Received: 19 December 2019 | Revised: 13 March 2020 | Accepted: 12 April 2020
DOI: 10.1002/aoc.5775

FULL PAPER

Applied Organometallic Chemistry WILEY

Synthesis of Pd@graphene oxide framework nanocatalyst with enhanced activity in Heck-Mizoroki cross-coupling reaction

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Funding information
Shahid Chamran University of Ahvaz, Grant/Award Number: 1398

A new method was developed for producing a catalyst involving a Pd nanoparticle (NP) embedded in a graphene oxide framework (Pd@GOF) with ordered macro- and mesoporous structures. First, 5,5′-diamino-2,2′-bipyridine was selected as cross-linking for covalent modification of GO nanosheets to prepare a three-dimensional (3D) framework with interlayer spaces in which well-dispersed and ultra-small Pd NPs in situ grew and embedded the framework. The synthesized nanopores 3D Pd@GOF can act as nanoreactors to help the reaction substrates thoroughly come into contact with the surface of Pd NPs, thereby exhibiting high activity toward the Heck reaction, rarely reported concerning Pd NPs supported on one-side functionalized graphene. The Pd@GOF catalyst can be used 10 times without any significant loss in the catalytic activity, confirming the long-term stability of this catalyst. Therefore, the covalently assembled GOF was proposed as a universal platform for hosting noble metal NPs to construct the desired metal@GOF nanocatalyst with improved activity and stability that can be used in a broad range of practical applications.

KEYWORDS
graphene oxide frameworks, Heck reaction, heterogeneous catalyst, palladium nanoparticles

1 | INTRODUCTION

Three-dimensional graphene materials (3DGMs) with porous structures have a large specific surface area, tunable porosity, low density, and excellent mechanical strength.[1–3] These materials have shown promising support in the preparation of heterogeneous catalysts. Specifically, their structures are conducive to stabilizing metal nanoparticles (NPs) and restricting their growth, which are the basic features of heterogeneous catalysts.

The past several years have witnessed the development of various synthetic strategies toward 3DGMs with diverse morphologies, structures, and properties, including self-assembly, template-assisted preparation, and direct deposition.[2,3] Structures of 3DGMs are often formed based on noncovalent interactions such as electrostatic, hydrogen bonding, and Van der Waals interactions, which are insufficiently durable during the catalytic process.[4–8] An important strategy for improving the stability of 3DGMs is the covalent construction of frameworks in stabilizers as linkers.[9] Among the stabilizers, monomers with two functional groups such as polyethylenimine and ethylenediamine,[10] *p*-phenylenediamine,[11] poly(oxypropylene)diamines,[12] triethylenetetramine,[2] benzene-1,4-diboronic acid or its derivatives,[13] 1,4-phenylenediisocyanate,[14] *n*-alkylamines,[15] and 1,2,4,5-benzenetetraamine[16] have been recently reported for cross-linking to the preparation of graphene oxide frameworks (GOFs). However, to our knowledge, only a few studies have reported a coordination-assisted synthetic approach toward encapsulated NPs inside the space of GOFs.[2,13] Most recently,

https://doi.org/10.1002/aoc.5775

Tran et al.[13] reported a new synthetic method comprising Pd NPs encapsulated in GOF (Pd@GOF) prepared through the cross-linking of GO with benzene-1,-4-diboronic acid. The catalytic activity of the nanocatalyst was investigated in the Suzuki-Miyaura cross-coupling reaction.

Herein, we demonstrate a novel and facile method for confining Pd NPs inside the space of a new GOF. In this fabrication process, GO layers are primarily intercalated by two-side covalent linkers with 5,5′-diamino-2,2′-bipyridine to form a new GOF. The porous structures of the GOF are utilized for the in situ growth of Pd NPs. Therefore, the formed Pd NPs are dispersed with a narrow particle-size distribution. Pd@GOF can effectively prevent the direct exposure of trapped Pd NPs and preserve their stabilization. The coordination effect between the N atom of bipyridine and Pd can further suppress the accumulation of the Pd NP. The catalytic activity of the well-defined nanocatalyst is then investigated in the Heck-Mizoroki cross-coupling reaction.

