FULL PAPER

Effect of addition of iron on morphology and catalytic activity of PdCu nanoalloy thin film as catalyst in Sonogashira coupling reaction

S. Jafar Hoseini | Nahal Aramesh | Mehrangiz Bahrami

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Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj 7591874831, Iran

Correspondence

S. Jafar Hoseini, Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj 7591874831, Iran. Email: jhosseini@yu.ac.ir; sjhoseini54@yahoo. com Palladium-supported catalysts are complex assemblies with a challenging preparation. Minor changes in their preparation conditions can affect the activity, selectivity and lifetime of these catalysts. PdCuFe nanoparticle (NP) thin films were supported on reduced graphene oxide (RGO) by the reduction of the organometallic complex [PdCl₂ (cod)] (cod = *cis,cis*-1,5-cyclooctadiene), and [Cu(acac)₂] and [Fe(acac)₃] (acac = acetylacetonate) complexes at a toluene–water interface. We have investigated the application of the liquid–liquid interface method for preparing ultrathin films of catalysts and have evaluated the catalytic activity of the prepared NPs for the Sonogashira coupling reaction in micelle media. Also, we have investigated the effect of the addition of iron on the morphology, size and catalytic activity of PdCu/RGO NPs. Our study shows that both of the prepared catalysts (PdCu/RGO and PdCuFe/RGO) are efficient and recoverable catalysts for the Sonogashira carbon–carbon coupling reaction. This method has advantages compared to other routes, such as short reaction times, high to excellent yields, facile and low-cost method for the preparation of the catalysts, and easy separation and reusability of the catalysts.

KEYWORDS

carbon-carbon coupling, graphene oxide, palladium/copper nanoalloys, Sonogashira reaction, thin film

1 | INTRODUCTION

Homogeneous palladium catalysis has attracted much interest for C–C coupling reactions such as Suzuki–Miyaura, Sonogashira, Heck and Stille reactions. This methodology has some advantages such as high reaction rate, turnover number, selectivity and yield. Also, some products can be synthesized in this way for the first time.^[11] The properties of these catalysts are dependent on ligand type such as amines^[21] and phosphines^[31] that are expensive. Recent investigations of ligand-free palladium-based catalysts have shown them as promising alternatives to ligand-assisted methods.^[4,5] Homogeneous palladium catalysts have some disadvantages: recycling problem for reusing the catalysts that leads to loss of expensive metal and ligands and produces impurities in products.^[6] Such problems have to be overcome by replacing homogeneous palladium catalysts with heterogeneous ones. In this case, palladium is stabilized on a solid support such as activated carbon,^[7,8] metal oxides,^[9–11] zeolites,^[12] clays^[13] and so on. In this manner, the heterogeneous catalysts can be separated after the reaction and can be reused in a few catalytic cycles. There are some reports of solid-supported palladium catalysts showing higher activities than homogeneous ones due to their higher stability.^[14]

Palladium-supported catalysts are complex assemblies and their preparation is a challenging task. Minor changes in their preparation conditions can affect the activity, selectivity and lifetime of these catalysts. Palladium catalysts can be stabilized on the supports using various methods such as wet or dry impregnation,^[15] deposition– precipitation,^[16] deposition–reduction,^[17] ion exchange methods,^[18] sol–gel processes^[19] and liquid–liquid interface self-assembly.^[20–22]

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In recent years, the interface between two immiscible solutions has been studied as it plays a key role for the assembly of nanostructures and a large variety of solid particles.^[23–25] In this strategy, reducing the surface tension between the fluid phases can lead to stable structures at the liquid–liquid interface formed by solid particles.^[26–30] In contrast to many synthetic processes, the liquid–liquid interface strategy does not need a calcination process. Also, this assembly method can be applied for the *in situ* synthesis of materials, template preformed structures and alloys.

