Revised: 1 August 2019

# FULL PAPER



# Immobilizing Pd nanoparticles on the ternary hybrid system of graphene oxide, $Fe_3O_4$ nanoparticles, and PAMAM dendrimer as an efficient support for catalyzing sonogashira coupling reaction

# Mehrasa Tarahomi<sup>1</sup> | Heshmatollah Alinezhad<sup>1</sup> | Behrooz Maleki<sup>2</sup>

<sup>1</sup>Faculty of Chemistry, University of Mazandaran, P.O. Box 47416-95447, Babolsar, Iran

<sup>2</sup>Department of Chemistry, Faculty of Sciences, Hakim Sabzevari University, 96179-76487 Sabzevar, Iran

#### Correspondence

Heshmatollah Alinezhad, Faculty of Chemistry, University of Mazandaran, P.O. Box 47416-95447, Babolsar, Iran. Email: heshmat@umz.ac.ir

Behrooz Maleki, Department of Chemistry, Faculty of Sciences, Hakim Sabzevari University, 96179-76487, Sabzevar, Iran. Email: b.maleki@hsu.ac.ir

**Funding information** Hakim Sabzevari University; Research Council of University of Mazandaran

## **1** | INTRODUCTION

The Sonogashira reaction is a cross-coupling reaction which used to form carbon–carbon bonds between a terminal alkyne and an aryl or vinyl halide and it employs a palladium catalyst. Palladium-based catalyst is one of the most promising agent for a classic C-C bond formation in organic chemistry.<sup>[1–4]</sup>

Palladium-catalyzed cross-coupling reactions which employ the formation of biphenyl compounds have become one of the most important and powerful synthetic procedures.<sup>[5]</sup> Among various coupling reactions, one of the most widely used reaction to form a new C-C bond is the palladium catalyzed Sonogashira coupling reaction. Due to the importance of palladium-catalyzed coupling reaction, it has been applied in many different areas of science, including pharmacological agents,

An alternative approach to develop a Pd catalyst based on dendrimerfunctionalized graphene oxide for C-C cross-coupling reactions is reported. Pd@MGO-D-NH<sub>2</sub> has been synthesized by incipient wet impregnation method. The structure of the catalyst was thoroughly characterized by a set of analytical techniques such as TEM, BET, SEM/EDS, FTIR, and elemental mapping analysis. Then, the catalytic activity of the catalyst was scrutinized for promoting sonogashira C-C coupling reaction. The results manifested that Pd@MGO-D-NH<sub>2</sub> was able to catalyze the coupling reaction to obtain high coupling yields in short reaction time. The results of present work are hoped to aid the development of new class of heterogeneous catalysts as the high performance candidate for industrial applications.

#### KEYWORDS

dendrimer, graphene oxide, Pd nanoparticles, Sonogashira coupling reaction

herbicides, the synthesis of natural products, and drug industry.  $^{\left[ 4,6-8\right] }$ 

Graphene oxide as a chemically modified and highly oxidized form of graphene with a giant aromatic macromolecule and a large number of oxygen functionalities on their basal plant, can simply disperse in organic solvents, water, and different matrixes. The popularity of graphene oxide (GO) promotes extensively, due to its unique physicochemical properties such as thermal and electrical conductivity, superior dispersibility, facile modification, and etc.<sup>[9–13]</sup> Combining the GO with polymer or ceramic matrixes can enhance their mechanical and electrical properties. Up to now, the utility of graphene based composite for energy research,<sup>[14–16]</sup> catalysis,<sup>[17,18]</sup> and electrochemical analysis<sup>[19]</sup> has also been widely confirmed.

Dendrimers are an important class of organic compounds due to their defined hyperbranched nanoarchitecture, monodispersity, abundance of functional groups at the periphery and biocompatibility,<sup>[20–22]</sup> So, it is visualized that the interface of graphene oxide with dendrimer would provide physico chemical advantages such as a solution/dispersion state.<sup>[23]</sup> So, developing a multicomponent graphene-based nanocarriers for organic transformation can be very important.

The combination of activity and high reaction rates can be attained when Pd is supported on an appropriate material. Then, research on novel Pd-based catalyst has received much attention.<sup>[24–29]</sup>

In the last decades, several Pd-based catalyst with different supports have been reported in cross-coupling reactions such as graphene-supported Pd/Fe<sub>3</sub>O<sub>4</sub> nanoparticles,<sup>[30]</sup> dendrimer-stabilized Pd nanoparticles,<sup>[31]</sup> palladium catalysts deposited over donor-functionalized silica gel.<sup>[32]</sup> polymer-supported palladium/N-heterocyclic carbene complex,<sup>[33]</sup> active palladium nanoparticles from multilayer films,<sup>[34]</sup> discharged palladium nanoparticle-graphene hybrids,<sup>[35]</sup> Pd@MTiO<sub>2</sub>.<sup>[36]</sup> pallaanchored to SBA-15 functionalized with dium melamine-pyridine groups,<sup>[37]</sup> Pd-Ni bimetallic synergistic catalyst on ZIF-8,<sup>[38]</sup> Pd immobilized on dendrimer decorated halloysite clay,<sup>[39]</sup> and etc.

