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FULL PAPER

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Synergetic catalytic effect of rGO, Pd, Fe_3O_4 and PPy as a magnetically separable and recyclable nanocomposite for coupling reactions in green media

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In this paper, rGO/Pd–Fe_3O_4@PPy as an efficient stable nanocomposite was synthesized. To understand the synergetic effects of rGO, Pd, Fe_3O_4 and Poly-Pyrrole, the performance of rGO/Pd–Fe_3O_4@PPy as a heterogeneous recyclable nanocatalyst in the green synthesis of C-C and C-O coupling products, as well as different conditions are studied. Synthesized rGO/Pd–Fe_3O_4@PPy was characterized by FT-IR, XRD, FE-SEM, EDS, TGA and AFM analysis. Best results are obtained under sonication in H_2O for C-C coupling and by ball-milling for C-O coupling. The benefits of this method include: green solvents and conditions, absence of external base, low reaction times with high yield and easy work-up method.

KEYWORDS
rGO/Pd–Fe_3O_4@PPy, coupling reactions, sonochemical condition, ball-mill

1 | INTRODUCTION

Increasing attention has been paid to nanocomposites in recent years due to their abundant potential applications in different categories especially in catalysis science. The synergetic catalytic effect in nanocomposites which is collaborations or interactions between certain catalytic components and the support can improved catalytic activity and reduced side effects to achieve more environmental-friendly performance. The catalytic performance in nanocomposite is fundamentally dependent on the structure of components, so selecting proper components are the determining stage in the synthesis of these compounds.[1]

Graphene, new charming member of carbonaceous materials, discovered and isolated as a single atomic layer of carbon in 2004 which lead to Nobel Prize in Physics in 2010. This world's first two-dimensional substance may be the most adaptable material accessible to researchers. Hummers and Offeman advanced Hummers' method to synthesize Graphene and is still used commonly.[2] The fascinating tough, strong and thin character of graphene, make it an extraordinary support material for the catalytic application. Most ordinarily used form of graphene for catalytic application is reduced graphene oxide (rGO). rGO interacts with metals simply, so despite the difficulty in formation of nanocomposite with inorganic materials, nanocomposite of rGO with metal can be synthesized effectively without any noteworthy problems.[2,3] The main problem in metal nanoparticle applications include nanoparticle agglomeration, this can decrease the catalytic ability as nanocatalyst. Metal particles must be produced with ultrafine sizes with a high surface area which increase their catalytic ability. Particularly, rGO are a promising material in order to disperse metal nanoparticles since loading metal nanoparticles on rGO surface can avoid aggregation.[4–11]

The foundations of many natural products and pharmaceuticals contain substituted aromatic structures, biaryls and diaryl ethers. Palladium complexes can carry out various kinds of C-X (C, O and N) coupling reactions starting from aryl and heteroaryl halides. An important C-C coupling reaction is Suzuki reaction that's because of that in 2010, Heck, Negishi and Suzuki were awarded the

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Nobel Prize in Chemistry. Due to air- and moisture-stability of organoboranes, Suzuki–Miyaura cross-coupling is the most effective approach for the synthesis of C-C bonding and biaryl compounds. This cross coupling reaction has many advantages over other coupling methods for creating C-C bonding containing steadiness of its reagents and raw materials, mild conditions and the ease of handling.[12] The Suzuki reaction has been used broadly in the synthetic organic chemistry, synthesis of natural products and pharmaceuticals.[13] Another important coupling reaction is C-O coupling. Several compounds have C-O bond in their structures such as: ethers, epoxides, lactones and carbonate derivatives. A synthetic challenge was shaped to form aryl-oxygen linkage under mild condition owing to the importance of aryl ethers. One solution could be raised to this challenge: Pd-catalyzed system. There is some literatures using Pd for C-O coupling with excellent results.[14]

In chemical reactions, big quantities of organic solvents are used to gain final products. Eco-friendly media and solvent free reactions are effective steps to reduce the toxic solvent effects. In the field of green coupling reactions, solvent and media selection for waste management are based on economic and safety considerations. Around sustainable development and sustainability, presenting an easy applicable method simplifies the access way to green chemistry.[15]

Here, due to palladium applications in coupling reactions,[16–19] and together to benefit of the abundant chemical properties of graphene, we decided to use Pd-GO nanocomposite to use in coupling reactions. To improve the dispersity of Pd nanoparticles and to avoid agglomeration of nanoparticles, polypyrrole as a special reducing agent was selected to synthesize efficient nanocomposite. In addition of this, to take advantageous of easy separating method and reusability of Fe_3O_4, Fe_3O_4/rGO supports was prepared to load Pd nanoparticles.[4] Synergistic effect of rGO, Pd, Fe_3O_4 and PPy was led to well-defined and high impact nanocomposite.