Nanoalloys of transition metals exhibit superior activity over their monometallic counterparts in many organic transformations ^[31–33] due to the strong synergy between the metals that leads to a higher catalytic performance. Graphene oxide (GO) can be used as a stabilizer with oxygen-containing surface groups to enhance the interaction with a metal at a liquid–liquid interface. These structures exhibit a wide variety of applications especially in catalysis.^[34–36] Previously, some platinum- and palladium-based nanostructures were synthesized at a liquid–liquid interface from organometallic precursors and their applications were investigated in *p*-nitrophenol reduction reaction, methanol oxidation in fuel cells and Suzuki–Miyaura reactions.^[20–22,37–42]

In this paper, we report a synthesis of trimetallic PdCuFe nanoalloy thin film supported on GO from the organometallic precursor $[PdCl_2(cod)]$ (cod = *cis,cis*-1,5-cyclooctadiene), and an investigation of the effect of the addition of iron on the morphology and catalytic activity of PdCu/reduced graphene oxide (RGO) nanostructures. These nanoalloys were applied as an efficient catalyst in the Sonogashira coupling reaction (reaction of alkynes with aryl or vinyl halides for the formation of $C(sp^2)$ —C(sp) bonds) under mild reaction conditions and in an environmentally friendly aqueous medium to investigate the effect of the addition of Fe on PdCu/RGO bimetallic alloy. In this study, we adopted a strategy using ligand-free palladium-based catalysts that show interesting catalytic activity with low palladium loading. There are some reports of palladium-based catalysts such as Pd/C that was first investigated by Guzman and coworkers,^[43] but PdCuFe/RGO catalyst produces a higher yield compared to Pd/C catalyst in the Sonogashira reaction.^[43] Also, Pd/C-PPh₃-CuI mixture exhibited very interesting catalytic activity in this case in which two cooperative catalytic cycles of palladium and copper were accepted as a plausible mechanism,^[44] but our strategy involves the synthesis of ligand-free catalyst that has lower cost and lower toxicity.

2 | EXPERIMENTAL

 $PdCl_2$, phenylacetylene and bromobenzene were purchased from Merck Company. $[PdCl_2 (cod)]$ and $[Fe(acac)_3]$ (acac = acetylacetonate) complexes were prepared according to reported procedures^[45,46] and the $[Cu(acac)_2]$ complex was purchased from Merck. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker AXS (D8 Advance) instrument employing the reflection Bragg–Brentano geometry with Cu K α radiation ($\lambda = 1.54184$ Å). Energy-dispersive analysis of X-rays (EDAX) was carried out using a Philips XL30 instrument with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained with a Philips CM-10 microscope operated at 100 kV. The loading amount of palladium was determined using an inductively coupled plasma (ICP) analyser (Varian Vista-Pro). ¹H NMR spectra were obtained with a Bruker 400 MHz Ultra-shield spectrometer using CDCl₃ as the solvent. Products were characterized by comparison of their spectral and physical data with those of known samples (supporting information). All yields refer to isolated products.

2.1 | Preparation of PdCu/RGO and PdCuFe/RGO Thin films at toluene–water interface

GO was prepared from graphite powder in accordance with the modified Hummers-Offeman method.^[40] GO was first exfoliated by dispersing GO (10 mg) in double-distilled water (25 ml) with sonication for 10 min. To prepare PdCuFe/RGO thin film, an equimolar solution of $[PdCl_2(cod)]$, $[Cu(acac)_2]$ and [Fe(acac)₃] (0.33 M, 25 ml) in toluene was sonicated for 5 min to prepare an orange-coloured solution. This solution was placed in contact with the solution of GO in a beaker (100 ml). Once the two layers were stabilized, a freshly prepared aqueous solution of NaBH₄ (15 ml, 0.1 M) was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a coloration of the liquid-liquid interface. With the passage of time, a thin film formed at the liquid-liquid interface. A similar procedure was applied for the synthesis of PdCu/RGO nanoparticle (NP) thin films. The catalyst was obtained from the liquid-liquid interface as follows: (i) the toluene top phase was removed using a syringe; (ii) ethanol was added to the mixture and centrifuged after 30 min; (iii) precipitates were washed with ethanol two times; and (iv) a drying procedure was performed under nitrogen.