2 | RESULTS AND DISCUSSION

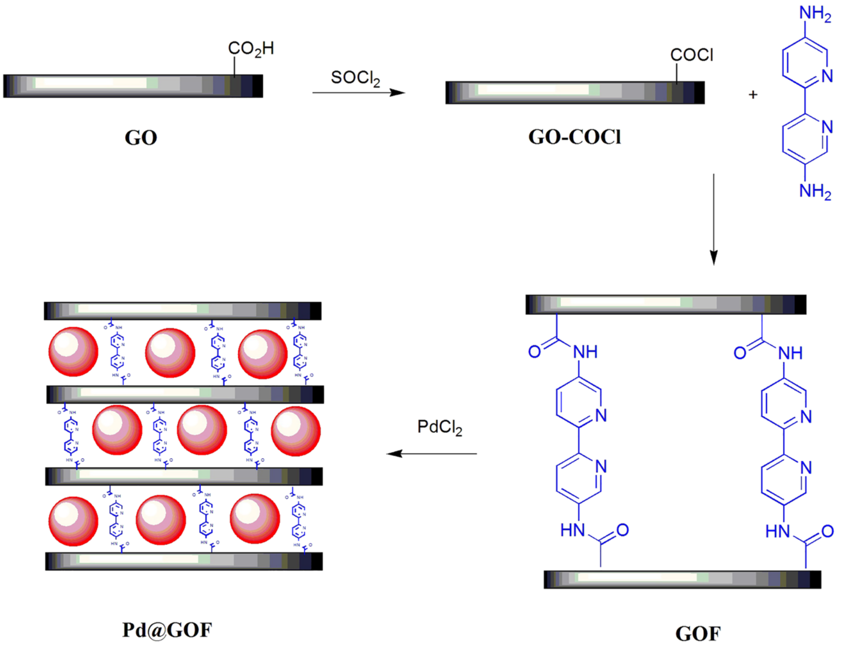
Regarding the synthesis and use of metal NPs in organic reactions,[17] we report here the synthesis of Pd@GOF nanocatalyst to use in the Heck reaction of various aryl iodides, bromides, and chlorides with styrene.

The synthesis of Pd@GOF is shown in Scheme 1. The framework was generated by the covalent linking of carboxyl (–COOH) groups of GO with the amino (–NH_2) groups of bipyridine. As shown, the first graphene oxide refluxed in $SOCl_2$ generated intermediate GO–COCl. Next, 5,5′-diamino-2,2′-bipyridine was reacted with GO–COCl layers for the synthesis of GOF. After GOF was washed and dried, the structures were analyzed using Fourier-transform infrared (FT-IR) spectroscopy (Figure 1).

The IR spectrum of GO revealed the characteristic stretching vibrations corresponding to O–H at 3300–3500 cm^{-1}, C=O at 1736 cm^{-1}, C=C at 1624 cm^{-1}, and C–O at 1054 cm^{-1}. After cross-linking with 5,5′-diamino-2,2′-bipyridine, the peak at 1736 cm^{-1} almost disappeared, and a new peak appeared at about 1700 cm^{-1}, which represents C=O in the amide group. To synthesize Pd@GOF, $PdCl_2$ was added to the ethanol solution of the GOF. Palladium was coordinated with the N atom of bipyridine present in the GOF. The chemical structure, framework, and morphology of the catalyst were characterized using FT-IR, X-ray diffraction (XRD), atomic absorption spectrometry (AAS), and transmission electron microscopy (TEM) spectroscopy. In the IR spectrum of Pd@GOF, a new peak emerged at 528 cm^{-1} corresponding to the N–Pd band.

Figure 2 represents the XRD spectra of Pd@GOF where GOF showed a characteristic peak at $2\Theta = 26°$, which is the same as that of GO,[18] confirming that the composite preserves the structure of GO. A significant Pd characteristic peak was obtained at 40.1°, indicating a successful reduction in palladium ion to Pd(0). The other two peaks at 47° and 68° are attributed to crystalline plane diffraction peaks of Pd(0). The particle size was calculated at 20.25 nm for the Pd@GOF catalyst based on the Scherrer equation.