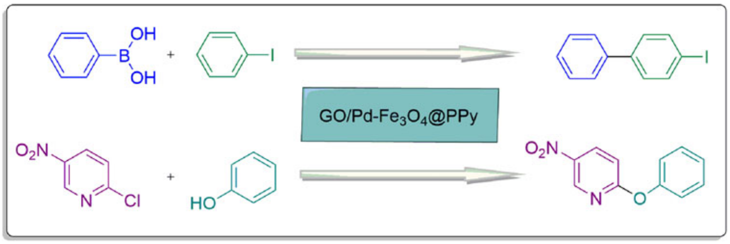
Previously, other graphene-based catalysts have been reported to have had very good results for coupling reaction,[20] so we decided to study this reaction with rGO/Pd–Fe_3O_4@PPy nanocomposite. To use synergistic effect of rGO, Pd, Fe_3O_4 and PPy, rGO/Pd–Fe_3O_4@PPy nanocomposite was synthesized successfully[4] and the catalytic property of synthesized nanocomposite was studied first in Suzuki C-C coupling reaction under sonication in H_2O and second in C-O coupling reaction by ball-milling. To the best of our Knowledge, there is no report about using the heterogeneous rGO/Pd–Fe_3O_4@PPy nanocomposite for catalysing the Suzuki C-C and C-O coupling reactions. It is necessary to mention that there have been a few reports for coupling reactions in the absence of external base. Moreover, this method has other advantages such as green solvents and conditions, low reaction times with high yields, good catalytic activity, magnetically separable and reusable catalyst, and easy work-up method (Scheme 1).

2 | EXPERIMENTAL

All chemicals and solvents were purchased from Merck and Aldrich. The ultrasonic reactions are carried out in an Elmasonic S 60 H (220–240 v) with a frequency of 37 kHz, ultrasonic power effective of 150 W and power consumption total of 550 W, and ball-mill device was Retsch Mixer Mill MM 400. Field emission scanning electron microscopy (FE-SEM) images were recorded by Sigma Zeiss, energy dispersive X-ray (EDX) spectra were taken on a Numerix DXP-X10P, the FT-IR spectroscopy were recorded by Shimadzu IR-470 spectrometer, NMR spectra were recorded by Bruker DRX-500 Avance spectrometer, X-ray diffraction (XRD) measurements were taken on a JEOL JDX-8030, Atomic force microscopy (AFM) analysis were recorded by DUALSCOPETM DS 95 series, TGA analysis was recorded by Netzsch - TGA 209 F1 and melting points were checked out by Electrothermal 9100 apparatus.

2.1 | Preparation of the rGO/Pd–Fe_3O_4@PPy nanocomposite

GO was prepared using Hummer's method.[21] For the synthesis of rGO/Pd–Fe_3O_4@PPy, 0.5 g of GO was dispersed in 30 ml of water for 30 min, 1 ml of pyrrole was added into it and stirred for 30 min. To this mixture, 10 ml solution of 0.035 g $PdCl_2$ and 0.4 g of $FeCl_3{\cdot}6H_2O$ was added and stirred for 5.0 h. 0.1 g of $FeCl_2{\cdot}4H_2O$ and 10 ml of $NH_3{\cdot}H_2O$ were added to above mixture under N_2 atmosphere at room temperature for 2.0 h. The synthesized products were isolated and washed with ethanol and dried by vacuum.[4]



SCHEME 1 Suzuki and C-O coupling catalyzed by rGO/Pd–Fe_3O_4@PPy

2.2 | General procedure for the C-C coupling reaction

In a typical reaction, 2 mmol of aryl halide, 2 mmol of phenylboronic acid and the 30 mg of rGO/Pd–Fe_3O_4@PPy were sonicated together in 5 ml of H_2O at 70 °C (Table 1). The catalyst was easily separated with an external magnet. Then, the products were extract with ethyl acetate. The products in the form of crystals were obtained by filtration and washing with n-hexane. Other products were obtained by chromatography with n-hexane: EtOAc - 9:1. The isolated products were analyzed by their melting points and some of them were analyzed by NMR spectroscopy.

2.3 | General procedure for the C-O coupling reaction

Vibrational frequency of ball-milling device was 50 Hz, its grinding jars were stainless steel and the size of each of them was 10 ml. Two balls for ball-milling were used and size of milling balls are 10 mm. In a typical reaction, 2 mmol of substituted phenols, 2 mmol of 2-chloro-5-nitropyridine and the 30 mg of catalyst were milled in 30.0 Hz and the completion of the reaction was monitored by TLC (Table 2). After completion of the reaction, the contents of ball mill vessel were transferred to a 10 ml beaker containing 5 ml of ethanol. The catalyst was easily separated with an external magnet. The products were obtained by filtration and washing with hexane. The isolated products were analyzed by their melting points and some of them were analyzed by NMR spectroscopy.

2.4 | Selected spectral data

2.4.1 | [1,1′:3′,1”-Terphenyl]-2′-ol (3d)

65% yield. White solid. M.p.: 103–105 °C. ^1H NMR (500 MHz, $CDCl_3$) 7.63–7.65 (m, 4H), 7.54–7.57 (m, 4H), 7.45–7.48 (tt, J = 4.2 Hz, J = 1.3 Hz, 2H), 7.36–7.37 (d, J = 7.6 Hz, 2H), 7. 13-7.16 (dd, J = 7.6 Hz, 1H), 5.50 (s, 1H, OH).

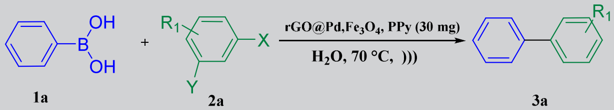
2.4.2 | Benzophenone (3e)

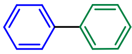
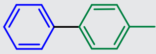
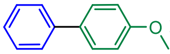
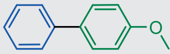
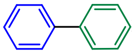
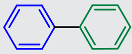
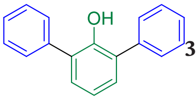
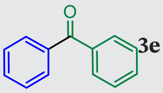
60% yield. White solid. M.p.: 50–51 °C. ^1H NMR (500 MHz, $CDCl_3$) 7.81–7.83 (m, 4H), 7.57–7.61 (m, 2H), 7.47–7.50 (m, 4H).

