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# Magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/reduced-graphene oxide nanohybrid as an efficient and recoverable catalyst for Suzuki-Miyaura coupling reaction in water

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#### Abstract

Palladium nanoparticles were supported on magnetic  $Fe_3O_4$ /reduced-graphene oxide( $Fe_3O_4$ /r-GO) nanohybrid by reduction of dichloropalladium (II) complex in water. Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction, and transmission electron microscopy (TEM). Our study shows that Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid was suitable for Suzuki-Miyaura carbon-carbon coupling reaction in water. Compared to the classical reactions, this method consistently has the advantages of green solvent, short reaction times, little catalyst loading, high yields, easy magnetically separation and reusability of the catalyst. Furthermore, Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid shows a high catalytic activity toward aryl chloride derivatives.

Keywords: Magnetic nanohybrid, Suzuki-Miyaura reaction, Carbon-carbon coupling, Catalyst

#### 1. Introduction

Nano-scale palladium particles make them attractive in catalysis due to their large surface area. Several palladium nanoparticles (NPs) as catalysts for carbon-carbon coupling reactions such as the Suzuki-Miyaura reaction have been reported [1-3].

In recent decade, as an important family of separation materials, magnetic  $Fe_3O_4$  NPs have attracted considerable interest in chemistry and material sciences, due to their potential

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applications in catalysis and biomedicine [4]. The paramagnetic and insoluble properties of  $Fe_3O_4$  NPs enable the catalyst to be easily separated with an external magnetic field.  $Fe_3O_4$  NPs, in particular, are environmentally benign, economic and comparatively non-toxic [5]. Recently, magnetic NPs were used as an efficient catalyst in many organic reactions [6-8]. However, to realize the successful applications of these magnetic NPs, at least two aspects need to be considered. First, the magnetic properties, which usually depend on several factors such as size, size distribution, shape and the chemical/biological stability of iron oxide NPs, should be improved. Second, these inherently instable NPs should be stabilized by matrix materials and the aggregation of  $Fe_3O_4$  NPs due to strong magnetic dipole–dipole attractions between particles must be reduced.

Graphene is one-atom-thick layer of  $sp^2$  hybridized carbon tightly packed into a two dimensional honeycomb lattice, and is a basic building unit for graphitic materials of all other dimensionalities [9]. Recently, many types of metal oxides NPs such as Fe<sub>3</sub>O<sub>4</sub> [10], Co<sub>3</sub>O<sub>4</sub> [11], TiO<sub>2</sub> [12] and ZnO [13] could be deposited on graphene oxide (GO) sheets to impart new functionality to this increasingly popular 2D nanomaterials in consideration of its large surface area.

Palladium catalyzed Suzuki cross-coupling reaction between an aryl halide and a phenyl boronic acid has been among the most powerful tools for constructing carbon–carbon bonds in organic synthesis [14]. Because biaryl moieties are used as the building block of a wide range of pharmaceuticals, herbicides, natural products, polymers, and etc, much effort has been spent on the development of simple and practical conditions for the Suzuki–Miyaura coupling reaction [15]. Generally, phosphine ligands are often used in Pd-catalyzed processes, but most of them are toxic, expensive and water or air sensitive [16]. Recently, employing readily available aryl

chlorides in these transformations have received increasing attention, and a number of effective catalytic systems have been developed for this purpose [17-18].

In this study, a successful method has been demonstrated for the synthesis of magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/reduced-graphene oxide (r-GO) nanohybrid. Then, Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid is used as non-phosphine catalyst for Suzuki-Miyaura reaction in water. This catalyst showed two main advantages in studying of its catalytic activity for Suzuki-Miyaura reaction. First, it has high surface area due to both Pd NPs and r-GO sheets, so the contact between reactants and catalyst increases considerably. Second, due to their insolubility in the reaction mixture and paramagnetic properties of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid, they can be separated easily from the reaction mixture by applying an external magnet. Recently, we have investigated thin film formation of Pd/r-GO and Pd NPs at oil-water interface as effective catalyst for Suzuki-Miyaura reaction in water [19]. In comparison to the previous work, although Pd loading decreased in this work but reaction between aryl halides and phenyl boronic acid performed in higher isolated yields at less times.