According to our interest to graphene-based nanostructured system,<sup>[40]</sup> in the present study, we describe the design, synthesis and evaluation of novel Pd supported on the dendrimer-functionalized graphene oxide to develop cross coupling reaction.

#### **2** | EXPERIMENTAL SECTION

#### 2.1 | Materials and instruments

All chemicals were purchased from Merck and Aldrich. Solvents were purified by conventional methods. The structure of Pd@MGO-D-NH<sub>2</sub> was characterized by TEM, BET, SEM/EDS, FTIR, and elemental mapping measurements. The progress of the reaction was checked with thin layer chromatography (TLC) using commercial plates coated with silica gel 60 F254.

Fourier transform infrared (FT-IR) spectra of the catalyst and the synthesized compounds were recorded on a TENSOR BRUKER 27 spectrometer in the frequency range of 400–4000 cm<sup>-1</sup> using KBr pellets. The SEM/EDX analysis were recorded with MIRA3 XMU instrument in which the specimens were sputter-coated with a thin layer of gold. The applied transmission electron microscope (TEM) images were recorded on a Philips CM30 transmission electron microscope. Nitrogen adsorption–desorption isotherms were performed on a BELSORP Mini II apparatus to characterize the textural

properties of the synthesized catalyst. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-400 AVANCE (MA, USA) spectrometer at 400.13 and 100.61 MHz, respectively. Mass spectra were determined on a Finnigan-Matt 8430 (Waltham, USA) mass spectrometer operating at an ionization potential of 70 eV.

#### 2.2 | Preparation of GO/Fe<sub>3</sub>O<sub>4</sub> (MGO)

GO was prepared by oxidizing graphite with a modified method.<sup>[41,42]</sup> To Hummers synthesize magnetic graphene oxide nanocomposite (MGO-NCs) an effective chemical precipitation method was used. To form a well-distributed suspension, 30 mg GO was sonicated in 10 ml distilled water for 20 minutes. It was heated to 50 °C, followed by purging with  $N_2$  to remove  $O_2$  in the solution. After that, 80 mg FeCl<sub>2</sub>·4H<sub>2</sub>O and 216 mg FeCl<sub>3</sub>·6H<sub>2</sub>O were added to the suspension and ultrasonicated for 30 min. One ml solution of NH<sub>3</sub>·H<sub>2</sub>O was dropwise added to the mixture with vigorous mechanical agitation and kept on reacting for 40 min at 50 °C protected by N<sub>2</sub>. When it was cooled to room temperature, the obtained composites were magnetically separated by a supermagnet and washed with doubledistilled water for several times. The resulting product was dispersed in 20 ml water, and the homogeneous product of the magnetic nanoparticles was obtained.

## 2.3 | Functionalization of MGO-NCs with a modified PAMAM dendrimer (MGO-D-NH<sub>2</sub>)

The modified PAMAM dendrimer was synthesized according to previous work.<sup>[22,40,43]</sup> The second generation dendrimer which contains 10-NH<sub>2</sub> terminal groups (G2) as pale yellow oil was obtained. The main steps of the experimental procedure are described in details below. MGO (0.3 g) was dispersed in 200 ml of deionized water by sonication for 30 min. Then, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC.HCl) of 0.052 g and N-hydroxysuccinimide (NHS) of 0.015 g were added to the solution and stirred for 10 min to activate the carbonyl group on MGO. Finally, modified PAMAM dendrimer (3 ml) was added dropwise to the system, and the reaction was allowed to proceed at 25°C for 1 day. The precipitate was collected by an external magnetic field, washed with deionized water and ethanol 3 times, and finally dried in a vacuum at 343(k). The resulting dark-brown precipitates of modified G2 PAMAM-MGO were ready to use.

## 2.4 | Immobilization of Pd nanoparticles on MGO-D-NH<sub>2</sub> (Pd@MGO-D-NH<sub>2</sub>)

Pd supported on dendrimer-functionalized graphene oxide-based catalyst (MGO-D-NH<sub>2</sub>) was obtained by incipient wet impregnation method. In this procedure, the dried support (0.5 g) was impregnated with dried dichloromethane solution (15 ml) of PdCl<sub>2</sub> (0.02 g, Aldrich 99%), and then stirred at 25°C overnight. The chemical reduction process reduced Pd (II) to Pd nanoparticles. In this procedure, a solution of sodium borohydride in methanol (10 ml, 0.2 M) was prepared. Then the prepared solution was added dropwise to the suspension under vigorous stirring for 4 hr to complete the reduction process. As a final point, the resulting precipitate was filtered and three times washed with methanol, and then dried in oven vaccum at 343 (k) for 24 hr to obtain Pd@MGO-D-NH<sub>2</sub>.

