# Formation of PdNiZn thin film at oil-water interface: XPS study and application as Suzuki-Miyaura catalyst

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S. Jafar Hoseini, Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj 7591874831, Iran. Email: jhosseini@yu.ac.ir; sjhoseini54@yahoo.com Nanosheet of PdNiZn and nanosphere of PdNiZn/reduced-graphene oxide (RGO) with sub-3 nm spheres have been successfully synthesized through a facile oil-water interfacial strategy. The morphology and composition of the films were determined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive analysis of X-ray (EDAX) and elemental mapping. In the present study, we have developed a method to minimize the usage of precious Pd element. Due to the special structure and intermetallic synergies, the PdNiZn and PdNiZn/RGO nanoalloys exhibited enhanced catalytic activity and durability relative to Pd nanoparticles in Suzuki-Miyaura C-C cross-coupling reaction. Compared to classical cross-coupling reactions, this method has the advantages of a green solvent, short reaction times, low catalyst loading, high yields and reusability of the catalysts.

### **KEYWORDS**

graphene oxide, oil-water interface, Suzuki-Miyaura catalyst, thin film, trimetallic alloy nanosheets

### **1** | INTRODUCTION

Trimetallic nanoparticles (NPs) alloy have attracted increasing interest due to their special morphology, size and high surface- to- volume ratios.<sup>[1]</sup> Enormous effort has been dedicated to the synthesis of multimetal alloys due to their various advantages.<sup>[2]</sup> A higher degree of selectivity, higher activity and chemical/physical stability are some of the advantages of trimetallic nanoalloys compare to their monometallic or even bimetallic counterparts.<sup>[3,4]</sup> Ultrathin noble metal nanocrystals have a potential to exhibit novel properties, especially in the area of catalysis which is related to their high specific surface area.<sup>[5]</sup> Tremendous efforts have been dedicated to the synthesis of ultrathin nanostructures of noble metals which is limited in comparison with nanostructures of metal hydroxides or sulfides.<sup>[6]</sup> The importance of trimetallic alloys as a catalyst in one hand and the importance of ultrathin nanostructures on the other hand,

encouraged our group to investigate new strategies for the synthesis of ultrathin trimetallic alloy structures like nanosheets or nanospheres. Nanosheets have attracted intensive interest due to their wide range of applications.<sup>[7]</sup> To obtain these structures, generally specific conditions should be applied such as using stabilizers or capping agents to control the growth process.<sup>[8]</sup> Bao and Tang et al. have synthesized ultrathin Pd nanosheets by using surfactants.<sup>[9,10]</sup> Till now, there are limited reports on the one-step synthesis of ultrathin trimetallic nanosheets or NPs in the absence of stabilizers. Kang et al. have synthesized Au@PdPt NPs with high catalytic activity in the presence of ascorbic acid and hydrazine.<sup>[11]</sup> Wu et al. have synthesized Au nanostructures on pre-formed PtNi nanostructures in two steps.<sup>[12]</sup> Among trimetallic nanocrystals, Pd-based nanocatalysts have attracted attention because of their physical and chemical performances compare to pure Pd or its bimetallic nanoalloys.<sup>[13]</sup> Palladium components are the best choice catalysts for various cross-coupling reactions, such as the Suzuki-Miyaura reaction (one of the most important synthetic transformations developed in the twentieth century) which exhibits a key role for the synthesis of symmetrical and unsymmetrical biaryl compounds.<sup>[14]</sup> Pd components have a high activity for a wide range of substrates but they suffer from leaching or aggregation after few cycles of the reaction progress.<sup>[15]</sup> Furthermore, high-cost and scarcity of Pd encourage the researchers to replace Pd partially or completely with low-costing metals. Several recent investigations evidenced the importance of bimetallic NP catalysts, such as PdAu, PdNi, PdZn and PdCu as effective catalysts for the Suzuki-Miyaura reaction.<sup>[16-19]</sup> Among the Pd alloy catalysts, alloys with lower metal costs and abundantly available metals (Ni and Zn) are extracted more attention. In C-C cross-coupling catalytic reactions, the main facts that affect the catalytic activity are structure and electronic properties. Therefore, besides the components, the size and surface morphology facts have an important role.<sup>[20]</sup> Nanostructures with different morphologies exhibit different atomic arrangements on the surface resulting in distinct electronic and geometric structures which improve the catalytic activity.<sup>[21]</sup> In this study, we highlight a new developed method for the synthesis of ultrathin trimetallic alloys with promising catalytic activity in Suzuki-Miyaura reaction as expanded by Rao's group and us.<sup>[22–32]</sup>