#### 2. Experimental

All of the chemical compounds were purchased from Merck Company. The powder X-ray diffraction patterns (XRD) were obtained by a Bruker AXS (D8, Advance) instrument employing the reflection Bragg–Brentano geometry with Cu-Kα radiation. Transmission electron microscopy (TEM) images were taken with a Philips CM-10 microscope operated at 100 kV. The FT-IR spectra were taken with a Jasco FT/IR-680 plus spectrometer. <sup>1</sup>H NMR spectra were taken with a Bruker 400 MHz Ultra-shield spectrometer using CDCl<sub>3</sub> as the solvent and TMS as the internal standard. Ultrasonication was performed in a TECNO-GAZ Tecna 3 ultrasonic bath.

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#### 2.1. Preparation of GO

GO was prepared using modified Hummers method from flake graphite (Merck Company) [20]. Briefly, a flask containing 1 g of graphite and 0.75 g of NaNO<sub>3</sub>, was placed in the ice-water bath. 75 mL of H<sub>2</sub>SO<sub>4</sub> was added with stirring and then 4.5 g of KMnO<sub>4</sub> were slowly added over about 1 h. After the mixture was stirred vigorously for 5 days at room temperature, 140 mL 5 % H<sub>2</sub>SO<sub>4</sub> aqueous solution was added over about 1 h with stirring , and the temperature was kept at 98 °C. The temperature was reduced to 60 °C, 3 mL of H<sub>2</sub>O<sub>2</sub> (30 wt% aqueous solution) was added, and the mixture was stirred for 2 h at room temperature. As-prepared GO was suspended in ultra-pure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. Resulting purified GO powders were collected by centrifugation and air-dried. GO powders were dispersed in water to create 0.05 wt% dispersion. Then, the dispersion was exfoliated through ultrasonication for 1 h, which the bulk GO powders were transformed into GO nanoplatelets.

#### 2.2 Preparation of Fe<sub>3</sub>O<sub>4</sub> NPs

To prepare Fe<sub>3</sub>O<sub>4</sub> NPs, 5.2 g of FeCl<sub>3</sub> and 2.0 g of FeCl<sub>2</sub> were successively dissolved in 25 mL of distilled water containing 0.85 mL of 12.1 N HCl. The resulting solution was added dropwise into 250 mL of 1.5 M NaOH solution under vigorous stirring. The last step generated an instant black precipitate. The precipitate was isolated in the magnetic field, and the supernatant was removed from the precipitate by decantation [6f].

#### 2.3 Preparation of Fe<sub>3</sub>O<sub>4</sub>/γ-Aminopropyltriethoxysilane (APTES)

In order to coat the  $Fe_3O_4$  NPs with APTES, NPs were ground into powder in an agate mortar and placed in a clean and dry round-bottom flask. To this, 20 mL of dry toluene was added and the mixture placed in a sonic bath for 30 minutes. The APTES reagent was added to the  $Fe_3O_4$ 

NPs at a 1:1 molar ratio from a micropipette in a nitrogen atmosphere. The mixture was stirred at 60  $\degree$ C for 12 h after which the mixture was cooled down and the residue washed with dry toluene and then with a water-acetone mixture (20% of H<sub>2</sub>O). The functionalized Fe<sub>3</sub>O<sub>4</sub> NPs were dried under vacuum for one day at ambient temperature [21].

#### 2.4 Preparation of Fe<sub>3</sub>O<sub>4</sub>/GO nanohybrid

0.02 g of GO was dispersed in distilled water and placed in a sonic bath for 10 minutes. Finally, a mixture contains 0.02 g Fe<sub>3</sub>O<sub>4</sub>/APTES and 0.02 g NaOH in water was added. The reaction mixture was heated under a reflux condenser in the presence of N<sub>2</sub> gas at 80  $^{\circ}$ C for 24 h.