## 2.5 | Typical procedure for the catalytic Sonogashira cross-coupling reaction

Pd@MGO-D-NH<sub>2</sub> (20 mg) and K<sub>2</sub>CO<sub>3</sub> (4.0 mmol) were added to reaction mixture of H<sub>2</sub>O: EtOH (1:1, v:v), followed by 1 mmol of phenylacetylene and 1 mmol of Aryl halide. The reaction mixture was refluxed at 100 °C, stirred vigorously, and monitored using TLC in n-hexane as eluent until the start is completely disappeared. After completion of the reaction, the catalyst was removed from the reaction mixture via an external magnetic field, and then the mixture was allowed to cool down to room temperature. The product was purified by column chromatography over deactivated silica gel using pure n-hexane as eluent to furnish a crude product.

### 2.6 | Selected spectral data

### 2.6.1 | 1,2-diphenylethyne (entry 1)

<sup>1</sup>H NMR (400.13 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 7.52 (ddd, J = 6.4, 4.0, 2.8 Hz, 4H), 7.28–7.40 (m, 6H). <sup>13</sup>C NMR (100.6 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 131.2, 128.6, 127.2, 122.1, 89.1. IR (KBr) /vcm<sup>-1</sup>); 3061, 2930, 1580, 1489, 1450, 1284, 1072, 762, 677. MS (EI, 70 eV) m/z (%): 178 [M<sup>+</sup>], 152, 126, 76.

### 2.6.2 | 1-methoxy-4-(phenylethynyl)benzene (entry 4)

<sup>1</sup>H NMR (400.13 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 7.50 (dd, J = 8.1, 1.5 Hz, 2 H), 7.42 (d, J = 8.9 Hz, 2 H), 7.30–7.42 (m, 3 H), 6.92 (d, J = 8.9 Hz, 2 H), 3.63 (s, 3 H) ppm. <sup>13</sup>C NMR (100.6 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 160.15, 133.58, 132.30, 129.60, 128.79, 128.32, 124.03, 115.88, 89.95, 88.22, 55.08 ppm. IR (KBr)/ (cm<sup>-1</sup>); 2231, 1592, 1241, 1169, 1142, 830, 758, 698. MS (EI, 70 eV) m/z (%): 208 [M<sup>+</sup>], 193, 177, 76.

## 2.6.3 | 1-nitro-4-(phenylethynyl)benzene (entry 5)

<sup>1</sup>H NMR (400.13 MHz, DMSO-d<sub>6</sub>), δ: 8.18–8.30 (m, 2H), 7.60–7.83 (m, 2H), 7.50 (dt, J = 5.5, 2.1 Hz, 2H), 7.23– 7.31 (m, 3H). <sup>13</sup>C NMR (100.6 MHz, DMSO-d<sub>6</sub>), δ: 146.8, 132.5, 132.2, 130.8, 129.5, 128.4, 123.2, 122.2, 94.4, 87.3. IR (KBr) /ν (cm<sup>-1</sup>); 2942, 2220, 1585, 1522, 1368, 850. MS (EI, 70 eV) m/z (%): 223 [M<sup>+</sup>], 193, 177, 165,151, 76.

## 2.6.4 | 4-(phenylethynyl)benzaldehyde (entry 7)

<sup>1</sup>H NMR (400.13 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 10.14 (s, 1 H), 7.78 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2 H), 7.48–7.69 (m, 2 H), 7.32–7.49 (m, 3 H) ppm. <sup>13</sup>C NMR (100.6 MHz, DMSO-d<sub>6</sub>),  $\delta$ : 192.22, 192.16, 136.21, 132.78, 132.59, 130.39, 130.30, 129.68, 129.15, 123.24, 94.32, 89.02 ppm. IR (KBr)/ $\nu$  (cm<sup>-1</sup>); 3058, 2854, 2216, 1700, 1600. MS (EI, 70 eV) m/z (%): 206 [M<sup>+</sup>], 177, 76.

# 2.7 | Recyclability evaluation of Pd@MGO-D-NH<sub>2</sub>

The catalyst was recovered from the reaction mixture after completion of the reaction using an external magnetic, and then it was washed with hot ethanol 3 times and vacuum-dried at 333 k overnight.

### **3** | **RESULTS AND DISCUSSION**

With respect to our interest in the design, synthesis and characterization of novel heterogeneous nanocatalysts,<sup>[22,40,44]</sup> we report a novel experimental protocol for *preparation* of Pd@MGO-D-NH<sub>2</sub>. As illustrated in scheme 1, the catalyst was prepared using an approach which includes several steps. In the first step, GO and MGO was prepared. The following step was the covalent attachment of modified PAMAM dendrimer (G. 2) with MGO using EDC/NHS.<sup>[40]</sup> In the final step, Pd NPs were immobilized on the dendrimer-functionalized graphene oxide through graft interactions between free chelating amino groups of dendrimer and Pd precursor. Then, the catalyst was characterized by FT-IR analysis, SEM-EDS, elemental mapping analysis, BET, and TEM.



SCHEME 1 The synthetic procedure for the preparation of pd@MGO-D-NH2.

#### 3.1 | Catalyst characterization

The characterization of Pd@MGO-D-NH<sub>2</sub> was performed using various kinds of techniques including SEM-EDS, elemental mapping, BET, TEM, and FT-IR. To characterize the structure of the catalyst, a detailed SEM-EDS analysis was implemented to elucidate the composition of the catalyst, Figure 1.