### 2 | EXPERIMENTAL

### 2.1 | Materials and methods

All of the chemical compounds were purchased from Merck and Sigma-Aldrich Companies. The  $[PdCl_2(cod)]$  (cod = *cis*, *cis*-1,5-cyclooctadiene) was synthesized using

reported procedure.<sup>[33]</sup> The powder X-ray diffraction patterns (XRD) were obtained by a Bruker AXS (D8, Advance) instrument employing the reflection Bragg– Brentano geometry with Cu-K $\alpha$  radiation. Transmission electron microscopy (TEM) images were collected with a JEOL JEM-3010 with an accelerating voltage of 300 kV. The elemental composition of the compounds and scanning electron microscopy (SEM) images were obtained from Nova Nano SEM 600, FEI company. X-ray photoelectron spectroscopy (XPS) spectra were recorded in an Omicron Nanotechnology Spectrometer with Mg K $\alpha$  as the X-ray source.<sup>1</sup>H NMR spectra were obtained with a Bruker 400 MHz Ultra-shield spectrometer in CDCl<sub>3</sub>. Infrared spectra were recorded with a JASCO FT/IR-680 plus spectrometer.

### 2.2 | Preparation of the PdNiZn/RGO thin film at toluene-water interface

Graphene oxide (GO) was synthesized from graphite powder by using modified Hummers method (supporting information file)<sup>[34,35]</sup> and characterized by FE-SEM, XRD and FT-IR techniques (Figures S1-S3). In the case of formation of PdNiZn/RGO at the interface of two immiscible liquids, according to Scheme 1a, in the first step GO (10 mg) was exfoliated and dispersed in 25 mL of distilled water by using ultrasonic waves for 10 min. Toluene solution (25 ml) contain an equimolar solution of  $[PdCl_2(cod)]$ ,  $[Ni(acac)_2]$  and  $[Zn(acac)_2]$  (acac = acetylacetonate) (0.33 mM) was prapared and sonicated for 10 min (Scheme 1a, yellow solution). This solution was contacted with aqueous solution contain GO in a beaker (100 ml) (Scheme 1b). After the stabilization of toluene and water layers, sodium borohydride aqueous solution (10 ml, 0.1 M) was injected by a syringe (Scheme 1c).

> SCHEME 1 Schematic illustration of the formation of PdNiZn/RGO trimetallic nanoalloy thin film at the interface between toluene and water, (a) dispersion of GO in water and metallic precursors in toluene, (b) stabilized mixture of  $[PdCl_2(cod)]$ ,  $[Ni(acac)_2]$  and  $[Zn(acac)_2]$ complexes in toluene (top phase, yellow) and GO in water (bottom phase, brown), (c) addition of the reducing agent to the stabilized mixture, (d) movement of RGO sheets and metallic NPs toward the interface. (e) formation of the PdNiZn/ RGO thin film at the toluene-water interface after 24 h, (f) extraction of the catalyst by removing the toluene (top phase) by a dropper



Addition of NaBH<sub>4</sub> leads to the reduction of both two phases: metallic precursor reduction and GO reduction. The functional groups on GO, which makes this compound dispersible homogeneously in water, decreases and makes it insoluble in water. This is the reason for the movement of RGO sheets toward the interface (Scheme 2d). The produced RGO sheets and reduced metallic NPs are self-assembled at the interface (Scheme 2d). The reduction was begun by the color change of the toluene phase from yellow to colorless which leads to the formation of the gray thin layer at the interface. Finally, the aqueous and organic phases below and above of the gray film were transparent (Scheme 1e). For the extraction of the catalyst from the interface, the toluene phase is removed by using a dropper after 24 h, ethanol is added to the aqueous phase and centrifuged (Scheme 1f). The obtained product can apply as an efficient catalyst for the Suzuki-Miyaura reaction. This procedure is continued similarly for the synthesis of PdNiZn trimetallic alloy thin film in the absence of GO as a stabilizer in the aqueous phase. Also, the amount of aqueous NaBH<sub>4</sub> is (5 ml, 0.1 M) in this step.

