

FULL PAPER

Buchwald-Hartwig amination reaction of aryl halides using heterogeneous catalyst based on Pd nanoparticles decorated on chitosan functionalized graphene oxide

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In this work, graphene oxide was functionalized with chitosan (GO-Chit) followed by a simple approach for immobilization of palladium nanoparticles onto a chitosan grafted graphene oxide surface. The Pd-nanocomposite (GO-Chit-Pd) was characterized using Transmission Electron Microscopy (TEM), Fourier transforms infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) measurements. The catalytic activity of the prepared heterogeneous graphene oxide functionalized chitosan-palladium (GO-Chit-Pd) was investigated in term of C-N coupling reaction (Buchwald-Hartwig amination reaction of aryl halides) yielding products of N-arylamines. The easy purification, convenient operation, and environmental friendliness, combined with a high yield, render this method viable for use in both laboratory research and larger industrial scales. Studying the reusability of the catalyst in this work showed that it could be reused for five times without obvious loss in catalytic activity.

KEYWORDS

amination, Buchwald-Hartwig reaction, C-N coupling reaction, graphene, heterogeneous catalyst, palladium nanoparticles

1 | INTRODUCTION

Transition-metal-catalyzed amination of aryl halides is a powerful methodology in organic synthesis. Therefore, there is particular attention on the introduction of new catalyst systems and their applicability in the cross coupling of aryl halides with amines. Typically, C-N bonds are formed by copper-mediated Ullmann reaction and palladium catalyzed Buchwald-Hartwig reaction.^[1–3] The palladium-catalyzed Buchwald-Hartwig amination of aryl halides has been successfully established as a highly valuable method for the formation of C(aryl)-N bond. The formation of this bond by cross coupling reactions represents a powerful means for the preparation of numerous compounds in biological, pharmaceutical, and material sciences.^[4,5] Typically, the cross-coupling reactions are performed under homogeneous situation using soluble palladium organic complex as the

catalyst.^[6] However, the high cost, low yield in separation and reusability of homogeneous transition metal catalysts remains a scientific challenge. In this regard, solidly supported metal nano particles (heterogeneous catalyst) are the best alternative for homogeneous systems. A variety of heterogeneous solid supported palladium catalysts such as silica, zeolite, mesoporous materials and others is reported to perform these coupling reactions.^[7–11] However, with these supports, inorganic materials have high sensitivity towards acid and base conditions. Owing to good stabilities in both alkaline and acid conditions, carbons as supports have attracted much attention.^[12]

In the last years, natural polymers, such as chitosan have attracted many scientists. Due to the distinguished properties of chitosan, such as non-toxic, hydrophilic features, biocompatibility, and antibacterial activity, it has been extensively used in several fields, such as biomaterials,

textile, environmental protection, and drug delivery.^[13–19] Graphene is also another material highly interested by researchers in the recent years. Graphene oxide (GO), as one of the graphene derivatives, is highly used in heterocatalysis applications because of its remarkable two-dimensional structures, huge surface areas, tunable electrical properties, and other excellent properties.^[20,21] Graphene oxide possesses various functional groups such as hydroxyl, carboxyl, and epoxy groups. Based on favourable properties of chitosan and natural properties of GO, some researchers have explored the facility of GO-chitosan composite as a heterogeneous catalyst.^[22]

In this research, we focused on the preparation of porous chitosan-GO composites with Pd nanoparticles immobilized on its surface in order to synthesize a reusable Pd catalyst for the application in the cross-coupling reaction of aryl halides with amines.