The SEM-EDS images of the catalyst Figure 1, showing the distribution of the N, Fe, O, C, N and Pd elements. Therefore the immobilization of Pd(0) nanoparticles was confirmed. The presence of N atoms in the EDS pattern,



FIGURE 1 The SEM-EDS of Pd@MGO-D-NH2

can be ascribed to the incorporation of polyamidoamine on the catalyst (Figure 1). Also the percentage of elements in proved our claim (Table 1). However, the structure of the catalyst cannot be confirmed solely by SEM-EDS, other measurement techniques have been employed. Further, the elemental mapping analysis of Pd@MGO-D-NH<sub>2</sub> (Figure 2) demonstrates the uniform distribution of N, C, Fe, O and Pd elements which is confirmed by the TEM observation, Figure 3.

TABLE 1	The percentage	of elements with	EDS-analysis
	The percentage	or erennenno mitti	LD D analyond

Elt	С	N	0	Fe	Pd
W%	13.66	2.48	26.55	53.09	4.22
A%	28.68	4.47	41.86	23.98	1:00

Also, the catalyst was evaluated by an inductively – optical emission spectrometry (ICP-OES) to measure the accurate content of Pd. The content of pd was calculated



FIGURE 2 The elemental mapping of Pd@MGO-D-NH2

to be 5.57 %W (1.04 mol%) which is another proof for the fact that palladium nanoparticles was be immobilized onto the Pd@MGO-D-NH<sub>2</sub> catalyst.

In order to characterize the morphology of the Pd@MGO-D-NH<sub>2</sub> catalyst, TEM images of catalyst were acquired, Figure 3a & b. According to TEM images of the catalyst (Figure 3.), the layered morphology of the GO was preserved upon decoration of PAMAM dendrimer and incorporation of palladium NPs. Moreover, the small spots on GO sheet, on the surface of the dendrimer and in the dendritic cavity in the TEM images can be ascribed to the Pd NPs. According to the results of TEM images, it can be concluded that MGO-D-NH<sub>2</sub> catalyst was effective in suppression the aggregation of the Pd NPs. Additionally, the Pd particle size distribution was determined based on TEM characterization, Figure 3c.

In the FT-IR pattern of MGO-D-NH<sub>2</sub> (Figure 4a) the bands at 2923 and 2863 cm<sup>-1</sup> are assigned to alkyl group(C-H stretch) in the Modified polyamidoamine. The characteristic peaks of MGO-D-NH<sub>2</sub> at 1639, 1547 and 1434 cm<sup>-1</sup> were attributed to NH deformation vibration of primary amine, the coupling of N-H bending and C–N stretching of amide. Also, the peak  $3435 \text{ cm}^{-1}$  proves the existence of the nitrogen-containing functional groups.<sup>[40,45]</sup>

The BET surface area (S<sub>BET</sub>), average pore diameter and total pore volume of the catalysts was determined via nitrogen adsorption/desorption isotherms, Figure 5. As indicated in Table 2, the measured S<sub>BET</sub> of the MGO-D-NH<sub>2</sub> and Pd@MGO-D-NH<sub>2</sub> were 86.4  $m^2 g^{-1}$  and 77.9  $m^2 g^{-1}$ . It is possible to deduce that upon decoration of PAMAM dendrimer and incorporation of palladium NPs, the  $S_{BET}$  of the catalyst was decreased, Table 2.

Moreover, it can be concluded that the total pore volumes and average pore diameter of the catalysts decreased in the order of MGO-D-NH<sub>2</sub> > Pd@MGO-D-NH<sub>2</sub>, which confirmed that the inner cavity of PAMAM dendrimer and graphene oxide could be occupied by Pd NPs.

TGA can evaluate the thermal stability and bond formation of materials. The TGA results of MGO, MGO-D-NH<sub>2</sub>, and Pd@MGO-D-NH<sub>2</sub> is indicated in Figure 6. A slow weight loss at low temperature (<100 °C) can be observed, which can be assigned to the loss of adsorbed water. Then the stage of weight reduction occurred around 200 °C, indicating the decomposition and vaporization of various oxygen-containing functional groups at



FIGURE 3 The TEM image of Pd@MGO-D-NH2



**FIGURE 4** The FTIR spectrum of prepared a) MGO-D-NH2 and b) Pd@MGO-D-NH2

different positions on the surface of the MGO. The TGA curve of MGO-D-NH<sub>2</sub> (4b) indicates a weight loss between 200 and 600 °C is assigned to modified PAMAM dendrimer.<sup>[40]</sup> Also, same weight-loss profile is achievable for Pd@MGO-D-NH<sub>2</sub>.

The TGA curve of the  $Pd@MGO-D-NH_2$  reveals an initial ascending behavior, unlike MGO and MGO-D-NH<sub>2</sub>, due to the buoyancy effect of the instrument in which the differences in heat capacity and thermal conductivity of the purging gas can lead to initial weight gain for the sample and platinum pan.