2.4.3 | 5-Nitro-2-phenoxypyridine (6a)

92% yield. Yellow solid. M.p.: 8 6-87°C. ^1H-NMR (500 MHz, $CDCl_3$) 9.09 (d, J = 2.7 Hz, 1H, Py-6-H),

TABLE 1 Suzuki cross-coupling catalyzed by rGO/Pd–Fe_3O_4@PPy[a]

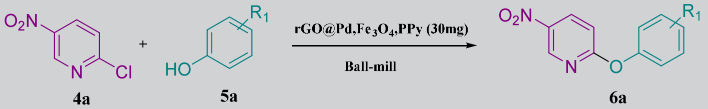


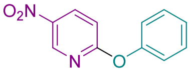
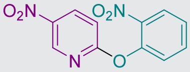
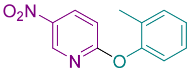
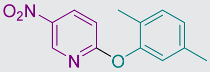
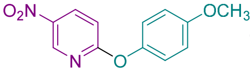
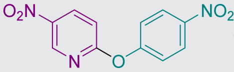
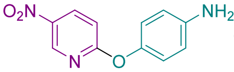
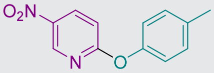
Entry	R_1	X	Y	Product	Time (min)	Yield[b] (%)
1	H	I	H	 3a	30	95
2	4-CH_3	I	H	 3b	60	91
3	4-OCH_3	I	H	 3c	45	93
4	4-OCH_3	Br	H	 3c	70	88
5	H	Br	H	 3a	60	85
6	H	Cl	H	 3a	180	50
7	4-OH	Cl	Cl	 3d	180	65
8	H	COCl	H	 3e	150	60

[a] rGO/Pd–Fe_3O_4@PPy catalyst, 70 °C, under sonication, H_2O as solvent,

[b] isolated yield.

TABLE 2 C-O-coupling catalyzed by rGO/Pd–Fe_3O_4@PPy[a]



Entry	R_1	Product	Time (min)	Yield[b] (%)
1	H	 **6a**	90	92
2	2-NO_2	 **6b**	120	80
3	2-CH_3	 **6c**	75	85
4	2, 5-CH_3	 **6d**	60	87
5	4-OCH_3	 **6e**	60	90
6	4-NO_2	 **6f**	120	82
7	4-NH_2	 **6g**	90	88
8	4-CH_3	 **6h**	75	90

[a] rGO/Pd–Fe_3O_4@PPy catalyst, ball-milling, room temperature,

[b] isolated yield.

8.51–8.53 (dd, J = 9.0 Hz, J = 2.7 Hz, 1H, Py-4-H), 7.50–7.52 (m, 2H, Ph-2-H, Ph-6-H), 7.3 4-7.37 (m, 1H, Ph-4-H), 7. 20-7.22 (m, 2H, Ph-3-H, Ph-5-H), 7.08 (d, 1H, J = 9.0 Hz, Py-3-H).

2.4.4 | 4-(5-Nitropyridin-2-yl-amino) phenol (6 g)

Yield: 88%. Brown solid. ^1H NMR (500 MHz, $CDCl_3$) 9.09 (d, J = 2.7 Hz, 1H, Py-6-H), 8. 22-8.24 (dd, J = 9.1 Hz, J = 2.7 Hz, 1H, Py-4-H), 7. 24-7.25 (dd, J = 6.5 Hz, J = 2.1 Hz, 2H, Ph-2-H, Ph-6-H), 7.07 (br, NH_2), 6.91–6.93 (dd, J = 6.5 Hz, J = 2.2 Hz, 2H, Ph-3-H, Ph-5-H), 6.61 (d, J = 9.3 Hz, 1H, Py-3-H).

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the rGO/Pd–Fe_3O_4@PPy catalyst

Driving force for the assembly of Pd, PPy and Fe_3O_4 nanoparticles are the electrostatic force, π– π^* interactions, and also based on ionic interactions and depends on the negative charges of the carboxylic and hydroxyl groups and positive charges of Pd^{2+} and Fe^{3+}.

In the synthesis of rGO/Pd–Fe_3O_4@PPy nanocomposite, the reduction of GO, the polymerization of the pyrrole, the synthesis of Pd and Fe_3O_4 nanoparticles and the reduction of GO were completed in one stage. $PdCl_2$ and $FeCl_3.6H_2O$ were used as the initiator for the pyrrole polymerization. The Pd^{2+} were reduced to Pd nanoparticles and Fe^{3+} ions were reduced to Fe^{2+} ions during the polymerization process. By NH_3 and under basic condition, Fe_3O_4 nanoparticles were prepared and together

FIGURE 1 FE-SEM image of rGO/Pd–Fe_3O_4@PPy

with Pd were deposited on the GO and covered by the PPy layer. By polymer and $NH_3.H_2O$, GO nanosheet were converted to rGO nanosheet.

From FE-SEM image of rGO/Pd–Fe_3O_4@PPy in Figure 1, we have realized that the Pd and Fe_3O_4 nanoparticles deposited on the graphene surface and covered with polypyrrole. So, nanaoparticles are not observed in FE-SEM image. Also, no aggregation appears outside of the GO nanosheet and nanoparticles uniformly occupy the GO surface. As well, it indicates a complete perfect combination of GO and the nanoparticles.