### 2.3 | General procedure for Suzuki-Miyaura reaction

Aryl halide (1.0 mmol) and phenylboronic acid (1.5 mmol) were added to a round bottom flask containing the trimetallic nanoalloy catalyst and  $K_2CO_3$  (2.0 mmol) in distilled water (5.0 ml). The mixture was stirred in 80 °C oil bath. After completion of the reaction (monitored by thin layer chromatography (TLC)), dichloromethane (3 × 5 ml) was added to the reaction vessel. The organic phase was separated and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent leads to the formation of the pure desired product. The obtained compounds were

characterized using FT-IR and <sup>1</sup>H NMR spectra which is in good agreement with the reported data. The details are given in the Supporting Information file.

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

### 3.1 | Physicochemical characterization of the catalysts

The as-synthesized trimetallic nanoalloy Thin films were characterized by XRD, XPS, FE-SEM, TEM and EDAXelemental mapping analysis. Figure 1(a, b) shows the XRD patterns for the PdNiZn and PdNiZn/RGO thin films, respectively. The five main diffraction peaks can be assigned to [(111), (200), (220), (311) and (222)] indices of face-centred cubic (*fcc*) Pd(0) at  $2\theta = 40^{\circ}$ , 48°, 68°, 82°, 86°.<sup>[34]</sup> The diffraction peaks with indices [(002), (100), (101), (102), (103), (110) and (004)] confirm the presence of Zn(0).<sup>[18]</sup> Other diffraction peaks, [(111), (200), (220) and (311)] correspond to the Ni(0).<sup>[36]</sup> Furthermore, in the XRD pattern of PdNiZn/RGO (Figure 1b), a clear diffraction band was observed at  $2\theta \sim 25^{\circ}$ , corresponding to the (002) plane of RGO.<sup>[34]</sup>

Figure 2 (a, b) shows the FE-SEM images of the PdNiZn and PdNiZn/RGO trimetallic nanoalloy thin films, respectively. Interestingly, PdNiZn has a sheet-like morphology which is consistent throughout the sample.

In the presence of RGO, the morphology of PdNiZn trimetallic nanoalloy changes from nanosheet to ultrathin nanospheres stabilized on RGO surface which is further confirmed by TEM images. Figure 3a shows the TEM image of PdNiZn alloy which has nanosheet like morphology while in the case of PdNiZn/RGO (Figure 3b), spherical ultrathin NPs is observable on the RGO surface with the mean diameter of 3 nm (Figure 3c). It is interesting that presence of GO changes the morphology of



SCHEME 2 Schematic illustration of formation of PdNiZn nanosheets and PdNiZn/RGO ultrathin spherical NPs at toluene-water interface



**FIGURE 1** XRD patterns of the (a) PdNiZn and (b) PdNiZn/RGO trimetallic nanoalloy thin films deposited on a glass

PdNiZn from nanosheet to spherical ultrathin NPs. Scheme 2 exhibits the proposed mechanism.

### 3.2 | Proposed mechanism for the synthesis of PdNiZn nanosheets and PdNiZn/RGO ultrathin spherical NPs

In this study, PdNiZn thin film exhibits nanosheet structure whereas PdNiZn/RGO shows ultrathin spherical NPs stabilized on RGO at the interfaces. Due to the different lattice structures of Pd and Ni (*fcc*), and Zn (*hcp*), different assembly and growth will happen. In general, according to Scheme 2a, the reduction was initiated by dropwise addition of NaBH<sub>4</sub> and Pd precursor reduced in the form of a sphere (Scheme 2b). This



**FIGURE 2** FE-SEM images of the (a) PdNiZn and (b) PdNiZn/ RGO trimetallic nanoalloy thin films

reduction was followed by the reduction of the second metal, (Ni(II)) (Scheme 2c), and Zn(II) to Zn (0) as a third metal (Scheme 2d) due to their standard electrode potentials. After the nucleation process (Scheme 2b,c,d), two routs are exist: In the case of PdNiZn thin film (in the absence of GO), reduced Pd, Ni and Zn were self-assembled (Scheme 2e) and grew with each other to form a nanosheet structure (Scheme 2f) (route 1). In the case of PdNiZn/RGO, simultaneous to nucleation process (Scheme 2b,c,d), GO sheets are also reduced. GO sheets with hydroxyl, epoxide and carboxyl functional groups which make this component hydrophile, lose its hydrophilicity due to the reduction of these functional groups. The decrease in the polar functionality is the driving force for the



**FIGURE 3** (a) TEM images of the (a) PdNiZn nanosheet, (b) PdNiZn/RGO ultrathin spherical NPs and (c) diagram of particles size distribution for PdNiZn/RGO

Diameter (nm)

movement of GO toward the interface (Scheme 2g). The prepared spherical NPs from nucleation process do not have time for self-assembly and crystal growth. They WILEY Chemistry

adsorb on the RGO surface at a time they formed and stabilize on the RGO surface (Scheme 2h).