#### 3.2 | Activity assessment of Pd@MGO-D-NH<sub>2</sub> catalyst

The activity, recovery and reuse of the catalyst is highly preferable due to the importance of expanding eco-



**FIGURE 5** A: Nitrogen adsorption/desorption isotherms (a) and BJH-plot (b) of the MGO-D-NH2. B: Nitrogenadsorption/desorption isotherms (c) and BJH-plot (d) of the pd@MGO-D-NH2

**TABLE 2**Textural properties of the MGO-D-NH2 and Pd@MGO-D-NH2

Catalyst	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)
$MGO-D-NH_2$	86.4	0.34	15.79
Pd@MGO-D- NH <sub>2</sub>	77.9	0.23	11.83

friendly procedures for Sonogashira coupling reaction. Also, the catalytic activity of  $Pd@MGO-D-NH_2$  was scrutinized. The reaction of iodobenzene (1 mmol) with



FIGURE 6 The TGA curves of MGO, MGO-D-NH2 and Pd@MGO-D-NH2

phenylacetylene(1 mmol) was chosen as a model reaction to evaluate the catalytic activity of  $Pd@MGO-D-NH_2$  (scheme 2).

According to the section 2.4. (experimental section) the catalyst was prepared with different loading, Table 3 . Then, the reaction parameters, such as different catalysts, bases, solvents, duration, temperature, and catalyst loading were investigated and optimized to gain the optimal reaction parameters. The optimized reaction conditions were applied to cross-coupling reaction and the results are summarized in Table 4.

As tabulated in Table 4, solvent screening demonstrated that the mixture of water/ethanol (1:1,  $\nu/\nu$ ) was the best choice in the reaction. Also, among the screened bases (KOH, NaOH, K<sub>2</sub>CO<sub>3</sub>, DABCO and KO-tBu), K<sub>2</sub>CO<sub>3</sub> proved to be the best and was thus chosen as the base in the coupling reaction. Also, the optimal amount of the Pd@MGO-D-NH<sub>2</sub> catalyst was 20 mg (A, 0.52 mmol/g, 1.04 mol%) at reflux and water/ethanol (1:1,  $\nu/\nu$ ) conditions.

As can be seen in the Table 4, the doping of trace palladium into MGO-D-NH<sub>2</sub> can amazingly increase the yield of the desired reaction products (Table 4, entry 8).

In an attempt to confirm the utility of this catalyst, the coupling reaction of phenylacetylene and a broad variety



**SCHEME 2** Pd@MGO-D-NH2–catalyzed synthesis of Diphenylacetylene derivatives.

**TABLE 3** Preparation of  $Pd@MGO-D-NH_2$  with different amount of  $PdCl_2$ 

Entry	Α	В	С	D	Е
Amount of PdCl <sub>2</sub> (mg)	20	10	5	2	1

#### **TABLE 4** Optimization of reaction conditions<sup>a</sup>

Entry	Reaction condition	Time (h)	Yield (%)
1	GO (30 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	10	trace
2	MGO (30 mg), K <sub>2</sub> CO <sub>3</sub> ,water/ethanol (1:1, $\nu/\nu$ ), reflux	8	trace
3	MGO-D-NH <sub>2</sub> (30 mg), K <sub>2</sub> CO <sub>3</sub> ,water/ethanol (1:1, $\nu/\nu$ ), reflux	5	20
4	Pd@MGO-D-NH <sub>2</sub> (A, 30 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), 25 °C	2:15	60
5	Pd@MGO-D-NH <sub>2</sub> (A, 30 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	1	95
6	Pd@MGO-D-NH <sub>2</sub> (A, 30 mg), $K_2CO_3$ , water/ethanol (1:4, $\nu/\nu$ ), reflux	1	95
7	Pd@MGO-D-NH2 (A, 20 mg), K2CO3,water/ethanol (1:1, $\nu/\nu$ ), 25 °C	2:30	55
8	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	1	95
9	Pd@MGO-D-NH <sub>2</sub> (B, 20 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	1	92
10	Pd@MGO-D-NH <sub>2</sub> (C, 20 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	1	90
11	Pd@MGO-D-NH <sub>2</sub> (D, 20 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	1	85
12	Pd@MGO-D-NH <sub>2</sub> (E, 20 mg), K <sub>2</sub> CO <sub>3</sub> , water/ethanol (1:1, $\nu/\nu$ ), reflux	1	82
13	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), K <sub>2</sub> CO <sub>3</sub> , water, reflux	2	60
14	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), K <sub>2</sub> CO <sub>3</sub> , ethanol, reflux	1	85
15	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), $K_2CO_3$ , water, 25 °C	3	45
16	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), K <sub>2</sub> CO <sub>3</sub> , CHCl <sub>3</sub> , reflux	1:30	60
17	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), K <sub>2</sub> CO <sub>3</sub> , Toluene, reflux	2	65
18	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), KOH, water/ethanol (1:1, $\nu/\nu$ ), reflux	2	50
19	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), NaOH, water/ethanol (1:1, $\nu/\nu$ ), reflux	2	45
20	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), DABCO, water/ethanol (1:1, $\nu/\nu$ ), reflux	2	30
21	Pd@MGO-D-NH <sub>2</sub> (A, 20 mg), KO-tBu, water/ethanol (1:1, $\nu/\nu$ ), reflux	2	50