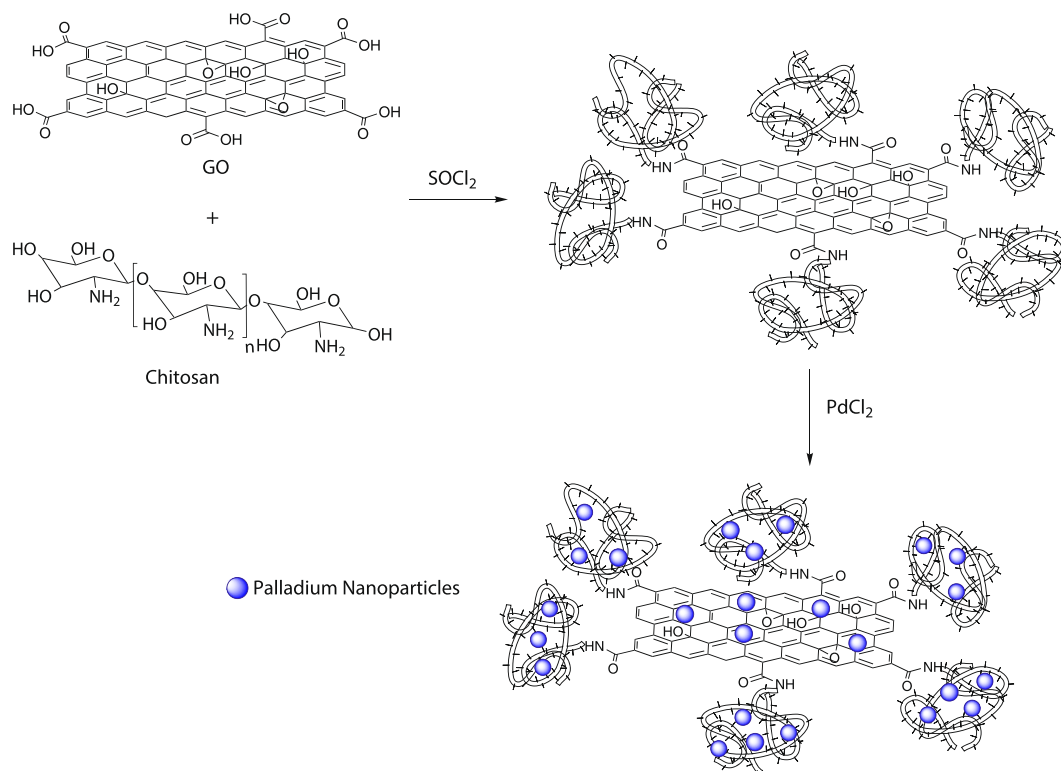
2 | RESULTS AND DISCUSSION

In a continuation of our studies on the preparation and application of palladium nanoparticles deposited on a functionalized graphene support in cross coupling reaction,^[23] we report the preparation of chitosan-grafted graphene oxide (GO-Chit), and Pd nanoparticles immobilization on GO-Chit in order to synthesize a reusable Pd catalyst (GO-Chit-Pd) to use in Buchwald-Hartwig reaction

of aryl halides with secondary amines. The process for the synthesis of immobilized Pd nanoparticles on chitosan-functionalized graphene oxide (GO-Chit-Pd) is shown in Scheme 1.

The scaffolds were synthesized by covalent linking of the carboxyl (–COOH) groups of GO with the amino (–NH₂) groups of chitosan. As shown in Scheme 1, the obtained graphene oxide was refluxed in SOCl₂ give the intermediate graphene oxide-COCl. Afterward, GO-COCl was reacted with chitosan for the synthesis of chitosan-functionalized graphene oxide (GO-Chit).^[24] After washing and drying GO-Chit, the structure was analyzed using Fourier Transition Infrared (FT-IR) spectroscopy. Different functional groups were observed in all graphene samples through FT-IR analysis (Figure 1). As clearly shown in Figure 1, the absorbance bands of GO at 3435 cm⁻¹, 1723 cm⁻¹, 1605 cm⁻¹, and 1078 cm⁻¹ are indexed to a hydroxyl group (–OH) stretching, the stretching vibration of C=O, the stretching vibration of C=C, and the stretching vibration of C–O (orange line), respectively. In the GO-Chit spectrum, the peak at 1723 cm⁻¹ approximately disappeared. Besides, a new broad band emerged at 1638 cm⁻¹, 1086 cm⁻¹, and 3440 cm⁻¹, corresponding to the C=O characteristic stretching band of the amide groups, the stretching vibration of C–O, and the stretching vibration of free –NH and –OH groups of grafted chitosan (green line), respectively.