2.2 | General procedure for Sonogashira coupling reaction

Phenylacetylene (1.0 mmol) was added to a flask containing catalyst and KOH (2 mmol) in 4 ml of H₂O– cetyltrimethylammonium bromide (CTAB) with a critical micelle concentration of 1 (1 CMC). This mixture was placed in an oil bath at 60 °C. Once the mixture reached this temperature, the reaction was initiated by the addition of aryl halide (1.0 mmol). After completion of the reaction (monitored using TLC), the reaction mixture was cooled to room temperature and then dichloromethane (3 × 5 ml) was added to the reaction vessel. The organic phase was separated and dried over anhydrous MgSO₄. Subsequently, the solution was

evaporated and the resulting compound was washed with cool hexane to afford the desired pure product. The catalyst was recovered from the reaction mixture by decantation of the solution and remained at the bottom of the round-bottom flask. Finally, the catalyst was washed with dichloromethane, water and diethyl ether and dried with nitrogen.

3 | RESULTS AND DISCUSSION

The liquid–liquid interface strategy was used for the synthesis of PdCu/RGO and PdCuFe/RGO. GO was used as a stabilizer with oxygen-containing surface groups, thus enhancing the interaction with the metal. Reduction of GO sheets was started after the addition of the reducing agent of NaBH₄ and they moved to the interface from the bottom phase due to the decrease of the hydrophilicity of the GO and decrease in the polar functionality on the surface of the sheets (Figure 1b). Also, metallic precursors started to reduce and moved from the top phase to the interface (Figure 1b). The effect of the addition of Fe on the morphology of the nanoalloy was investigated. Also, these catalysts were applied in the Sonogashira coupling reaction to evaluate their catalytic activity. These coupling reactions were performed in a water and CTAB medium. Figure 1 shows the reaction steps.

3.1 | PdCu/RGO and PdCuFe/RGO characterizations

The crystal structure and composition of the PdCu/RGO ^[22] and PdCuFe/RGO thin films were confirmed using XRD. In the XRD pattern of PdCu/RGO thin film (Figure 2a), five main diffraction peaks at $2\theta = 40.2^{\circ}$, 47° , 67° , 82.6° and 87° can be assigned as the (111), (200), (220), (311) and (222) planes corresponding to the face-centred cubic Pd structure.^[40] The other diffraction peaks at $2\theta = 45.2^{\circ}$, 52.08° and 75.6° correspond to the (111), (200) and (220) planes of Cu (0) lattice.^[47]



FIGURE 1 Schematic of PdCuFe/RGO trimetallic thin film formation at toluene–water interface. (a) Stabilized mixture of $[PdCl_2 (cod)]$, $[Cu(acac)_2]$ and $[Fe(acac)_3]$ in toluene (orange) and GO in water (brown) followed by dropwise addition of NaBH₄ to the stabilized mixture. (b) Thin film of PdCuFe/RGO nanoalloy appeared at the toluene–water interface after adding NaBH₄. (c) Sonogashira C–C coupling reaction in H₂O–CTAB medium



FIGURE 2 XRD patterns of (a) PdCu/RGO NP thin film^[22] and (b) PdCuFe/RGO NP thin film deposited on glass

RGO shows a broad and weak diffraction peak at $2\theta = 25.25^{\circ}$ that can be assigned as the (002) plane.^[40]

Figure 2(b) shows the XRD pattern of PdCuFe/RGO NP thin film. In addition to the five main diffraction peaks of face-centred cubic Pd, the weak and broad peak of RGO and three peaks that belong to Cu(0), weak diffraction peaks are observed at $2\theta = 44^{\circ}$, 65.1° and 84° corresponding to the (110), (200) and (221) planes of Fe(0).^[41] Relative to the same reflections for Pd, the diffraction peaks of these thin films are shifted to higher 2θ values, revealing decreased lattice parameters and a high level of alloying.^[48]

As shown in Figure 3(a,b), TEM images of the PdCu/ RGO NPs exhibit spherical structures with an average diameter of 8.8 nm (Figure 3c). Figure 4(a–c) shows TEM images of the PdCuFe/RGO NP thin film. The average diameter of the thin-film particles is approximately 7.2 nm (Figure 4(d)).

The chemical composition of the PdCuFe/RGO thin film was characterized using EDAX, confirming the presence of Pd, Cu, Fe and C elements (Figure 5).

3.2 | Investigating effect of addition of Fe on morphology of PdCu/RGO thin film

One of our main purposes in the work reported was in fact to improve the catalytic performance of the thin films and



FIGURE 3 (a, b) TEM images of PdCu/RGO NP thin film with (c) an average diameter of 8.8 nm $^{\left[22\right]}$

reduce the usage of precious and expensive metals for commercialization of the catalysts by developing a suitable route for the synthesis of alloy nanostructures having well-defined shapes (Table 1).