The composition of the PdNiZn nanosheets was investigated by EDAX analysis and elemental mapping (Figure 4a-d). Also, Figure 4e shows the EDAX spectra of PdNiZn/RGO trimetallic nanoalloy which shows the presence of Pd, Ni, Zn and C in the sample.

PdNiZn alloy was further characterized by XPS. Figure 5 shows XPS spectra of Pd, Ni and Zn in PdNiZn alloy, the signal at 335.5 and 340.8 eV can be assigned corresponding to the  $d_{5/2}$  and  $d_{3/2}$  states of Pd, respectively. The signal at 853.0 eV is corresponding to Ni 2p orbital, whereas signal at 1020.16 is due to the Zn 2p orbitals (Figure 5a-c).

The Pd, Ni and Zn loadings in the catalysts was obtained using ICP that was 6.69% for Pd, 6.97% for Ni and 5.84% for Zn in the case of PdNiZn nanosheets. Also, in the case of PdNiZn/RGO ultrathin spherical NPs, the loading of Pd, Ni, and Zn is 1.21%, 4.08% and 5.09%, respectively.

### 3.3 | Investigating the catalytic activity of trimetallic nanoalloy thin films

The PdNiZn nanosheet and PdNiZn/RGO ultrathin spherical NP thin films were investigated for the Suzuki-Miyaura C-C cross-coupling reaction as the efficient recoverable catalysts (Scheme 3).

To optimize the reaction conditions of the cross-coupling reaction of phenylboronic acid and bromobenzene, PdNiZn/RGO ultrathin spherical NPs is used in different solvents and temperatures (Table 1).

K<sub>2</sub>CO<sub>3</sub> was used as a base for optimizing the conditions of the reaction. According to Table 1, the biphenyl product is obtained in a high yield (97 %) when the reaction is progressed in water at 80 °C (Table 1, entry 2). The reactions were performed with various amounts of catalyst to test the reaction feasibility with catalyst concentration. Due to the high cost of Pd, the optimum amount of Pd in alloy catalyst was investigated for the reaction of phenylboronic acid with bromobenzene at optimized solvent and temperature condition (Table 2). As shown in Table 2, the optimum amount of the Pd in alloy catalyst was found to be 1.74 mol% of Pd in the case of PdNiZn nanosheet, whereas interestingly for the PdNiZn/RGO catalyst, 0.29 mol% of Pd was found to be optimum. It is noteworthy that presence of RGO increases the reaction yield and decreases the cost of catalyst.

More studies were focused on the application of the optimized reaction conditions to Suzuki-Miyaura cross coupling reactions of aryl halides. As shown in Table 3, various substrates including those with electron-with-drawing and electron-donating groups can be coupled in good reaction yields (70-97 %) in short reaction times. Also, the study of the efficacy of the present catalysts



**FIGURE 4** (a) EDAX elemental mapping analysis of (a) Pd, (b) Ni and (c) Zn nanosheet EDAX spectra of PdNiZn and (b) PdNiZn/rGO nanocomposite

compared with previous reports in the coupling of phenylboronic acid and bromobenzene in Table 4.

According to the following reasons, PdNiZn nanosheet and PdNiZn/RGO ultrathin spherical NPs are better catalysts for Suzuki- Miyaura C-C coupling reaction:

- i. **Synergistic effects:** The as-prepared trimetallic ultrathin nanoalloy thin films exhibit superior catalytic performance than their monometallic analogous. This behavior is due to the interesting synergistic interactions between the metals. The excellent synergic interactions between Ni, Pd, and Zn in trimetallic PdNiZn nanocatalysts are considered to play an important role in the observed high catalytic activity. Scheme 4 exhibits the synergic effect between the three metals (Pd, Ni, Zn) and formation of PdNiZn trimetallic alloy with higher catalytic activity, stability and new properties.
- ii. The number of active sites and specific surface area of the catalyst: The morphology, shape and size of nanostructures play an important role in the field of catalysis. Different atomic arrangements on the surface are the result of nanostructures with different morphologies which leads to distinct geometric structures and improve the catalytic activity.<sup>[45]</sup> Nanosheets exhibit higher catalytic activity due to their large specific surface area and more active sites (Table 4). In the presence of PdNiZn nanosheets and