PdCl₂ was added to the ethanol solution of GO-Chit in order to create the GO-Chit-Pd nanocomposite. Pd was



SCHEME 1 Synthesis of GO-Chit–Pd

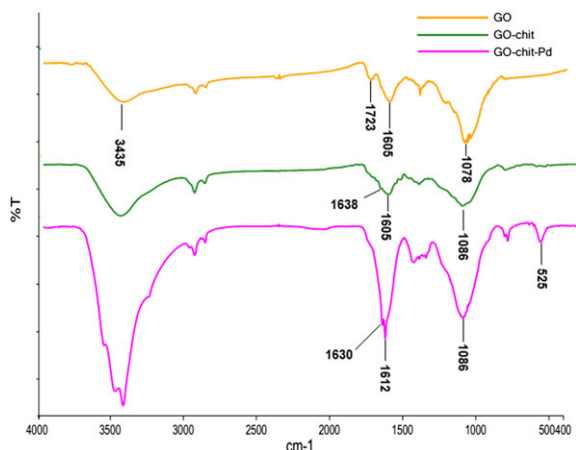


FIGURE 1 FT-IR spectra of GO, GO-Chit, and GO-Chit-Pd

immobilized at the chitosan region of GO-Chit through the formation of an N-Pd complex. The chemical structure, composition, and morphology of the synthesized GO-Chit-Pd nanocomposite were fully characterized using FT-IR, XRD, AAS and TEM spectroscopy, respectively. In the IR spectrum of GO-Chit-Pd, a new band emerged at 525 cm^{-1} corresponding to the N-Pd band (violet line in Figure 1).

The XRD spectra of GO-Chit-Pd nanocomposites are shown in Figure 2. From the XRD patterns it is observed that GO-Chit-Pd give a characteristic peak at $2\theta = 26.7^\circ$, which is the same as that of GO,^[13] confirming that the composite nevertheless preserves the structure of GO. Also, the broad peaks at $2\theta = 20.9^\circ$ are due to the amorphous state of the chitosan. This angle of the composite film is similar to that of the pure chitosan. However, the chemical structure of the chitosan in the composite barely changes with the increasing content of graphene oxide, indicating that there was mainly a physical interaction but a limited chemical reaction between chitosan and graphene oxide. A significant characteristic peak of Pd is obtained at 40.1° , suggesting a successful reduction of palladium ion to Pd(0). The other two peaks at 46.7° and 68.1° are attributed crystalline plane diffraction peaks of Pd(0). According to the Scherrer equation B

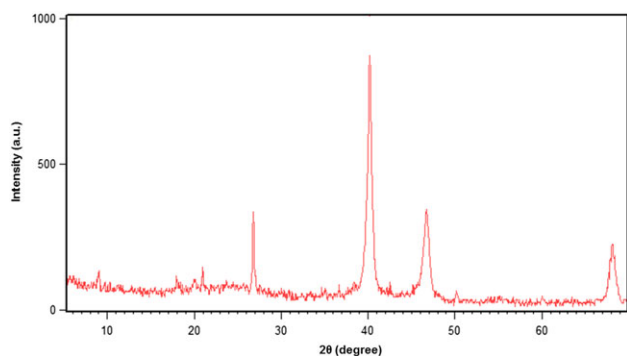


FIGURE 2 XRD pattern of GO-Chit-Pd

$(2\theta) = K\lambda/L\cos\theta$, the Pd particle size is calculated at 28.66 nm for the GO-Chit-Pd catalyst.