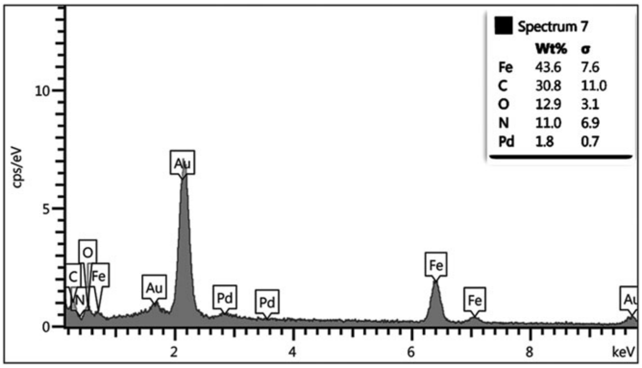


FIGURE 2 EDX image of rGO/Pd–Fe_3O_4@PPy

From EDX spectra in Figure 2, we can identify what is synthesized rGO/Pd–Fe_3O_4@PPy nanocomposite particular elements are and their relative proportions. X-ray energies are used to identify and quantify the elements present in a nanocomposite. From its peaks positions, existence of C (43.6%), Fe (30.8%), O (12.9%), N (11%) and Pd (1.8%) in this nanocomposite can be confirmed.

Fourier-transform infrared (FT-IR) spectrum was shown in Figure 3. The stretching mode of the C=C in the graphene ring was observed at 1560 cm^{-1}, the peak at 1178 cm^{-1} is related to the vibrations of C-H, the band at 1035 cm^{-1} is assigned to the C-H bending mode and the band at around 557 cm^{-1} corresponds to the stretching mode of Fe-O. Also the characteristic peak at 912 cm^{-1} is attributed to pyrrole-ring deformation.

X-ray diffraction (XRD) pattern of rGO/Pd–Fe_3O_4@PPy was shown in Figure 4. Six sharp diffraction peaks appear at 2θ = 30.00, 34.75, 42.48, 53.36, 56.53, and 61.88, which are respectively indexed to (220),

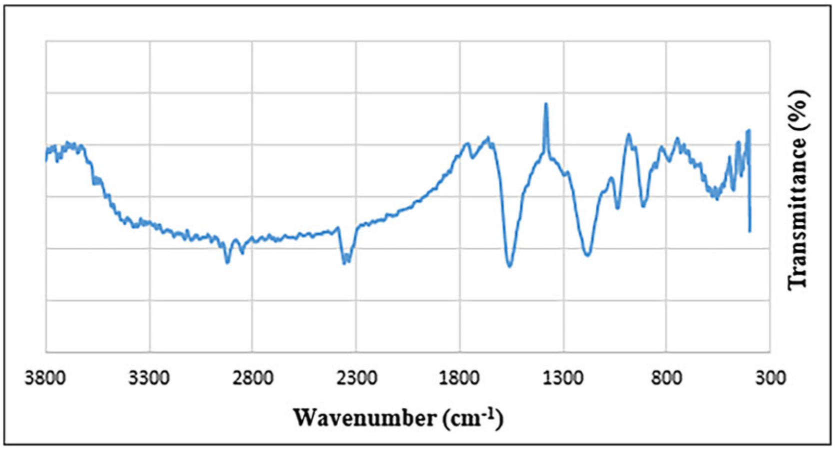


FIGURE 3 FT-IR spectra of rGO/Pd–Fe_3O_4@PPy

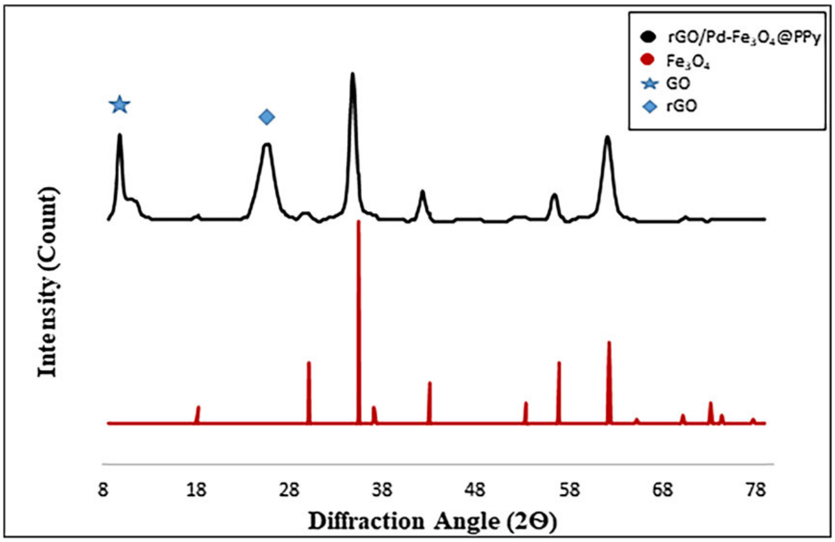


FIGURE 4 XRD pattern of rGO/Pd–Fe_3O_4@PPy

(311), (400), (422), (511), and (440) and confirmed the face-centered cubic lattice of Fe_3O_4 nanoparticles (JCPDS no. 19-0629). As well, for rGO, the peak at around $2\theta = 9.8$ for GO has noticeably less sharpness than pure GO, and a new peak appears at $2\theta = 26.04$ owing to the reduction of intercalated oxygen functionalities of GO. Due to the synchronous addition of $FeCl_3$, $FeCl_2$ and Pd, Pd was placed between the crystalline layers of Fe_3O_4. The atomic radius of palladium is larger than iron, so according to Bragg's law which is $2d\sin\theta = n\lambda$, insertion of Pd in structure cause to increase in d and decrease in θ. This cause the shift to smaller degree in XRD pattern.