PdNiZn/RGO ultrathin spherical NPs, the Suzuki-Miyaura reaction was progressed in milder and green condition. Also, PdNiZn/RGO ultrathin spherical NPs exhibits a better catalytic activity than PdNiZn due to its high surface-to-volume ratio which is due to the small particle size and presence of RGO.

- iii. Stabilization of the metal atoms on the RGO support: GO with its large surface area can apply as an effective stabilizer for fabrication of less aggregated ultrathin spherical NPs. Furthermore, the synergistic catalytic interaction can be obtained between graphene and metal NPs.
- iv. **Preparation strategy:** The PdNiZn nanosheets and PdNiZn/RGO spherical NPs are ultrathin films that prepared at the toluene-water interface. These structures contain a large number of surface atoms that lead to a higher catalytic activity. This is the reasons for their better catalytic activity. Also, PdNiZn/RGO ultrathin spherical NPs exhibit better catalytic activity in Suzuki-Miyaura reaction even than PdNiZn due to the small particle size (3 nm), large surfaceto-volume ratio and presence of RGO with its large specific surface area.
- v. Accelerating the oxidative-addition and reductive-elimination steps by using trimetallic catalysts: In general, three steps are present in the catalytic cycle of each Suzuki-Miyaura C-C coupling reaction: (1) oxidative addition, (2) transmetallation





and (3) reductive elimination (Scheme 5).<sup>[19]</sup> From Table 3, it is obvious that the oxidative addition of the Pd-based catalysts into a carbon-halogen bond



**SCHEME 3** PdNiZn nanosheet and PdNiZn/RGO spherical NPs thin films catalyzed Suzuki-Miyaura cross-coupling reaction of aryl halide with phenylboronic acid in water

**TABLE 1**Suzuki-Miyaura cross-coupling reaction in various solvents and temperatures in the presence of PdNiZn/RGO ultrathinspherical NPs<sup>a</sup>

Entry	Solvent	Temp (°C)	Yields (%) <sup>b</sup>
1	H <sub>2</sub> O	r.t.	80
2	H <sub>2</sub> O	80	97
3	H <sub>2</sub> O/EtOH (1:1)	r.t.	65
4	H <sub>2</sub> O/EtOH (1:1)	80	75
5	EtOH	r.t	60
6	EtOH	70	70
7	Toluene	100	25

<sup>a</sup>Reaction conditions: 1.0 mmol of bromobenzene, 1.50 mmol of phenylboronic acid, 2.0 mmol of  $K_2CO_3$ , 5.0 ml of solvent, reaction time 0.25 h;

<sup>b</sup>Isolated yield.

**TABLE 2** Investigating the effect of catalyst amount in the synthesis of biphenyl from phenylboronic acid and bromobenzene at  $80 \ ^{\circ}$ C in water

Entry	PdNiZn/mol% <sup>a</sup> ; yields <sup>b,c</sup> (%)	PdNi/Zn/RGO/mol% <sup>a</sup> ; yields <sup>b,c</sup> (%)
1	0.58; 80	0.10; 90
2	1.74; 90	0.29; 97
3	5.22; 90	0.87; 97

<sup>a</sup>mol% of Pd;

<sup>b</sup>Isolated yields;

<sup>c</sup>Reaction time 0.25 h.

occurs in the order I > Br >> Cl, which is due to the carbon-halogen bond strength. Another important fact is that electron-withdrawing groups on the aryl halide structure enhance the reactivity compared to electron-donating groups. This observation is due to this fact that the oxidative addition step is often the rate-determining step (RDS) in the catalytic cycle. Consider to this fact that Pd(0) acts as a nucleophile and preferentially attacks the most electrondeficient position in the oxidative addition step; So, the presence of high electron density groups on Pd nanocatalysts increase the rate of oxidative addition. Therefore, the presence of Ni and Zn with Pd(0) can **TABLE 3** Suzuki-Miyaura C-C cross-coupling reactions of aryl halides with phenylboronic acid in the presence of PdNiZn nanosheet andPdNiZn/RGO ultrathin spherical NPs