In the next step, the GO-Chit-Pd catalyst was studied using Transmission Electron Microscopy (TEM) in order to represent the morphology and size of immobilized Pd nanoparticles on the surface of GO-Chit. The TEM images in Figure 3 showed the GO-Chit-Pd nanocomposite and GO. The average particle sizes in the Figure 3b are consistent with

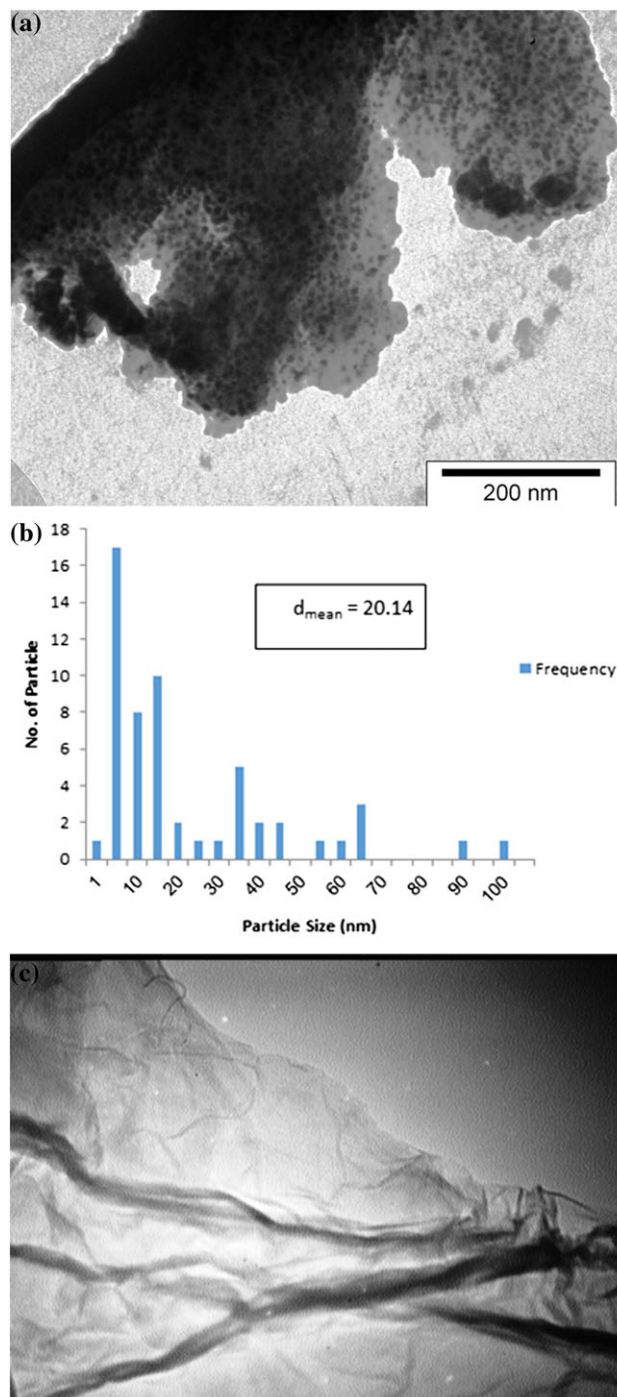


FIGURE 3 (a) TEM image of GO-Chit-Pd catalyst, (b) The histogram of particle size distribution of GO-Chit-Pd catalyst, (c) TEM image of GO

those estimated by XRD. The results show that our methodology is highly efficient for the synthesis of PdNPs in small size on the surface of chitosan-graphene oxide sheets with no significant particle aggregation, which is suitable for the catalytic application. The amount of Pd in the catalyst (GO-Chit-Pd) measured by atomic adsorption spectrometry (AAS) is 18 wt.%.