<sup>a</sup>iodobenzene(1 mmol), phenylacetylene(1 mmol).

of halobenzene with different electronic and steric properties were investigated to the synthesis of desired products, Table 5. Hence, it can be deduced from the Table 5, that a wide range of halobenzenes can be used for this purpose. Moreover, it has also been demonstrated, within the

Applied Organometallic-Chemistry

WILEY

9 of 13

```
TABLE 5
Effect of Pd@MGO-D-NH2 catalyst for Sonogashira reaction
```

Entry	Aryl halide	product	Time (h)	Yield (%)	Melting point
1		Br	1	95	58-60 <sup>[46]</sup>
2	O <sub>2</sub> N-Br	H <sub>3</sub> CO-	2	85	58-60 <sup>[46]</sup>
3	0 <sub>2</sub> N-	H3COC	1:45	88	112-114 <sup>[46]</sup>
4	онсСІ	ОНС-	2	70	61-63 <sup>[46]</sup>
5			1:45	90	112-114 <sup>[46]</sup>
6	0 <sub>2</sub> N-	Н₃СО-√	1:15	90	97–99 <sup>[47]</sup>
7	0 <sub>2</sub> N-{		00:40	95	101-103 <sup>[46]</sup>
8	онс-	онс-	00:50	90	101-103 <sup>[46]</sup>

10 of 13 WILEY-Organometallic

TABLE 6 Comparison of catalytic activity of Pd@MGO-D-NH<sub>2</sub> with some reported catalysts in the Sonogashira coupling reaction<sup>a</sup>

Entry	Reaction condition	Time (h)	Yield (%)
1	Pd(0)/MCoS-1, Et <sub>3</sub> N,H <sub>2</sub> O,90 °C <sup>[48]</sup>	6	94
2	Nanopolymer-supported palladium (II) complex, $Et_3N$ , TBAB, $H_2O$ , 70 °C <sup>[49]</sup>	6	94
3	PdNPs@EDACs, K <sub>2</sub> CO <sub>3</sub> , CuI, H <sub>2</sub> O,80 °C <sup>[50]</sup>	7	98
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /Schiff base/Pd (II), K <sub>2</sub> CO <sub>3</sub> , DMF, 90 °C <sup>[51]</sup>	1	93
5	Pd@Hal-P-CD, H <sub>2</sub> O:EtOH (1:1), 60 °C <sup>[52]</sup>	1:15	95
6	Pd@MGO-D-NH <sub>2</sub> , K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O:EtOH (1:1), reflux (This work)	1	95

<sup>a</sup>iodobenzene(1 mmol), phenylacetylene(1 mmol).



SCHEME 3 The plausible mechanism of the sonogashira coupling reaction.

halobenzene series, iodobenzenes exhibited the higher yields and shorter reaction times due to their more reactivity.

According to Table 5, using of the catalyst Pd@MGO-D-NH<sub>2</sub> produced the desired products in higher yields and shorter reaction times, compared to several reported protocols. Additionally, this procedure avoids hazardous material and can be used as a promising alternative to the existing procedures. Also the reactions proceeded under mild reaction conditions. Remarkably, Compared to homogeneous catalysts traditionally applied in organic transformation, the heterogeneous Pd@MGO-D-NH<sub>2</sub> catalyst can be recovered and reused for subsequent reactions without significant loss in its activity.

Moreover, the efficiency of  $Pd@MGO-D-NH_2$  catalyst was confirmed with comparing the yield of the model



**FIGURE 7** Recycling of Pd@MGO-D-NH2. Reaction conditions: phenylacetylene (1 mmol), Aryl halide (1mmol), K2CO3 (4.0 mmol), Pd@MGO-D-NH2 (20 mg) with water/ethanol (1:1,  $\nu/\nu$ ) at reflux 100 °C.

reaction under  $\ensuremath{\text{Pd}}\ensuremath{\text{@MGO-D-NH}}\xspace_2$  catalyst and other reported catalysts, Table 6. As presented in Table 6, Pd@MGO-D-NH2 illustrated the best catalytic performance in comparison to the other counterparts according to the values of time and yield.

A plausible mechanism for the Pd@MGO-D-NH<sub>2</sub>-catalyzed coupling reaction is illustrated in Scheme 3.

Applied Organometallic Chemistry According to the reaction procedure, initially the Pd@MGO-D-NH2 catalyst activates the terminal C-H of phenyl acetylene. Then, terminal C-H of phenyl acetylene can be deprotonated by K2CO3 to form potassium acetylide. Also Pd@MGO-D-NH2 catalyst activates ArX and forms arylpalladium halide complex (ArPdX). For the next step, the halide can be displaced to form

WILEY

11 of 13



FIGURE 8 The TEM images of Pd@MGO-D-NH2 a) before use and b) after four runs

**TABLE 7** Textural properties of the Pd@MGO-D- $NH_2$  a) before use b) after 4 runs

Catalyst	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)
Pd@MGO-D- NH2 <sup>a</sup>	77.9	0.23	11.83
Pd@MGO-D- NH2 <sup>b</sup>	77.6	0.20	11.79

arylpalladium acetylide. In the last step, the desired coupling product can be produced by reductive elimination.