Figure 3 shows the energy-dispersive X-ray spectroscopy (EDS), which verifies the presence of a large



SCHEME 1 Synthesis of Pd@GOF (GO, graphene oxide; GOF, graphene oxide framework)

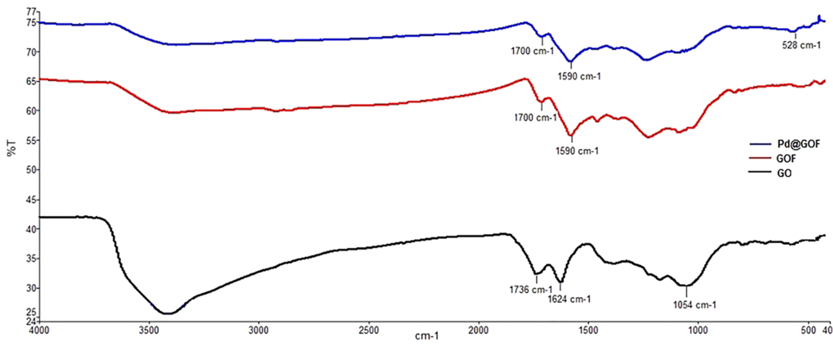


FIGURE 1 Fourier-transform infrared spectra of graphene oxide (GO), graphene oxide framework (GOF), and palladium nanoparticle embedded in a graphene oxide framework (Pd@GOF)

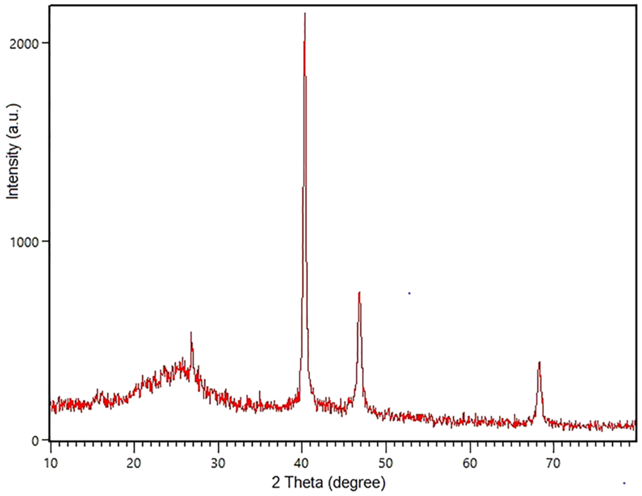


FIGURE 2 X-ray diffraction pattern of Pd@GOF

number of Pd NPs on graphene. The figure also shows the presence of nitrogen, therefore the existence of 5,5′-diamino-2,2′-bipyridine in the Pd@GOF. The amounts of elements detected by EDS analysis are summarized in Table 1. The amount of Pd in the catalyst measured using the AAS was 21.68 wt%.

Figure 4 shows the TEM image of Pd@GOF catalyst, based on which dispersed Pd NPs were trapped by the graphene network and homogeneously embedded between the sheets of GO. Further, it is also clear from Figure 4b that the sizes of Pd NPs are 15.5 nm that are consistent with those estimated by XRD.

The catalytic activity of the prepared catalyst was systematically tested through the Heck-Mizoroki cross-coupling reaction. For this purpose, the coupling reaction of bromobenzene with styrene was chosen as the model reaction, and the effects of several solvents were also examined to specify the most optimal solvent. According to the results summarized in Table 2, the best conversion was observed for H_2O–EtOH (1:1) in the presence of Pd@GOF (1 mg, 0.2 mol% Pd) (Table 2, entry 3). K_2CO_3 (1.5 mmol) was used as a base for optimizing the reaction conditions. In the next step, the optimum amount of the catalyst was monitored to achieve the maximum yield of the product, and 1 mg (0.2 mol% Pd) of the catalyst was selected as the optimum amount (Table 3, entry 2).

TABLE 1 Elemental composition of Pd@GOF determined by EDS analysis

C	O	N	Pd
32.27	28.42	6.63	32.67

Abbreviations: EDS, energy-dispersiveX-ray spectroscopy; Pd@GOF, palladium nanoparticle embedded in a graphene oxide framework.