Entry	Substrate	Product	Catalyst	Time (min)	Yields (%) <sup>a</sup>	TON	TOF (h <sup>-1</sup> )
1	C <sub>6</sub> H <sub>5</sub> I	[1a]	PdNiZn PdNi/Zn/RGO	10 5	90 98	51.72 337.92	323.25 4071.32
2	$C_6H_5Br$	[1a]	PdNiZn PdNi/Zn/RGO	15 10	90 97	51.72 334.47	206.88 2090.43
3	4-MeC <sub>6</sub> H <sub>4</sub> Br	[1b]	PdNiZn PdNi/Zn/RGO	100 80	80 80	45.97 275.85	27.69 207.41
4	C <sub>6</sub> H <sub>5</sub> Cl	[1a]	PdNiZn PdNi/Zn/RGO	70 55	73 78	41.95 268.95	36.16 295.54
5	$4-NO_2C_6H_4Cl$	[1d]	PdNiZn PdNi/Zn/RGO	60 45	70 75	40.22 258.61	40.22 344.81
6	C <sub>5</sub> H <sub>4</sub> NCl	[1c]	PdNiZn PdNi/Zn/RGO	280 145	80 82	45.97 282.75	9.86 117.32

<sup>a</sup>Isolated yields;

<sup>b</sup>See section 3.5 for the calculation of TONs and TOFs.

TABLE 4 Catalytic performance of different Pd-based catalysts in the coupling of phenylboronic acid and bromobenzene

Entry	Catalyst	Solvent	Base	Temp (°C)	Time (h)	Yield (%)	Ref.
1	PdNi NPs	(H <sub>2</sub> O/EtOH 1:1)	K <sub>2</sub> CO <sub>3</sub>	50	7	65	[37]
2	Pd/SBA-15 <sup>a</sup>	(H <sub>2</sub> O/EtOH 1:3)	K <sub>2</sub> CO <sub>3</sub>	85	10	88	[38]
3	Pd/SiO <sub>2</sub> /TEG <sup>b</sup>	toluene	K <sub>3</sub> PO <sub>4</sub>	110	12	86	[38]
4	Pd-G-3 <sup>c</sup>	EtOH	NaOAc <sup>d</sup>	reflux	24	42	[38]
5	Pd NPs	Ionic liquid <sup>e</sup>	$\rm NBu_4\rm OH^{f}$	60	1.5	93	[38]
6	PdCu	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	1.33	87	[19]
7	PdCu/RGO	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	0.5	87	[19]
8	Pd <sub>1</sub> Ni <sub>2</sub>	DMF	NaOH	140	10	93.8	[39]
9	Pd/Fe <sub>3</sub> O <sub>4</sub> NPs	МеОН	K <sub>3</sub> PO <sub>4</sub>	60	18	95	[40]
10	Pd-Ni/Fe <sub>3</sub> O <sub>4</sub>	EtOH	K <sub>2</sub> CO <sub>3</sub>	80	0.5	95	[41]
11	Pd thin film	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	80	1.5	90	[42]
12	Pd/RGO thin film	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	0.5	95	[42]
13	PtPdCu	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	0.42	94	[19]
14	PdZn	(H <sub>2</sub> O/EtOH 1:1)	K <sub>2</sub> CO <sub>3</sub>	80	1	94	[18]
15	PdPtZn	H2O-CTAB <sup>g</sup>	K <sub>2</sub> CO <sub>3</sub>	80	0.75	96	[18]
16	Diimine/Pd(II)	$DMA^h$	K <sub>2</sub> CO <sub>3</sub>	80	1	58	[43]
17	NHC-Pd <sup>i</sup>	EtOH	K <sub>3</sub> PO <sub>4</sub>	reflux	0.5	75	[44]
18	PdNiZn	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	0.25	90	This work
19	PdNiZn/RGO	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	0.16	97	This work

<sup>a</sup>SBA-15: Santa Barbara amorphous type silica;

<sup>b</sup>TEG: tetra(ethylene glycol);

<sup>c</sup>generation-3 palladium NP-cored dendrimer;

<sup>d</sup>NaOAc: sodium acetate;

<sup>e</sup>tetraalkylammonium-based ionic liquids;

<sup>f</sup>tetrabutylammonium hydroxide;

<sup>g</sup>: CTAB: cetyltrimethylammonium bromide;

<sup>h</sup>DMA: dimethyl acetamide.



