finally, we believe that 1, 3-diamino-graphene materials can also be used as heterogeneous ligand or support for other transition metals (Ru, Pd, Rh, etc) catalysis. And the 1, 3-diamino-graphene may react with salicylaldehyde, forming di-schiff base graphene materials. Further studies for the application of 1, 3-diamino-graphene materials are currently underway in our laboratory.

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1,3-diamino-graphene was synthesized and used as an efficient heterogeneous ligand for CuI-catalyzed C-N coupling reaction.