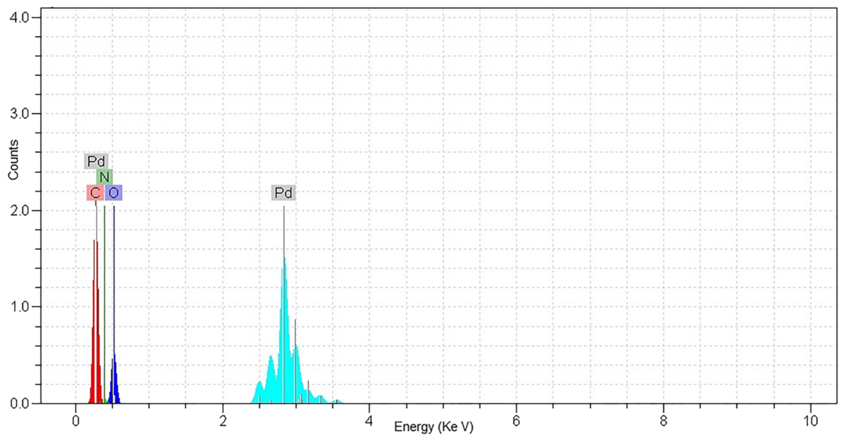


FIGURE 3 Energy-dispersiveX-ray spectroscopy analysis of Pd@GOF

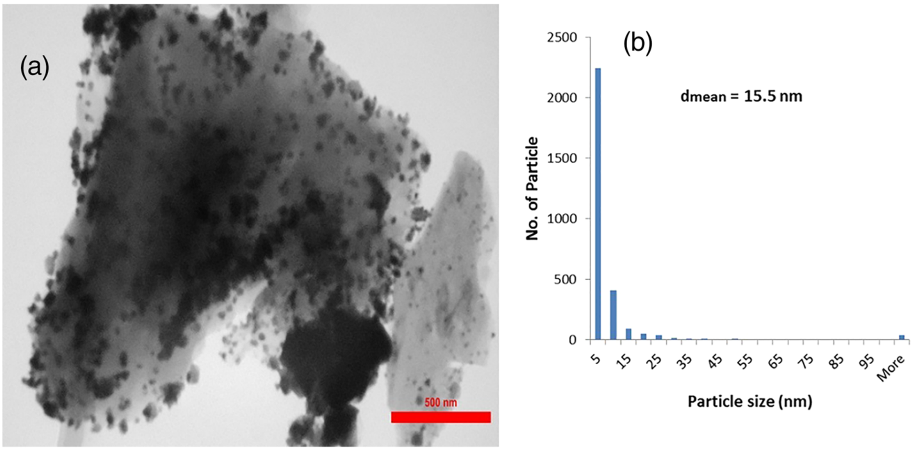


FIGURE 4 (a) Transmission electron microscopy image of Pd@GOF and (b) histogram of particle-size distribution of Pd@GOF catalyst

TABLE 2 Heck reaction in various solvents[a]

Entry	Solvent	Yield (%)[b]
1	H_2O	85
2	EtOH	93
3	H_2O–EtOH	98
4	Toluene	30
5	DMF	78

Abbreviation: DMF, dimethylformamide.

[a] Reaction was carried out with 1 mmol of bromobenzene, 1.2 mmol of styrene, 1.5 mmol of K_2CO_3, 1 mg (0.2 mol% Pd) of Pd@GOF, and 5 ml of the solvent at 80°C for 20 min.

[b] Isolated yield.

To study the catalytic activity of Pd@GOF under optimal conditions, the coupling reactions of various substituted aryl halides with styrene were accomplished in the presence of Pd@GOF catalyst, using K_2CO_3 as a base and H_2O–EtOH (1:1) as an environmentally benign solvent, and the results are summarized in Table 4.