From the TEM images (Figures 3 and 4), it is obvious that the addition of Fe to the PdCu/RGO nanoalloy thin film not only prevents particle aggregation, but also decreases the size of NPs having a very good dispersion.



FIGURE 4 (a-c) TEM images of PdCuFe/RGO NP thin film and (d) histogram of particle size distribution



FIGURE 5 EDAX spectrum of PdCuFe/RGO thin film

TABLE 1 Effect of alloying on morphology of thin films

Entry	Thin film	Morphology	Size (nm)	Ref.
1	Pd/RGO	Spherical NPs	7	[20]
2	PdCu/RGO	Spherical NPs	8.8	This work
3	PdCuFe/RGO	Spherical NPs	7.2	This work

3.3 ↓ Investigating effect of addition of Fe on catalytic activity of PdCu/RGO thin film using Sonogashira C–C coupling reaction

Synthesis of Pd(0) NPs from Pd(II) at a GO support can be advantageous due to the generation of species with a higher catalytic activity.^[1] In this study, the catalytic activity of PdCu/RGO and the effect of the addition of Fe to the thin film were investigated for the Sonogashira coupling reaction.

The PdCu/RGO and PdCuFe/RGO nanoalloy thin films were used as suitable and recoverable catalysts in the Sonogashira coupling reaction. We initiated our investigation by optimizing the reaction conditions. Phenylacetylene and bromobenzene were used in a model C–C coupling reaction. The solvent has an important effect on the reactivity of this type of coupling reaction. Therefore, the reaction of bromobenzene with phenylacetylene was performed in the presence of the nanoalloy thin films using various solvents. The results of the catalytic reactions are summarized in Table 2. Among the various solvents tested, the best conversion is observed for H₂O–CTAB (1 CMC) (Table 2, entry 6). The product is detected in a lower yield when the reaction is carried out with other solvents (Table 2).

Also, the Sonogashira coupling reaction of bromobenzene with phenylacetylene at various temperatures was investigated. According to the results summarized in Table 3, we choose 60 °C as the reaction temperature in aqueous solutions (Table 3, entry 2).

In the next step, the reaction of bromobenzene with phenylacetylene was performed in the presence of the nanoalloy thin films. Kotschy and co-workers used diisopropylamine as an alternative to K_2CO_3 , but the yields



TABLE 2 Sonogashira coupling reaction of bromobenzene with phenylacetylene (1:1 mmol) in various solvents and in the presence of K_2CO_3 as base at 80 °C in 20 min

Catabyst R_CCO_H_COLTAB						
Entry	Solvent	PdCu/RGO (mol%) ^a ; yield (%) ^b	PdCuFe/RGO (mol%) ^a ; yield (%) ^b			
1	DMF	0.006; 50	0.001; 20			
2	THF	0.006; 5	0.001; 5			
3	Toluene	0.006; trace	0.001; 30			
4	H_2O	0.006; 85	0.001; 40			
5	H ₂ O-EtOH (1:1)	0.006; 75	0.001; 35			
6	H ₂ O-CTAB	0.006; 90	0.001; 90			

^aPd mol%.

^bIsolated yield.

TABLE 3 Sonogashira coupling reaction of bromobenzene withphenylacetylene at various temperatures in micellar system of CTAB and inthe presence of K_2CO_3 as base for 20 min

Entry	Temp. (°C)	PdCu/RGO (mol%) ^a ; yield (%) ^b	PdCuFe/RGO (mol%) ^a ; yield (%) ^b
1	80	0.006; 90	0.001; 90
2	60	0.006; 90	0.001; 90
3	50	0.006; 50	0.001; 75
4	40	0.006; 20	0.001; 60

^aPd mol%.

^bIsolated yield.

were not very high.^[49] We used KOH as an efficient base with the best yield for this type of coupling reaction (Table 4, entry 4).

Finally, various amounts of catalysts were studied. The reaction yields a trace amount of product (below 5%) without catalyst after 24 h; it proceeds catalytically upon the addition of the NP thin films. The optimal amounts of the catalysts were determined from the reaction of bromobenzene with phenylacetylene at 60 °C in micellar system of CTAB (1 CMC). PdCuFe/RGO (0.001 mol%) and PdCu/RGO (0.006 mol%) give the best results in the Sonogashira coupling reaction.