# 3.3 | Recycling of catalyst and leaching test

Further, we investigated the possibility of recycling of the  $Pd@MGO-D-NH_2$  catalyst. To evaluate the recyclability of the catalyst, the reaction of iodobenzene and phenylacetylene in a 1:1 mole ratio was used as a model reaction for Sonogashira reaction. Upon completion the reaction in each run, the catalyst was recovered via a magnet, and then washed with hot ethanol. So, it was ready to be used for the next batch reaction under the same conditions.

The recyclability of the catalyst was investigated and the results are presented in Figure 7. Recycling tests show that the catalyst could be recycled up to four times with virtually no loss in catalytic activity.

Pd leaching from Pd@MGO-D-NH<sub>2</sub> into reaction solution was checked by ICP analysis. The result proved the heterogeneity of our catalytic processes and negligible leaching under the applied reaction conditions. Also these results truly confirmed the high stability, strong attachment of metal center onto the Pd@MGO-D-NH<sub>2</sub>, and also heterogeneous nature of our catalytic system. The ICP analysis of the catalyst before the reaction and after the fourth run was measured and the results were 5.57 W% and 5.24 W%. So, it can be deduced that the amount of pd leaching was negligible.

Figure 8 compares the TEM of the catalyst before and after four runs, which indicates the presence of Pd NPs on the surface of the recycled catalyst the same as the fresh one.

Moreover, the BET surface area ( $S_{BET}$ ), average pore diameter and total pore volume of the catalyst was determined before the reaction and after the fourth run. The results indicated that the measured  $S_{BET}$ , Total pore volume and Average pore diameter of the catalyst did not change significantly. It is another proof for the stability of the catalyst, Table 7.

## 4 | CONCLUSIONS

In summary, we have reported an efficient approach for immobilizing Pd nanoparticles on the ternary hybrid system of graphene oxide,  $Fe_3O_4$  nanoparticles, and PAMAM dendrimer as an efficient support for catalyzing sonogashira coupling reaction in H<sub>2</sub>O:EtOH (1:1) at reflux. The activity, recovery and reuse of the catalyst is highly preferable due to the importance of expanding eco-friendly procedures for Sonogashira coupling reaction.

The advantages of the present procedure are based on the high yields of products, simple operation, easy catalyst separation, and absence of any toxic solvents.

#### ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Research Council of University of Mazandaran and partial support from the Hakim Sabzevari University.

#### ORCID

Heshmatollah Alinezhad b https://orcid.org/0000-0002-7189-2961 Behrooz, Maleki b https://orcid.org/0000-0002-0322-6991

#### REFERENCES

- C. C. Tzschucke, C. Markert, H. Glatz, W. Bannwarth, *Angew. Chem. Int. Ed.* 2002, *41*, 4500.
- [2] A. Corma, H. García, A. Leyva, J. Catal. 2006, 240, 87.
- [3] R. G. Heidenreich, K. Koehler, J. G. Krauter, J. Pietsch, *Synlett* 2002, 2002, 1118.
- [4] C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, Angew. Chem. Int. Ed. 2012, 51, 5062.
- [5] J.-P. Corbet, G. Mignani, Chem. Rev. 2006, 106, 2651.
- [6] A. Chatterjee, T. R. Ward, Catal. Lett. 2016, 146, 820.
- [7] A. J. Lennox, G. C. Lloyd-Jones, Angew. Chem. Int. Ed. 2013, 52, 7362.
- [8] A. Molnar, Chem. Rev. 2011, 111, 2251.
- [9] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, Adv. Mater. 2010, 22, 3906.
- [10] D. R. Dreyer, Chem. Soc. Rev. 2010, 39, 228.
- [11] K. A. Mkhoyan, A. W. Contryman, J. Silcox, D. A. Stewart, G. Eda, C. Mattevi, S. Miller, M. Chhowalla, *Nano Lett.* 2009, 9, 1058.
- [12] J. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J. Tascon, Langmuir 2008, 24, 10560.
- [13] C. Hontoria-Lucas, A. López-Peinado, J. D. D. López-González, M. Rojas-Cervantes, R. Martin-Aranda, *Carbon* 1995, 33, 1585.
- [14] H. Wang, Y. Liang, T. Mirfakhrai, Z. Chen, H. S. Casalongue, H. Dai, *Nano Res.* 2011, *4*, 729.