The surface of rGO/Pd–Fe_3O_4@PPy nanocomposite was shown in AFM images in Figure 5. As can be seen, the thickness of rGO/Pd–Fe_3O_4@PPy is about 0.8 nm

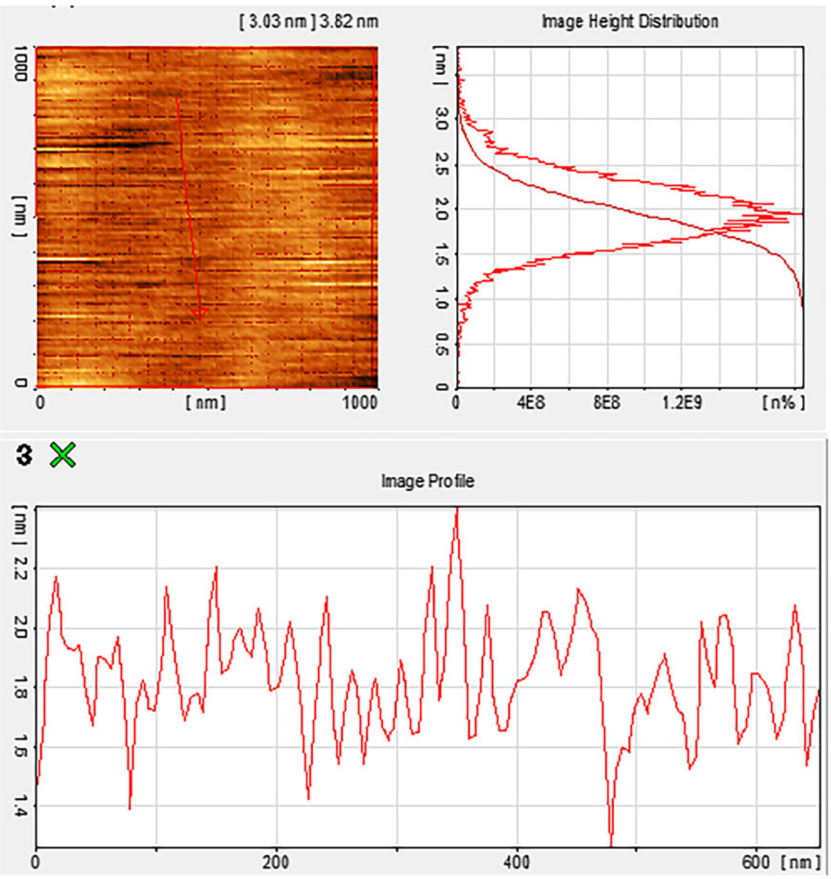


FIGURE 5 AFM analysis of rGO/Pd–Fe_3O_4@PPy

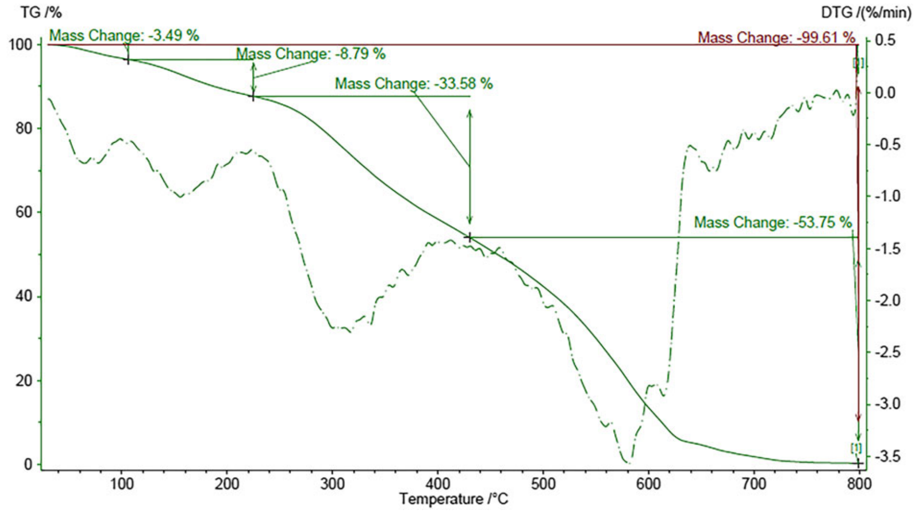
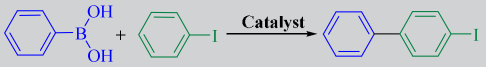


FIGURE 6 TGA analysis of rGO/Pd–Fe_3O_4@PPy

which completely in agreement with reported single layer GO. Studying AFM analysis also was done using the height distribution histograms which was about 2 nm.