TABLE 4 Variation of bases for Sonogashira coupling reaction ofbromobenzene with phenylacetylene at 60 °C in micellar system of CTAB for20 min

Entry	Base	PdCu/RGO (mol%) ^a ; yield (%) ^b	PdCuFe/RGO (mol%) ^a ; yield (%) ^b
1	K ₂ CO ₃	0.006; 90	0.001; 90
2	Na ₂ CO ₃	0.006; 90	0.001; 85
3	NEt ₃	0.006; 60	0.001; 40
4	KOH	0.006; 95	0.001; 95
5	NaOH	0.006; 60	0.001; 80

^aPd mol%.

^bIsolated yield.

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Bromobenzene mmol) treated with (1was phenylacetylene (1 mmol) and KOH (2 mmol) in the presence of the PdCuFe/RGO catalyst (0.001 mol%) and the PdCu/RGO catalyst (0.006 mol%) at 60 °C and after 20 min a quantitative yield was obtained (Table 5, entry 2). To investigate the scope of the reaction, the optimized conditions were utilized for the Sonogashira couplings of various aryl halides with phenylacetylene. The results for related investigations are summarized in Table 5. Different aryl halides bearing electron-withdrawing and electron-donating groups can react in short reaction times with good reaction yields (70-95%). The activity of aryl halides usually decreases in the order I > Br > Cl due to the stronger $C(sp^2)$ –Cl bond than the $C(sp^2)$ —Br and $C(sp^2)$ —I bonds. Aryl iodide is found to be more reactive than aryl chloride and bromide (Table 5, entries 1-3). We also investigated some aryl chlorides in the Sonogashira cross-coupling reaction, and products are found in good yields (Table 5, entry 5). These results clearly show that PdCu/RGO and PdCuFe/RGO are efficient catalysts for the Sonogashira coupling reaction.

Also, the efficacy of the present catalysts was compared with that of previously reported catalysts in the coupling of aryl iodides with phenylacetylene. The results are summarized in Table 6.

To compare the catalytic activity of PdCu/RGO with PdCuFe/RGO thin film we should consider the following important points that affect catalytic activity:

- 1. **Surface area.** Dispersion of nanostructures on the GO support in the form of thin films can increase the surface area. PdCu/RGO and PdCuFe/RGO thin films exhibit higher catalytic activity compared to other catalysts according to Table 6. Furthermore, in the presence of PdCu/RGO and PdCuFe/RGO, the Sonogashira reaction progresses under milder conditions. Also, PdCuFe/RGO exhibits a better catalytic activity than PdCu/RGO due to the smaller particle size.
- 2. **Dispersion of metal atoms on the support.** TEM images show a better dispersion of nanostructures on the RGO surface for PdCuFe/RGO and confirm its better catalytic activity.

- 3. **Size of the crystallites.** According to TEM images, the size of PdCuFe/RGO nanostructures is smaller than that of PdCu/RGO nanostructures. Therefore, the PdCuFe/RGO nanostructure thin film exhibits a better catalytic activity.
- 4. **Oxidation state of Pd.** Synthesis of Pd(0) NPs from Pd(II) at the GO support can be advantageous due to the generation of species with a higher catalytic activity.^[1] Both PdCu/RGO and PdCuFe/RGO catalysts contain Pd(0) and have higher catalytic activity than catalysts containing Pd(II) under similar conditions.^[1]
- 5. **Conditions of catalyst preparation.** PdCu/RGO and PdCuFe/RGO catalysts are nanostructures prepared at a toluene–water interface. Therefore, all the atoms are on the surface of the catalyst that can lead to a higher catalytic activity.
- 6. Turnover frequency (TOF) and turnover number (TON) calculations. The TON (moles of product per mole of catalyst) and TOF (= TON per time (h)) were calculated. The TOF and TON, which are measures of the efficiency of a catalyst, totally depend on the Pd concentration. Kohler and co-workers reported that the Pd/ C-catalysed Sonogashira reaction of iodobenzene with phenylacetylene without the addition of CuI or PPh3 gives TOF = 1184 h^{-1} and TON =592.^[50] Gholinejad and Ahmadi reported that the Sonogashira reaction over Pd-CuFe₂O₄/SiO₂ catalyst gives TOF = 10.97 h^{-1.[51]} Under similar conditions, Basu and co-workers,^[52] Metin and co-workers^[53] and Gao and co-workers^[54] reported the Sonogashira reaction with Pd/Cu-ARF(II) $(TOF = 43.43 h^{-1}), Cu_{48}Pd_{52}/RGO (TOF = 145.26 h^{-1})$ and MMT/Pd-Cu (TOF = 6.06 h^{-1}) catalysts, respectively. In the present study, PdCu/RGO and PdCuFe/RGO catalysts show higher TOF (68 839 and 593 750 h^{-1} , respectively) and TON (15 833 and 95 000, respectively) for the Sonogashira reaction of phenylacetylene with iodobenzene.