The results show that the catalyst system is efficient and the stilbene derivatives are obtained in a short time with high yields. Heck reactions of the deactivated aryl bromides proceeded with high yields over a short reaction period and high turnover frequencies (TOF) (Table 4, entries 6–11). The Heck reaction of the activated aryl bromides including 4-bromotoluene, 4-bromoanisole, 4-bromophenol, and 4-bromoaniline also provided 90%, 85%, 83%, and 85% yields, respectively, but over longer reaction times and lower TOF (2.25, 2.13, 1.38, and 1.42 h^{-1}, respectively) compared with deactivated aryl bromides (Table 4, entries 2–5). Moreover, iodobenzene reacted much faster than bromobenzene with higher TOF (Table 4, entry 12). The catalytic system was less effective on the reaction of aryl chlorides (Table 4, entries 14, 15).

TABLE 3 Influence of amount of catalyst on Heck reaction[a]

Entry	Amount of catalyst (mg)	Pd content (mol%)	Yield (%)[b]
1	0.5	0.1	60
2	1	0.2	98
3	2	0.4	98

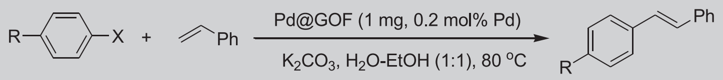
[a] Reaction was carried out with 1 mmol of bromobenzene, 1.2 mmol of styrene, 1.5 mmol of K_2CO_3, and 5 ml of the solvent H_2O–EtOH (1:1) at 80°C for 20 min.

[b] Isolated yield.

To investigate the reusability of the heterogeneous palladium catalyst, a set of experiments were performed under optimized conditions for the reaction of bromobenzene with styrene. After each catalytic cycle was completed, the reaction mixture was primarily cooled down to the room temperature, then filtered and washed with ethanol and acetone, and dried under vacuum for the next run. Finally, the reuse of Pd@GOF was investigated in the Heck reaction of bromobenzene with styrene. Table 5 shows that the Pd@GOF catalyst was recycled 10 times with a minor loss of catalytic activity, which clearly indicates the high catalytic activity and stability of Pd@GOF. Comparison of the Pd concentrations before the catalytic reaction (21.68 wt%) and after 10 runs (19.02 wt%) measured by atomic absorption shows that palladium leaching was negligible, probably due to the excellent binding of the N atom with Pd.

To investigate whether the catalytically active species is really heterogeneous, the hot filtration[19] experiment was carried out to get insight into Heck reaction catalyzed with apparently a heterogeneous Pd@GOF catalyst. The catalytically active nanocomposite was removed from the reaction of bromobenzene with styrene by filtration after 5 min using a hot frit, and the filtrate was monitored for continued activity. The hot filtrates were then transferred into another flask containing 1.5 mmol of K_2CO_3 and 5 ml of H_2O–EtOH (1:1) at 80°C. Upon further continuation of the catalyst-free reaction for 5 h, no

TABLE 4 Heck reaction of aryl halides with styrene catalyzed by Pd@GOF[a]



Entry	R	X	Time (h)	Yield (%)[b]	TON[c]	TOF (h^{-1})[d]
1	H	Br	15 min	97	4.85	19.40
2	CH_3	Br	2	90	4.50	2.25
3	OCH_3	Br	2	85	4.25	2.13
4	OH	Br	3	83	4.15	1.38
5	NH_2	Br	3	85	4.25	1.42
6	CN	Br	1	89	4.45	4.45
7	NO_2	Br	1	94	4.70	4.70
8	CO_2H	Br	2	90	4.50	2.25
9	COH	Br	2	85	4.25	2.13
10	$COCH_3$	Br	1	85	4.25	4.25
11	Cl	Br	1	88	4.40	4.40
12	H	I	5 min	95	4.75	57.00
13	OCH_3	I	0.5	90	4.50	9.00
14	H	Cl	7	65	3.25	0.46
15	COH	Cl	7	70	3.50	0.50

[a] Reaction conditions: aryl halides (1.0 mmol), styrene (1.2 mmol), K_2CO_3 (1.5 mmol), Pd@GOF (1 mg, 0.2 mol% Pd), and H_2O–EtOH (1:1) (5 ml) at 80°C.
[b] Isolated yield.
[c] TON, turnover number, moles of aryl halides converted per mole of Pd.
[d] TOF, turnover frequencies, TON/time of reaction.