**SCHEME 4** Schematic illustration of synergistic effect between three metals (Pd, Ni, and Zn)



**SCHEME 5** Important steps in the catalytic cycle of the Suzuki-Miyaura C-C coupling reaction



**FIGURE 6** Isolated yields for recycling of PdNiZn nanosheet and PdNiZn/RGO ultrathin spherical NPs as catalyst in the coupling reaction of phenylboronic acid with bromobenzene at 80 °C in water

lead to increase the catalytic activity due to the donation of electron to Pd centre. Furthermore, it is reported that the reductive elimination step (the final step in SuzukiMiyaura reaction) is facilitated by using elements of the first-row of transition metals such as Ni and Zn. So, the addition of non-precious Ni and Zn elements to the Pd film can accelerate the reductive elimination reaction in the last step of the reaction, additionally, reduces the expensive Pd dosage in the catalyst.

## 3.4 | Calculating the turnover number (TON) and turnover frequency (TOF)

The turnover number (TON = mole of product per mole of catalyst) and turnover frequency (TOF = TON per time (h)) were calculated for the as-prepared catalysts applied in Suzuki-Miyaura reaction. By comparing the TOF value of different catalysts, the efficiency of a catalyst can be measured. Fox *et al.*, reported that the Suzuki-Miyaura C-C coupling reaction over Pd-NP-cored G-3 dendrimer catalyst gives TOF = 1942 h<sup>-1</sup>.<sup>[46]</sup> In this study, not only the cost of catalyst is decreased by using non-precious metals alloying with Pd, but also ultrathin spherical NPs is synthesized with high active sites and better catalytic

10 of 11 WILEY-Organometallic Chemistry

activity. PdNiZn/RGO catalyst exhibits higher TOF (2090.43  $h^{-1}$ ) for the Suzuki-Miyaura reaction of phenylboronic acid with bromobenzene.

### 3.5 | Catalysts stability and reusability

The stability and reusability of the catalysts were examined in the reaction of phenylboronic acid with bromobenzene at 80 °C. In this step, the catalysts were separated by centrifugation and purified by washing with distilled water and diethyl ether. The catalysts were recycled at least seven times without any considerable loss of activity (Figure 6).

The Pd loading of the catalysts was also obtained using ICP that confirms no leaching happens.

In brief, some of the advantages of this study are: (i) unique morphology of the catalysts and good reusability without considerable loss of catalytic activity in the green and environmentally friendly medium (H<sub>2</sub>O solvent), (ii) preparation of the low-cost Pd-based trimetallic alloy catalysts by a facile, efficient and low-cost method, (iii) excellent results were obtained in short reaction times using low catalyst loading, (iv) reduce the amount of expensive Pd dosage by using alloy strategy at liquid-liquid interface and RGO as a stabilizer.

### 4 | CONCLUSIONS

Recent studies tend to the development of highly active, selective, stable, and cost-effective catalysts. So, in this study, self-assembly at the toluene-water interface was applied to produce PdNiZn nanosheet and PdNiZn/RGO ultrathin spherical NP catalysts at room temperature. This strategy is easy and inexpensive in comparison to other synthesis strategies. The as-synthesized thin films exhibit a high catalytic activity in Suzuki-Miyaura C-C coupling reaction. RGO affects the catalytic activity by altering the electronic properties. Nanosheets and ultrathin spherical NPs are suitable for superior catalytic performances due to their geometric properties. Herein, the addition of non-precious elements to Pd leads to the formation of trimetallic alloys. Metal-metal interaction has a significant effect on oxidative addition and reductive elimination as key steps in Suzuki-Miyaura C-C coupling reactions. Elements of the first-row of transition metals facilitate the reductive elimination step as the final step in Suzuki-Miyaura reaction. Some of the main advantages of this study are: applying a green medium (water) as a solvent and good yields with unactivated aryl halides in the cross-coupling reaction. Our goal was the synthesis of noble metal catalysts with both improved performance and low Pd dosage that leads to a low cost of catalysts using non-precious metals. Our method is promising for

the synthesis of high-performance catalysts for Suzuki-Miyaura C-C cross-coupling reaction.

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