The catalytic performance of the prepared catalyst was systematically examined through Buchwald-Hartwig reaction. To achieve optimal conditions, the reaction of bromobenzene with morpholine in the presence of GO-Chit-Pd catalyst was selected as a model reaction and the effect of various reaction parameters such as solvent, base, and the amount of catalyst were studied in detail. The results of optimization study are shown in Table 1 and 2. Through this optimization study, first, some solvents including DMF, H₂O, H₂O-EtOH (1:1) and toluene (Table 1, entries 1–4) were screened out. According to the results shown in Table 1, it is found that DMF is the best solvent for the reaction (Table 1, entry 4). In the next step, the effect of organic and inorganic bases such as t-BuOK, K₂CO₃, Cs₂CO₃, Et₃N, and NaOH on the model reaction was investigated. According to the results shown in Table 1 (entries 4–8), the product indicates a low yield when the reaction is carried out in the presence of K₂CO₃, Cs₂CO₃, Et₃N, and NaOH. As shown in Table 1 (entry 5), the best product yield was detected for t-BuOK in the presence of GO-Chit-Pd (3 mg, 0.5 mol% Pd). Additionally, temperature strongly affects the kinetics and efficiency of the coupling reaction, as an increase in temperature increases reaction productivity. The output of the reaction at room temperature is negligible (Table 1, entries 8–11).

TABLE 1 Optimization of reaction conditions for Buchwald-Hartwig amination reaction of bromobenzene with morpholine using GO-Chit-Pd catalyst^a

Entry	Solvent	Base	T (°C)	Yield (%) ^b
1	H ₂ O	K ₂ CO ₃	100	52
2	H ₂ O-EtOH	K ₂ CO ₃	100	58
3	Toluene	K ₂ CO ₃	100	10
4	DMF	K ₂ CO ₃	100	72
5	DMF	Cs ₂ CO ₃	100	83
6	DMF	Et ₃ N	100	62
7	DMF	NaOH	100	78
8	DMF	t-BuOK	100	95
9	DMF	t-BuOK	80	65
10	DMF	t-BuOK	60	55
11	DMF	t-BuOK	r.t. ^c	30

^aReaction conditions: bromobenzene (1 mmol), morpholine (1.2 mmol), GO-Chit-Pd (3 mg, 0.5 mol%), solvent (5 mL), base (1.5 mmol) for 12 h.

^bIsolated yield.

^cRoom Temperature.

TABLE 2 Optimization of catalyst loading for Buchwald-Hartwig amination reaction of bromobenzene with morpholine using GO-Chit-Pd catalyst^a

Entry	Amount of Catalyst (mg)	Pd loading (mol%)	Yield (%) ^b
1	0	0	0
2	1	0.17	44
3	2	0.34	62
4	3	0.51	95
5	4	0.68	93

^aThe reaction was carried out with 1 mmol of bromobenzene, 1.2 mmol of morpholine, 1.5 mmol of t-BuOK, and 5 mL of DMF at 100 °C for 12 h.

^bIsolated yield.

Afterward, the optimum amount of catalyst was monitored to get maximum yield of the product and 3 mg (0.5 mol%) of a catalyst selected as the optimum amount (Table 2, entry 4). The model reaction first took place in the absence of a catalyst and no product was formed, as the result (Table 2, entry 1).

To investigate the catalytic activity of PdNPs, under the optimized conditions, we probed the scope of various substituted aryl halides with morpholine in the presence of t-BuOK, using DMF (5 ml) as a solvent. Based on the results shown in Table 3, Buchwald-Hartwig amination reaction can be accomplished efficiently in the presence of GO-Chit-Pd catalyst system. Aryl bromides, Aryl iodides, Aryl chlorides were found as suitable in our methodology. However, iodobenzene exhibit a higher activity compared to bromobenzene (Table 3, entries 1–2). However, the catalytic system was less effective for the reaction of chlorobenzene

TABLE 3 Buchwald-Hartwig amination reaction of aryl halides with morpholine using GO-Chit-Pd catalyst^a

Entry	Aryl halides	Products	Yield (%) ^b
1		a	90
2		a	96
3		a	58
4		b	89
5		c	92
6		d	85
7		e	88
8		f	82
9		g	88
10		h	98
11		i	90
12		i	98
13		g	98
14		c	95
15			90
16			89
k			

^aReaction conditions: Aryl halides (1 mmol), morpholine (1.2 mmol), GO-Chit-Pd (3 mg, 0.5 mol%), t-BuOK (1.5 mmol), DMF (5 ml) at 100 °C for 12 h.^bIsolated yield.