In TGA analysis, the weight loss of sample mass is measured over increasing in temperature. From Figure 6, weight loss observed below 120 °C is because of the loss of moisture and the evaporation of water (−3.49%). In the temperature between 120-240 °C, the observed weight loss is due to the decomposition of the oxygen species present on the substrate surface which have not been reduced during synthesis (−8.79%). Between 240-400 °C, layers of PPy was decomposed on rGO surface (−33.58%). This analysis was carried out in air, so complete decomposition of nanocomposite is up to 660 °C.

TABLE 3 Optimizing condition for Suzuki cross-coupling catalyzed by rGO/Pd–Fe_3O_4@PPy[a]



Entry	Catalyst	Loading (mg)	Solvent	Condition/Temp. (°C)	Time (min)	Yield[b] (%)
1	-	-	EtOH	reflux	180	No product
2	rGO@Pd,Fe_3O_4,PPy	40	EtOH	reflux	180	40
3	rGO@Pd,Fe_3O_4,PPy	40	H_2O	reflux	180	55
4	rGO@Pd,Fe_3O_4,PPy	40	Solvent-free	100	180	45
5	rGO@Pd,Fe_3O_4,PPy	40	H_2O	60	180	30
6	rGO@Pd,Fe_3O_4,PPy	40	H_2O	25	180	20
7	rGO@Pd,Fe_3O_4,PPy	40	Solvent-free	Ball milling	180	60
8	rGO@Pd,Fe_3O_4,PPy	40	H_2O	Ultrasonic/25	180	60
9	rGO@Pd,Fe_3O_4,PPy	40	H_2O	Ultrasonic/50	180	75
10	rGO@Pd,Fe_3O_4,PPy	40	H_2O	Ultrasonic/70	30	95
11	rGO@Pd,Fe_3O_4,PPy	30	H_2O	Ultrasonic/70	30	95
12	rGO@Pd,Fe_3O_4,PPy	20	H_2O	Ultrasonic/70	180	70

[a] rGO/Pd–Fe_3O_4@PPy catalyst, Aryl halide and phenylboronic acid,

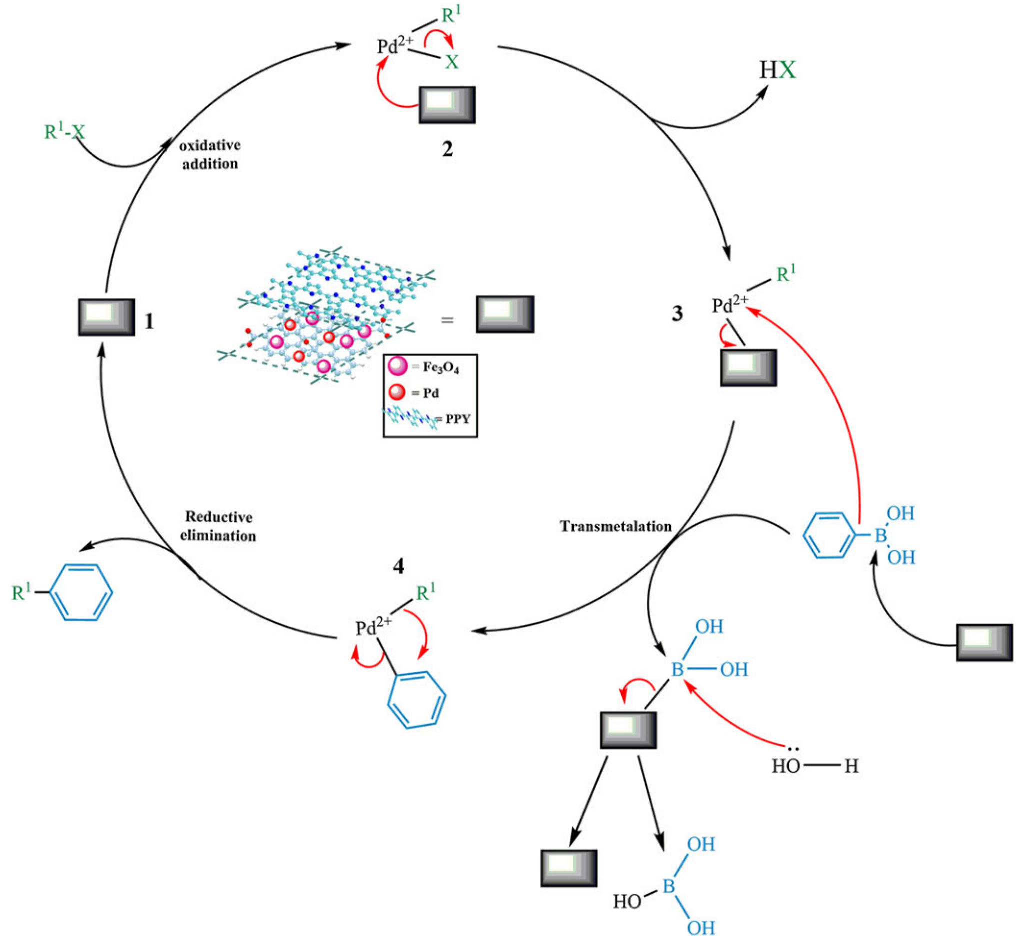
[b] isolated yield.