The size of PdCu/RGO (8.8 nm) and PdCuFe/RGO (7.2 nm) is very nearly equal. So the doping of Fe has changed the PdCuFe/RGO particles. The results show that

TABLE 5	Sonogasnira cross-coupling reaction between ar	yi nandes and phenylace	etylene in the presence of N	NP thin films under optimized rea	iction conditions

Entry	Substrate	PdCu/RGO: time (min); yield (%) ^b	PdCu/RGO: TON; TOF (h ⁻¹)	PdCuFe/RGO: time (min); yield (%) ^b	PdCuFe/RGO: TON; TOF (h ⁻¹)
1	PhI	14; 95	15 833; 68 839	10; 95	95 000; 593 750
2	PhBr	20; 95	15 833; 47 979	20; 95	95 000; 287 879
3	PhCl	90; 88	14 667; 9778	70; 91	91 000; 78 448
4	4-MeC ₆ H ₄ Br	80; 90	15 000; 11 278	35; 93	93 000; 159 520
5	4-NO ₂ C ₆ H ₄ Cl	80; 80	13 333; 10 025	55; 86	86 000; 93 886
6	$4-NO_2C_6H_4Br$	18; 70	11 666; 38 887	15; 75	75 000; 300 000
7	C ₅ H ₄ NCl	120; 70	11 666; 5833	80; 70	70 000; 52 632

^aReaction conditions: 60 °C, H₂O-CTAB and KOH as base.

^bIsolated yield.

TABLE 6 Study of efficacy of the present catalysts compared with previously reported catalysts



Entry	Catalyst	Catalyst (mol%)	Solvent	Base	Temp. (°C)	Time (min)	Yield (%)	Ref.
1	Pd/C	0.5	Piperidine	Piperidine	100	360	61	[50]
2	Pd/C	0.125	DMA ^a	Pyrrolidine	100	360	77	[50]
3	Pd/C	0.5	Pyrrolidine	Pyrrolidine	100	360	80	[1]
4	Pd-CuFe ₂ O ₄ /SiO ₂	0.3	DMA	1,4-Diazabicyclo[2.2.2]octane	50	1440	80	[51]
5	Pd/Cu-ARF(II) ^b	Not reported	CH ₃ CN	K ₂ CO ₃	80	360	85	[52]
6	Cu48Pd52/RGO	0.63	DMF	КОН	120	60	93	[53]
7	MMT ^c /Pd-Cu	1	Ethanol	K ₂ CO ₃	65	960	97 ^d	[54]
8	PdCu/RGO	0.006	H ₂ O-CTAB	KOH	60	14	95	This work
9	PdCuFe/RGO	0.001	H ₂ O-CTAB	КОН	60	10	95	This work

^aDMA: dimethylacetamide.

^bARF(II): Amberlite resins with formate, under N₂ condition.

^cMMT: montmorillonite.

^dIn the presence of 2 mol% PPh₃.

with increasing Fe amount in the NPs with nearly the same size, the efficiency of the reaction is increased.

There are some reports of the Sonogashira reaction in the absence of palladium and using other transition metals such as iron ^[55] and copper.^[56] In most of these reports, results are limited to the use of aryl iodides and activated bromides under high reaction temperature (130 °C) and high loading of catalysts. Therefore, there are few reports about the reaction in the presence of aryl chlorides, but the PdCu/RGO and PdCuFe/RGO thin films can react with aryl chlorides to give high yields of products.