TABLE 4 Buchwald-Hartwig amination reactions of bromobenzene with different primary and secondary amines using GO-Chit-Pd.^a

Entry	amines	Products	Yield (%) ^b
1		l	89
2		m	90
3		n	82
4	(PhCH ₂) ₂ NH	o	60
5	PhCH ₂ NHCH ₃	p	65
6	PhNH ₂	q	40
7	CH ₃ CH ₂ CH ₂ CH ₂ NH ₂	r	55

^aReaction conditions: bromobenzene (1 mmol), amine (1.2 mmol), GO-Chit-Pd (3 mg, 0.5 mol%), *t*-BuOK (1.5 mmol), DMF (5 ml) at 100 °C for 12 h.

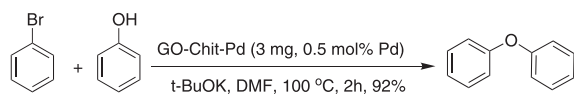
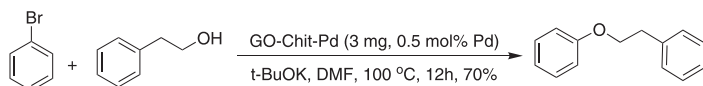
^bIsolated yield.

(Table 3, entry 3). The results also show that the catalyst provides a high product yield for both electron-withdrawing substituents (–NO₂, –COCH₃, –COOH, –CHO and –CN) and electron-donating substituents (–OMe, –CH₃ and OH) (Table 3, entries 4–14).

The reaction is substantially extensible to different primary and secondary amines (Table 4). We chose a variety of structurally divergent primary and secondary amines and investigated their reactions under the optimized reaction conditions with bromobenzene. The results showed that the primary amines and secondary amines with steric hindrance provide a low yield (Table 4, entries 4–7).

In order to show the more application of this catalytic system, the reactions of bromobenzene with phenol and 2-phenylethanol under similar reaction conditions have been also presented. The reactions were performed well as shown in Schemes 2 and 3 and the desired coupled products were isolated in 92% and 70%, respectively.

Recovery and recyclability is a noteworthy point about the use of heterogeneous catalysts. For this purpose, we performed recyclability of GO-Chit-Pd catalyst for the reaction of bromobenzene with morpholine under the same

**SCHEME 2** Coupling reaction of bromobenzene with phenol**SCHEME 3** Coupling reaction of bromobenzene with 2-phenylethanol

above-mentioned reaction conditions. After completion of each run, the mixture was cooled to room temperature, and then the catalyst was recovered by centrifugation and reused. The results showed that this catalyst system is reusable at least for 5 times without any significant decrease in its catalytic activities (Table 5).

To investigate whether the catalytically active species is really heterogeneous or not, the hot filtration experiment was carried out to get insight into Buchwald-Hartwig amination reaction catalyzed with apparently a heterogeneous GO-Chit-Pd catalyst. During the reaction of bromobenzene with morpholine, the catalytically active nanocomposite was removed from the reaction by filtration after 30 min using a hot frit, and the filtrate was monitored for continued activity. The hot filtrates were then transformed to another flask containing 1.5 mmol of *t*-BuOK, and 5 ml of DMF at 100 °C. Upon further heating of the catalyst-free solution for 12 h, no considerable progress was observed. Moreover, AAS of the same reaction solution at the midpoint of completion

TABLE 5 Reusability of the GO-Chit-Pd Nanoparticles^a

Run	1	2	3	4	5
Yield (%) ^b	90	90	89	87	87

^aReaction conditions: bromobenzene (1 mmol), morpholine (1.2 mmol), GO-Chit-Pd (3 mg, 0.5 mol%), *t*-BuOK (1.5 mmol), DMF (5 mL) at 100 °C for 12 h.

^bIsolated yield.

indicated that no significant quantities of palladium were lost to the reaction liquors during the process.