TABLE 4 Optimizing condition for C-O-coupling catalyzed by rGO/Pd–Fe_3O_4@PPy[a]

Entry	Catalyst	Loading (mg)	Solvent	Condition/Temp.(°C)	Time (min)	Yield[b] (%)
1	-	-	EtOH	reflux	180	No product
2	rGO@Pd,Fe_3O_4,PPy	40	EtOH	reflux	180	50
3	rGO@Pd,Fe_3O_4,PPy	40	H_2O	reflux	180	60
4	rGO@Pd,Fe_3O_4,PPy	40	Solvent free	100	180	40
5	rGO@Pd,Fe_3O_4,PPy	40	H_2O	60	180	45
6	rGO@Pd,Fe_3O_4,PPy	40	H_2O	25	180	25
7	rGO@Pd,Fe_3O_4,PPy	40	H_2O	Ultrasonic/25	180	40
8	rGO@Pd,Fe_3O_4,PPy	40	H_2O	Ultrasonic/50	180	55
9	rGO@Pd,Fe_3O_4,PPy	40	H_2O	Ultrasonic/70	180	70
10	rGO@Pd,Fe_3O_4,PPy	40	Solvent-free	Ball-mill	90	92
11	rGO@Pd,Fe_3O_4,PPy	30	Solvent-free	Ball-mill	90	92
12	rGO@Pd,Fe_3O_4,PPy	20	Solvent-free	Ball-mill	240	80

[a] rGO/Pd–Fe_3O_4@PPy catalyst, substituted phenols and 2-chloro-5-nitropyridine,

[b] isolated yield.



SCHEME 2 Proposed mechanism for Suzuki reaction

3.2 | Investigation of the catalytic ability of the rGO/Pd–Fe_3O_4@PPy nanocatalyst for C-C and C-O coupling reactions

After characterization of the catalyst, the catalytic ability of rGO/Pd–Fe_3O_4@PPy was investigated in C-C coupling reaction over a systematic study. Hence, the reaction of 2 mmol Aryl iodide and 2 mmol phenylboronic acid was studied as the model reaction. The reaction conditions were optimized to determine appropriate solvent, temperature, amount of catalyst and device for the synthesis of desired product.

To analyze the various conditions for the C-C coupling reaction, in the no-catalyst condition in EtOH and reflux, no product obtained in 180 min. But the reaction in 180 min and in the presence of rGO/Pd–Fe_3O_4@PPy in reflux had 40% and 55% yield of product in EtOH and H_2O, respectively. Also had 45% yield in solvent free condition and 100 °C. So H_2O was selected as a reaction media. Also the reaction was studied by ultrasonic and ball-milling technique that ultrasonic showed better results in 70 °C (30 min, 95%). To optimize the amount of catalyst, after addition of 20 mg of the catalyst, the yield of the desired product was about 70% in 180 min. Furthermore, higher yield was obtained in H_2O under sonication with 30 mg of catalyst in shorter reaction time. It was observed that more than 30 mg, there is no noticeable change in the yield of product (Table 3).

Studying the catalytic effect in C-O coupling was performed in various conditions. In the absence of catalyst, the product was not produced in 180 min and reflux.

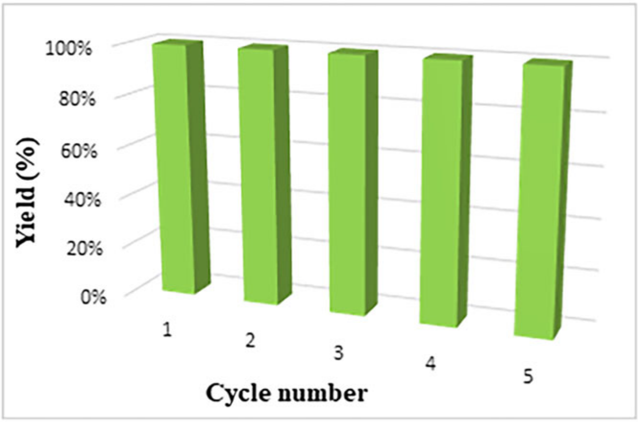


FIGURE 7 Recycling result of the Suzuki coupling reaction

TABLE 5 Study of the efficiency of the rGO/Pd–Fe_3O_4@PPy nanocatalyst compared with previous reports[a]

Entry	Catalyst	Base	Solvent	Temperature (°C)	Time (min)	Yield[b] (%)	Ref.
1	Pd-slGO-60	K_2CO_3	EtOH	25	60	44	[22]
2	f-GO [Pd (C^N) Cl (dmso)]nanohybride	K_2CO_3	Toluene	25	30	94	[23]
3	Pd@AGu@MGO	K_2CO_3	H_2O	25	60	95	[24]
4	Sr/Alg/CMC/GO/Au composites	NaOH	H_2O	80	240	98	[25]
5	rGO/Pd-Fe_3O_4@PPy	-	H_2O	70	30	92	This work

[a] Aryl halide and phenylboronic acid for Suzuki coupling,

[b] isolated yield.

The yield of the reaction in the presence of rGO/Pd–Fe_3O_4@PPy in the same condition is 50% in 180 min. to study the solvent effect, between EtOH, H_2O and solvent free condition, H_2O had the yield of 60% in 180 min which was the best among them. But by using ball-mill as a solvent free device, best yield (90 min, 92%) was gained compared to sonication and reflux (Table 4).

To study the scope of these methods for C-C and C-O couplings, the optimized reaction conditions were established to other derivatives and the results have been reported in Table (3, 4). After monitoring the reaction by TLC and completion of the reaction, the catalyst was isolated by external magnet from the reaction mixture and the product was filtrated by chromatography. Good to high yields of the desired products were obtained under the optimized conditions in reasonable reaction times. Both electron-withdrawing and electron-donating groups involved in the optimized reaction conditions to gain desired products. In general, the nature of the aryl substituents has an important impact on the reaction rate.