TABLE 5 Reusability of the Pd@GOF in Heck reaction[a]

Run	1	2	3	4	5	6	7	8	9	10
Yield (%)[b]	90	90	89	89	87	86	86	86	85	85

[a] Reaction conditions: bromobenzene (1.0 mmol), styrene (1.2 mmol), K_2CO_3 (1.5 mmol), Pd@GOF (1 mg, 0.2 mol% Pd), and H_2O–EtOH (1:1) (5 ml) at 80°C.
[b] Isolated yield.

TABLE 6 Comparison of efficiency of Pd@GOF with one-side functionalized graphene in Heck reaction of bromobenzene with styrene

Entry	Catalyst [ref]	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)[a]	TOF (h^{-1})
1	ERGO-Pd (0.3 mol%)[20]	DMF	Et_3N	120	4	88	0.73
2	Pd/Met/GO (0.1 mol%)[21]	DMF	Et_3N	110	3	96	3.2
3	Pd/GO (0.16 mol%)[22]	Toluene	Et_3N	110	5	63	0.78
4	TRGO-NPy-Pd (0.3 mol%)[23]	DMF	Na_2CO_3	140	5	97	0.65
5	PCA-GNS-Pd (0.2 mol%)[24]	H_2O	Na_2CO_3	90	12	85	0.35
6	Pd@GOF (0.2 mol%) [this work]	H_2O–EtOH	K_2CO_3	80	15 min	97	19.40

Abbreviations: DMF, dimethylformamide; TOF, turnover frequencies.
[a] Isolated yield.

substantial progress (by GC analysis) was observed. Furthermore, AAS of the same reaction solution at the midpoint of completion indicated that no significant quantities of palladium were lost to the reaction liquors during the process.

The catalytic performance of Pd@GOF was compared with the certain Pd NPs supported on one-side functionalized graphene reported in the literature for the reaction of bromobenzene with styrene (Table 6).[20–24] Table 6 shows that the high loading of palladium on Pd@GOF effectively made it possible to perform the reaction with only a small catalyst amount with higher reaction yield over shorter reaction times and higher TOF. The high catalytic activity is attributed to the small size and identical dispersion of Pd NPs on ordered pores that could be considered as nanoreactors to increase the contact area between the substrate and the catalyst.

3 | CONCLUSION

In summary, the GOF was successfully prepared by cross-linking of 5,5′-diamino-2,2′-bipyridine with GO as well-defined porous support in heterogeneous catalysis. The reaction of two amino groups of linker with the carboxylic group of GO sheets provided a GOF structure with a regularly expanded interlayer spacing. In situ dispersed Pd NPs were grown and encapsulated in the framework due to the strong coordination between the Pd atoms and bipyridine's N atom of 5,5′-diamino-2,2′-bipyridine, a process facilitating the immobilization and stabilization of Pd NP in the GOF matrix. The Pd@GOF catalyst exhibited a superior performance toward the Heck cross-coupling reaction. Also, the formed ordered pores were considered as nanoreactors to increase the contact area between the substrate and the catalyst. Accordingly, such a catalyst exhibits high activity, synergistic catalysis, and stable cycling toward the Heck reaction.

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 halides, styrene, potassium carbonate (K_2CO_3), 5-amino-2-bromopyridine, PEG 4000, and palladium(II) chloride were purchased from Merck Chemical Company (Kenilworth, NJ 07033, USA), without further purification. Double-distilled water was used throughout the experiments. FT-IR spectra were recorded in KBr pellets using a Spectrum One FT-IR spectrometer (PerkinElmer, Waltham, MA). High-field nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 250 MHz Avance Ultrashield instrument (Germany). ^{1}H NMR and ^{13}C NMR chemical shifts are quoted relative to solvent resonance(s) as the internal standard. TEM images were acquired using a Zeiss-EM10C transmission electron microscope with an acceleration voltage of 80 kV. Samples were prepared by dispersing Pd@GOF in water via ultrasonication. One drop of the suspension was applied to a formvar carbon-coated grid Cu mesh 300 and left dry in air. An Analytik Jena (Germany) flame AAS instrument was used for the determination of Pd. In addition, investigations using scanning electron microscopy were carried out by applying an EDS detector. The measurements were conducted using a Rontec scanning electron microscope (Bruker, Germany).