3 | CONCLUSIONS

In summary, a graphene oxide-chitosan composite was successfully prepared by covalent linking of the carboxyl groups of graphene oxide with the amine groups of chitosan. This process is a simple, low cost, and green pathway. Accordingly, we designed an efficient catalytic system via stabilizing palladium NPs on graphene oxide-chitosan sheets. The catalytic activity of this catalyst was investigated for the Buchwald–Hartwig amination reaction of aryl halides with different secondary amines. The catalyst showed superior activity for this C–N bond formation reaction. Easy purification, convenient operation, recyclability of catalyst, and environmental friendliness of this method, in addition to the high yields, are the main characteristic of this process.

4 | EXPERIMENTAL

4.1 | Materials and methods

Graphite powder, sulfuric acid (H_2SO_4), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), various aryl halide, secondary amines, *N,N*-dimethylformamide (DMF), potassium tert-butoxide (*t*-BuOK) and Palladium (II) chloride were purchased from Merck Chemical Company (USA), using without further purification. Double distilled water was used throughout the experiment.

FT-IR spectra were taken on a PerkinElmer Spectrum Version 10.4.4 spectrophotometer in KBr pellets and reported in cm^{-1} . ^1H and ^{13}C NMR spectra were measured on a Bruker 250 MHz spectrometer in CDCl_3 with chemical shift (δ) given in ppm. Transmission electron microscopy (TEM) image was acquired on a LEO912AB transmission electron microscope. An Analytik Jena (Germany) flame atomic absorption spectrometer (AAS) was used for designation of Pd. The crystalline phases of the composites were verified and compared by X-ray diffraction (XRD) using a Philips-PW1730. The diffraction angles (2θ) were set between 5° and 80° .

4.2 | Preparation of GO:

GO was synthesized from graphite by a modified Hummers' method.^[25] In brief, 2 g graphite powder was added into a 250 ml beaker, then 1 g of sodium nitrate and 50 ml concentrated H_2SO_4 (95%) was added into it sequentially under stirring in an ice bath, and then KMnO_4 (8 g) was added slowly into the beaker at lower than 20°C . Then the ice bath was removed after 10 min and the mixture was stirred at 35°C for 12 hour. Subsequently, deionized water (150 ml) was

slowly added under severe stirring and the diluted suspension was stirred at 90°C for 30 min. Finally 10 ml H_2O_2 was put into the mixture to convert the unreacted permanganate and manganese dioxide into soluble sulfate. The reaction mixture was centrifuged (10000 rpm for 30 min), and the supernatant was decanted away. The remaining solid material was washed 3 times with 5% HCl solution in order to remove the excess of manganese and washed with deionized water several times, and finally by filtration and air drying, graphite oxide was obtained. For using in the reactions, the graphite oxide aqueous suspension was ultrasonicated for 30 min to form graphene oxide.

4.3 | Synthesis of chitosan-functionalized graphene oxide (GO-Chit)^[24]:

To a canonical flask, a suspension was obtained by ultrasonic exfoliation of graphite oxide (150 mg) in SOCl_2 (30 ml) for 30 min. Then, the suspension was refluxed at 70°C for 24 hours. The product (GO-COCl) was gathered by filtration, washed with anhydrous tetrahydrofuran (THF) and then dried at room temperature. The carboxyl groups of GO were converted to acyl chloride (GO-COCl) *via* reaction with thionyl chloride. During this process, GO-COCl (140 mg) was first homogenized with 15 mL deionized water in an ultrasonic bath for 60 min. Then 20 ml of solution of acetic acid containing 1 g chitosan was added and the mixture was stirred for 1 h, followed sonicated for another 25 min and then the stirring was continued for another 24 h at room temperature. The product was washed three times with 2% acetic acid to remove the unreacted chitosan. The obtained chitosan grafted GO (GO-Chit) was filtered and washed with deionized water several times until the pH reached 7 and then dried at room temperature.