The proposed mechanism starts with addition of the organohalide to the Pd(0) to oxidized and form a Pd (II) complex which followed by participation of basic group of PPy. By this action, driving force for next action is supplied. By adding the catalyst to organoborane, this compound by nucleophilic addition is added to gain compound **3**. Because of H_2O media and after addition of H_2O to organoborane compound, acid boric as byproduct is formed and catalyst is returned to catalytic cycle. By transmetallation process, compound 4 is formed (Scheme 2).

Designing recoverable nanocatalysts is a highly challenging field from green chemistry, economic and environmental viewpoint. In many reported methods, catalysts are ruined and it loses its catalytic properties after one reaction. As can be seen in Figure 7, the recycled rGO/Pd–Fe_3O_4@PPy can be used in up to five cycles with negligible lose in the catalytic activity.

We compared our gained results of Suzuki reaction with reported results, taking the reactions of Aryl halide and phenylboronic acid for Suzuki coupling (Table 5).[22–25] These factors make our nanocomposite as nanocatalyst superior to the others: absence of base as co-catalyst, low reaction times with high yield in mild reaction conditions and easy work-up method.

4 | CONCLUSION

In summary, we have developed an efficient method for coupling reactions using rGO/Pd–Fe_3O_4@PPy nanocomposite with a very stable character of catalyst and high yield of products. These graphene-based nanocomposite exhibit great catalytic activity and stability for loading Pd nanoparticles. Coupling reactions has been setup and several functional groups studied, representing the high adaptability of the method. High yields and short reaction times have been gained in the absence of external base in this green procedure for C-C and C-O couplings in H_2O and ball-mill, respectively. Also this catalyst can be recycled easily from reaction media by external magnet. Catalytic activity of this nanocomposite was attributed to the synergetic effect of rGO, Pd, Fe_3O_4 and PPy.

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REFERENCES

[1] J. Shi, *Chem. Rev.* **2013**, *113*, 2139.

[2] a) A. K. Geim, *Science* **2009**, *324*, 1530. b) A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.

[3] T. Vats, S. Dutt, R. Kumar, P. F. Siril, *Sci. Rep.* **2016**, *6*, 33053.

[4] T. Yao, H. Wang, Q. Zuo, J. Wu, X. Zhang, F. Cui, T. Cui, *Chem. – An Asian J.* **2015**, *10*, 1940.

[5] H. Chen, Y. Li, F. Zhang, G. Zhang, X. Fan, *J. Mater. Chem.* **2011**, *21*, 17658.

[6] T. Wu, L. Zhang, J. Gao, Y. Liu, C. Gao, J. Yan, *J. Mater. Chem. A* **2013**, *1*, 7384.

[7] C. Huang, C. Li, G. Shi, *Energ. Environ. Sci.* **2012**, *5*, 8848.

[8] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262.

[9] X. Zhou, X. Huang, X. Qi, S. Wu, C. Xue, F. Y. C. Boey, Q. Yan, P. Chen, H. Zhang, *J. Phys. Chem. C* **2009**, *113*, 10842.

[10] P. Raveendran, J. Fu, S. L. Wallen, *J. Am. Chem. Soc.* **2003**, *125*, 13940.

[11] X. Chen, G. Wu, J. Chen, X. Chen, Z. Xie, X. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 3693.

[12] R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461.

[13] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

[14] G. Mann, C. Incarvito, A. L. Rheingold, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 3224.

[15] C. Capello, U. Fischer, K. Hungerbuhler, *Green Chem.* **2007**, *9*, 927.

[16] S. Li, W. Zhang, F. Chen, R. Chen, *Mater. Res. Bull.* **2015**, *66*, 186.

[17] W. Zhang, H. Zhao, Z. Lu, F. Chen, R. Chen, *Chem. Lett.* **2015**, *44*, 1371.

[18] S. Li, W. Zhang, M.-H. So, C.-M. Che, R. Wang, R. Chen, J. Mol, *Catal. A: Chem.* **2012**, *359*, 81.

[19] W. Zhang, Q. Wang, F. Qin, H. Zhou, Z. Lu, R. Chen, *J. Nanosci. Nanotechnol.* **2011**, *11*, 7794.

[20] S. J. Hoseini, H. G. Khozestan, R. H. Fath, *RSC Adv.* **2015**, *5*, 47701.

[21] H. Ghafuri, N. Joorabchi, A. Emami, H. R. Esmaili Zand, *Ind. Eng. Chem. Res.* **2017**, *56*, 6462.

[22] S.-i. Yamamoto, H. Kinoshita, H. Hashimoto, Y. Nishina, *Nanoscale* **2014**, *6*, 6501.

[23] R. Hashemi Fath, S. J. Hoseini, *J. Organomet. Chem.* **2017**, *828*(Supplement C), 16.

[24] L. Ma'mani, S. Miri, M. Mahdavi, S. Bahadorikhalili, E. Lotfi, A. Foroumadi, A. Shafiee, *RSC Adv.* **2014**, *4*, 48613.

[25] M. Thomas, M. U. D. Sheikh, D. Ahirwar, M. Bano, F. Khan, *J. Colloid Interface Sci.* **2017**, *505*(Supplement C), 115.

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