- [15] P. Wang, T. Jiang, C. Zhu, Y. Zhai, D. Wang, S. Dong, Nano Res. 2010, 3, 794.
- [16] X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang, H. Zhang, Small 2011, 7, 3163.
- [17] C. Xu, X. Wang, J. Zhu, J. Phys. Chem. C 2008, 112, 19841.
- [18] Y. Liang, H. Wang, H. S. Casalongue, Z. Chen, H. Dai, Nano Res. 2010, 3, 701.
- [19] C. Shan, H. Yang, J. Song, D. Han, A. Ivaska, L. Niu, Anal. Chem. 2009, 81, 2378.
- [20] S. Reichert, P. Welker, M. Calderón, J. Khandare, D. Mangoldt, K. Licha, R. K. Kainthan, D. E. Brooks, R. Haag, *Small* 2011, 7, 820.
- [21] K. J. Landmark, S. DiMaggio, J. Ward, C. Kelly, S. Vogt, S. Hong, A. Kotlyar, A. Myc, T. P. Thomas, J. E. Penner-Hahn, ACS Nano 2008, 2, 773.
- [22] H. Alinezhad, A. Amiri, M. Tarahomi, B. Maleki, *Talanta* 2018, 183, 149.
- [23] P. S. Wate, S. S. Banerjee, A. Jalota-Badhwar, R. R. Mascarenhas, K. R. Zope, J. Khandare, R. D. K. Misra, *Nanotechnology* **2012**, *23*, 415101.
- [24] K. Bester, A. Bukowska, W. Bukowski, J. Mol. Catal. A: Chem. 2013, 378, 124.
- [25] A. Grirrane, H. Garcia, A. Corma, J. Catal. 2013, 302, 49.
- [26] M. L. Kantam, M. Roy, S. Roy, B. Sreedhar, S. S. Madhavendra, B. M. Choudary, R. L. De, *Tetrahedron* 2007, 63, 8002.
- [27] H. Veisi, S. Hemmati, P. Safarimehr, J. Catal. 2018, 365, 204.
- [28] H. Veisi, P. Safarimehr, S. Hemmati, Mater. Sci. Eng. C 2019, 96, 310.
- [29] H. Veisi, M. Ghorbani, S. Hemmati, *Mater. Sci. Eng. C* 2019, 98, 584.
- [30] H. A. Elazab, A. R. Siamaki, S. Moussa, B. F. Gupton, M. S. El-Shall, *Appl. Catal.*, a 2015, 491, 58.
- [31] A. Tadjarodi, S. M. Ferdowsi, R. Zare-Dorabei, A. Barzin, Ultrason. Sonochem. 2016, 33, 118.
- [32] M. Semler, P. Štěpnička, Catal. Today 2015, 243, 128.
- [33] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. A. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 2004, *306*, 666.
- [34] J. Zhang, T. Li, X. Zhao, Y. Zhao, F. Li, X. Li, J. Colloid Interface Sci. 2016, 463, 13.
- [35] Y. Li, X. Fan, J. Qi, J. Ji, S. Wang, G. Zhang, F. Zhang, Nano Res. 2010, 3, 429.

- [36] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, *Nano Lett.* **2008**, *8*, 902.
- [37] H. Veisi, M. Hamelian, S. Hemmati, J. Mol. Catal. A: Chem. 2014, 395, 25.
- [38] Y. Wang, Y. Zeng, X. Wu, M. Mu, L. Chen, *Mater. Lett.* 2018, 220, 321.
- [39] N. Bahri-Laleh, S. Sadjadi, A. Poater, J. Colloid Interface Sci. 2018, 531, 421.
- [40] H. Alinezhad, M. Tarahomi, B. Maleki, A. Amiri, Appl. Organomet. Chem. 2019, 33, e4661. https://doi.org/10.1002/ aoc.4661
- [41] L. J. Cote, F. Kim, J. Huang, J. Am. Chem. Soc. 2008, 131, 1043.
- [42] D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, Nat. Nanotechnol. 2008, 3, 101.
- [43] S. Chandra, M. D. Patel, H. Lang, D. Bahadur, J. Power Sources 2015, 280, 217.
- [44] M. Baghayeri, H. Alinezhad, M. Tarahomi, M. Fayazi, M. Ghanei-Motlagh, B. Maleki, *Appl. Surf. Sci.* 2019, 478, 87.
- [45] Z. Lu, J. Yu, H. Zeng, Q. Liu, Sep. Purif. Technol. 2017, 183, 249.
- [46] H. Naeimi, F. Kiani, J. Organomet. Chem. 2019, 885, 65.
- [47] S. J. Sabounchei, M. Ahmadi, Z. Nasri, E. Shams, M. Panahimehr, *Tetrahedron Lett.* 2013, 54, 4656.
- [48] A. S. Roy, J. Mondal, B. Banerjee, P. Mondal, A. Bhaumik, S. M. Islam, *Appl. Catal.*, a 2014, 469, 320.
- [49] M. Nasrollahzadeh, M. Khalaj, A. Ehsani, *Tetrahedron Lett.* 2014, 55, 5298.
- [50] S. Keshipour, S. Shojaei, A. Shaabani, Cellulose 2013, 20, 973.
- [51] M. Esmaeilpour, J. Javidi, F. N. Dodeji, M. M. Abarghoui, *Transition Met. Chem.* 2014, 39, 797.
- [52] S. Sadjadi, M. Atai, Appl. Clay Sci. 2018, 153, 78.

How to cite this article: Tarahomi M, Alinezhad H, Maleki B. Immobilizing Pd nanoparticles on the ternary hybrid system of graphene oxide,  $Fe_3O_4$  nanoparticles, and PAMAM dendrimer as an efficient support for catalyzing sonogashira coupling reaction. *Appl Organometal Chem*. 2019; e5203. <u>https://doi.org/10.1002/aoc.5203</u>