One of the major advantages of the system under investigation is the easy separation of the catalyst from the reaction mixture for recovery and reuse. The reusability of the catalysts was investigated in the reaction of bromobenzene with phenylacetylene at 60 °C under optimized reaction conditions. When the reaction was completed, the catalyst could be easily separated and then it was washed with water and diethyl ether. The recovered catalyst was dried and can be reused successfully. As evident from Table 7, the catalytic activity of the alloy catalysts remains and they retain a good performance after four recycles.

In general, C–C coupling reactions catalysed by supported palladium follow the usual reaction mechanism with three main steps: (i) oxidative addition, (ii) transmetallation and (iii) reductive elimination. Addition of non-precious

 TABLE 7
 Recycling results of PdCu/RGO and PdCuFe/RGO NP thin films as catalyst at 60 °C for coupling reaction of phenylacetylene with bromobenzene^a

Cycle	PdCu/RGO: yield (%) ^b	PdCuFe/RGO: yield (%) ^b
Fresh catalyst	95	95
First recycle	95	95
Second recycle	90	95
Third recycle	80	90
Fourth recycle	80	85

 aReaction conditions: 60 °C, $H_2O\mathchar`-CTAB$ and KOH as base. bIsolated yield.

metals such as Cu and Fe to the Pd thin film is reduces the amount of expensive Pd content of the catalyst and improves the catalytic activity due to the synergistic effect of Cu and Fe that accelerates the reductive elimination reaction. Moreover, theoretical studies demonstrated that metals such as Cu can modify the Pd valence state via injection of charge into the sp subband.^[57] Due to electronic modification in the Pd–Cu alloys, it improves the catalytic activity of the alloy systems. ICP analysis shows no Pd leaching, but it has been accepted that most heterogeneous Pd catalysts catalyse via a homogeneous method (dissolved as colloids or complexes by leaching from the supported Pd) by leached Pd species, and can re-deposited on reaction completion.^[11]

4 | CONCLUSIONS

Palladium-based alloys exhibit promising catalytic activity in various organic transformations. Homogeneous Pd catalysts in C-C Sonogashira reactions exhibit some disadvantages such as the high cost of Pd, they cannot be recycled and reused and are difficult to extract from the reaction mixture that can cause a severe problems for pharmaceutical industries and limiting their application. Heterogeneous systems have high catalyst stability, and the catalysts are easily extracted from the reaction mixture by simple filtration and can be reused for several subsequent reactions. In this study, PdCuFe NPs supported on RGO thin films were prepared via a simple liquid-liquid interface self-assembly method as a heterogeneous catalyst (insoluble catalyst in the reaction medium and catalyst recovery is achieved by solvent decantation). In most cases of Sonogashira coupling catalysed by Pd/C, the presence of CuI and PPh₃ as ligands is necessary. There are few reports of the use of Pd/C catalysts for Sonogashira coupling reactions being successful in the absence of phosphine ligands. Also, cross-coupling reactions catalysed by supported Pd can be carried out in organic solvents or organic solvent-water mixtures. In this study we

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used a ligandless catalyst in a safe solvent and environmentally friendly medium of H_2O –CTAB via a reduction of an organometallic precursor, [PdCl₂ (cod)], and also [Cu(acac)₂] and [Fe(acac)₃] complexes. These recyclable heterogeneous catalysts show suitable and efficient properties for the Sonogashira carbon–carbon coupling reaction of a wide range of aryl halides with phenylacetylene. The size of these NPs is approximately 7–9 nm that affects the catalytic activity. Since PdCu/RGO and PdCuFe/RGO have similar size, the higher efficiency of PdCuFe/RGO in the Sonogashira coupling reaction is ascribed to the addition of Fe. The major advantages of these catalysts are as follows:

- 1. High surface area due to both GO sheets and nanoalloy thin films leads to an increase in the contact between reactants and catalyst.
- 2. The reactions were performed in a green solvent, H_2O , giving high to excellent yields in short reaction time.
- 3. The catalytic activity of PdCuFe/RGO is greater than that of PdCu/RGO (TOF = 593 750 and 68 839 h⁻¹, respectively), and greater than that of some other reported catalysts in the Sonogashira reaction of phenylacetylene with iodobenzene.

It can be expected that these kinds of catalysts will become of enhanced importance in future.

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