4.4 | Synthesis of graphene oxide-chitosan supported palladium complex (GO-Chit-Pd):

Pd nanoparticles were stabilized on the chitosan grafted GO (GO-Chit) based on the following procedure: the GO-Chit (50 mg) was dispersed in 20 ml of ethanol by sonication for 30 min. Subsequently, PdCl_2 (0.25 mmol, 44.3 mg) was added and the mixture was subjected to sonication for 5 min, then stirred for 24 h at room temperature. Then, the product was filtered and washed with distilled water for five times. The obtained catalyst (GO-Chit-Pd) was air-dried.

4.5 | General procedure for Buchwald-Hartwig amination reactions catalyzed by GO-Chit-Pd catalyst:

In a 25 ml round bottom flask, 3 mg of the catalyst GO-Chit-Pd was dispersed in 5 ml of DMF by sonication for 20 min at

room temperature, and then aryl halides (1 mmol), amines (1.2 mmol) and *t*-BuOK (1.5 mmol, 0.168 g) were added to this suspension and heated in an oil bath at 100 °C for required time. The reaction was followed by TLC. After completion of the reaction, the catalyst was separated by filtered. Then the mixture was cooled to room temperature and extracted with diethyl ether (3 × 10 ml). The products (**a-r**) were purified by column chromatography (n-hexane/ethyl acetate) to obtain the desired purity.

Products **a-r** are known compounds, and their NMR spectra are in accordance with those reported in the literature.^[26]

4.5.1 | 4-Phenylmorpholine (a)

¹HNMR (300 MHz, DMSO-*d*₆) 7.22–7.3 (2H, m), 6.80–6.91 (3H, m), 3.83 (4H, t, *J* = 4.6 Hz), 3.11 (4H, t, *J* = 4.5 Hz); ¹³CNMR (75 MHz, DMSO-*d*₆) 151.2, 129.0, 119.5, 115.3, 66.7, 49.0.

4.5.2 | 4-Morpholinobenzonitrile (c)

¹HNMR (250 MHz, CDCl₃) 7.47–7.53 (2H, m), 6.82–6.88 (2H, m), 3.82–3.86 (4H, m), 3.25–3.29 (4H, m).

4.5.3 | 4-(4-acetylphenyl)morpholine (d)

¹HNMR (250 MHz, CDCl₃) 7.83 (2H, d, *J* = 8.7 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 3.92–3.81 (4H, m), 3.33–3.21 (4H, m), 2.56 (3H, s); ¹³CNMR (62.9 MHz, CDCl₃) 196.3, 153.9, 130.3, 127.9, 113.2, 66.5, 47.5, 26.4.

4.5.4 | 4-(*p*-Tolyl)morpholine (h)

¹HNMR (250 MHz, CDCl₃) 7.07 (2H, d, *J* = 4.0 Hz), 6.85 (2H, d, *J* = 3.7 Hz), 3.85–3.89 (4H, m), 3.10–3.13 (4H, m), 2.27 (3H, s).

4.5.5 | 4-(4-Methoxyphenyl)morpholine (i)

¹HNMR (250 MHz, DMSO-*d*₆) 6.82–6.90 (4H, m), 3.86 (4H, t, *J* = 4.8 Hz), 3.77 (3H, s), 3.04 (4H, t, *J* = 4.8 Hz); ¹³CNMR (62.9 MHz, DMSO-*d*₆) 153.9, 145.6, 117.8, 114.4, 67.0, 55.5, 50.8.

4.5.6 | 1-Phenylpyrrolidine (l)

¹HNMR (250 MHz, CDCl₃) 7.26–7.31 (2H, m), 6.62–6.72 (3H, m), 3.32–3.37 (4H, m), 2.02–2.07 (4H, m).

4.5.7 | 1-Phenylpiperidine (m)

¹HNMR (250 MHz, DMSO-*d*₆) 7.22–7.30 (2H, m), 6.95 (2H, d, *J* = 7.9 Hz), 6.82 (1H, d, *J* = 7.8 Hz), 3.15 (4H, t,

J = 5.0 Hz), 1.65–1.75 (4H, m), 1.50–1.62 (2H, m); ¹³CNMR (62.9 MHz, DMSO-*d*₆) 152.5, 128.9, 119.5, 116.5, 50.5, 26.2, 24.2.

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