4.2 | Synthesis of GO

GO was synthesized from graphite using a modified Hummers method.[25]

4.3 | Synthesis of GO–COCl

GO–COCl was synthesized according to our previous procedure.[17b] GO (0.1 g) was dispersed in 15 ml $SOCl_2$ by sonication for 30 min. Subsequently, the suspension was refluxed at 70°C for 24 h. The product (GO–COCl) was gathered by filtration, washed with anhydrous tetrahydrofuran (THF), and dried at room temperature.

4.4 | Synthesis of 5,5′-diamino-2,2′-bipyridine by homocoupling of 5-amino-2-bromopyridine

The linker was prepared using a modification of the procedure described in Wang et al.[26] A mixture of 5-amino-2-bromopyridine (1.73 g, 10 mmol), $PdCl_2$ (17.7 mg, 0.1 mmol), K_2CO_3 (1.38 g, 10 mmol), and PEG 4000 (10 g) was stirred at 120°C for 24 h at which time the starting material could not be detected anymore by thin-layer chromatography (eluent ethyl acetate). After the reaction, the solution was cooled to room temperature, and the resulting solid was extracted with dichloromethane (4 × 35 ml). Further purification of the product was achieved using flash chromatography on a silica gel column. The product 5,5′-diamino-2,2′-bipyridine was separated as a yellowish solid and was sublimed as described earlier to yield a colorless powder (yield, 1.75 g; 85%). m.p. 206°C (Janiak et al.[27]205–206-°C). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.94 (d, 2H, J = 2.8 Hz, H6, H6′), 7.85 (d, 2H, J = 8.5 Hz, H3, H3′), 6.90 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz, H4, H4′), 5.38 [s (br.), 4H, NH$_2$]. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 147.3 (C2, C2′), 145.3 (C5, C5′), 135.7 (C6, C6′), 124.2 (C3, C3′), 121.8 (C4, C4′).

4.5 | Synthesis of GOFs

The GOF was prepared with the reaction between 5,5′-diamino-2,2′-bipyridine and GO–COCl according to the following procedure. At first, GO–COCl (0.1 g) was mixed in dimethylformamide (DMF) (30 ml) and sonicated for 30 min. Then, 5,5′-diamino-2,2′-bipyridine was added to 20 ml of DMF and stirred; the achieved solution was then slowly added to GO–COCl suspension. Consequently, the reaction temperature was raised to 100°C and the mixture was stirred for 24 h. Finally, the reaction temperature was reduced down to 80°C, and the mixture was kept under static conditions for 24 h. The resulting solid was filtered and washed several times with deionized water. Next, it was dried at room temperature before characterization.

4.6 | Synthesis of GOF-embedded Pd NPs (Pd@GOF)

The GOF (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. The reaction was then stirred for 24 h at room temperature. The final product was filtered and washed with distilled water five times, and the catalyst (Pd@GOF) was air-dried.

4.7 | General procedure for the Heck reaction

In a 25 ml round-bottom flask, 1 mg of Pd@GOF catalyst (0.2 mol% Pd) was dispersed in 5 ml of H$_2$O–EtOH (1:1) by sonication for 20 min at room temperature. To this suspension, aryl halides (1 mmol), styrene (1.2 mmol), and K$_2$CO$_3$ (1.5 mmol) were added, and the reaction mixture was stirred at 80°C for the required time. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled down to room temperature, filtered, and then washed with dichloromethane (3 ×10 ml). The organic phase was separated and dried over anhydrous Na$_2$SO$_4$, and the crude product was purified using column chromatography (n-hexane–ethyl acetate). The evaporation of the solvent generated pure desired products, all of which are known compounds whose NMR spectra are in accordance with those reported in the literature.[20–24]

ACKNOWLEDGMENT

We thank Shahid Chamran University of Ahvaz Research Council, Ahvaz, for financial support of this study (Grant Number 1398).

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How to cite this article: Shekarizadeh A, Azadi R. Synthesis of Pd@graphene oxide framework nanocatalyst with enhanced activity in Heck-Mizoroki cross-coupling reaction. *Appl Organomet Chem*. 2020;e5775. https://doi.org/10.1002/aoc.5775