#### 2.5 Preparation of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid

0.01 g of Fe<sub>3</sub>O<sub>4</sub>/GO was dispersed in 2 mL of distilled water and placed for 1 hour under ultrasonic waves. Subsequently, a solution contain PdCl<sub>2</sub> (0.14 mmol) dissolved in HCl was added. Finally, 0.1 g of NaBH<sub>4</sub> was added slowly to the resulting mixture and refluxed for 12 h at 60  $^{\circ}$ C under nitrogen atmosphere. The isolated solid was dried at room temperature for 24 h in vacuum. The solid contained 0.54% Pd by weight based on the inductively coupled plasma (ICP) analysis.

#### 2.6 General procedure for Suzuki-Miyaura coupling reaction

Arylhalide (1 mmol) and phenyl boronic acid (1.5 mmol) were added to a flask containing the Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO catalyst (0.36 mol% of Pd) and K<sub>2</sub>CO<sub>3</sub> (2 mmol) in distillated water (5 mL). The mixture was stirred in an oil bath at 80 °C. After completion of the reaction (monitored by TLC), the reaction mixture was cooled down to room temperature and then, dichloromethane (5×10 mL) was added to the reaction vessel and separated solid catalyst by a normal magnet. The organic phase was separated and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent gave the pure desired product. Characterization of these compounds was established by comparison of

their <sup>1</sup>H NMR spectra with those of authentic sample and the details are given in the supporting information.

#### 3. Results and Discussion

The  $Fe_3O_4/GO$  nanohybrid synthesized according to procedure titled in the experimental section and graphically summarized in Scheme 1.



Scheme 1. Picture shows the synthesis of Fe<sub>3</sub>O<sub>4</sub>/GO nanohybrid.

FT-IR spectra of GO, Fe<sub>3</sub>O<sub>4</sub>/APTES and Fe<sub>3</sub>O<sub>4</sub>/APTES/GO supplied in the supporting information (Figure S1). The results from FT-IR spectroscopy revealed that the characteristic band of the carboxyl group in GO appears at *ca*. 1731cm<sup>-1</sup> (C=O stretching) (Figure S1a) [22, 23]. The C–O vibrations of epoxy groups in GO appeared at *ca*. 1124 cm<sup>-1</sup> [22, 24].

As shown in Figure S1b, the peaks at 2865 cm<sup>-1</sup> and 2924 cm<sup>-1</sup> corresponds to symmetric  $v_s$  CH<sub>2</sub> and asymmetric  $v_{as}$  CH<sub>2</sub> of the alkyl chains, respectively, and is assigned to APTES. The absorbance band at 588 cm<sup>-1</sup> ascribed to Fe<sup>2+</sup>-O<sup>2-</sup> vibration and is consistent with the reported IR spectra for spinel Fe<sub>3</sub>O<sub>4</sub> [6f]. Moreover, appearance of the bands at *ca*. 1128 cm<sup>-1</sup> (v Si–O–C) provides more evidence for the presence of APTES [25]. The FT-IR result in Figure S1c shows that Fe<sub>3</sub>O<sub>4</sub>/APTES/GO nanohybrid is formed *via* a S<sub>N</sub>2 nucleophilic displacement reaction between epoxy groups of GO and amino moieties of Fe<sub>3</sub>O<sub>4</sub>/APTES NPs. Amine groups did not

reacted with carboxylic acid groups of GO through the amidation process because the amide v NH vibration expected at 3300 cm<sup>-1</sup> is not present and the 1650–1750 cm<sup>-1</sup> region does not show a strong v C=O band. The absorption band at around 1700 cm<sup>-1</sup> is attributed to the carboxyl groups. However, the corresponding absorption (Figure S1c) at this range is not observable, likely due to the overlapping of absorption of graphene sheets in this region [22]. Figure 1 shows a TEM image of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid. In this image, Pd/Fe<sub>3</sub>O<sub>4</sub> NPs appear as spherical particles with diameters of about 3 nm on a lighter shaded substrate corresponding to the planar r-GO sheets.



**Figure 1.** TEM images show (a and b) spherical  $Pd/Fe_3O_4/r$ -GO nanohybrid with 2-3 nm and (c) the Histogram of particle size distribution.

In the XRD pattern of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid (Figure 2) four clear diffraction bands centered at 20 of 40.2°, 46.6°, 68.1° and 82.1°, correspond to the (111), (200), (220) and (311) crystalline planes of Pd, respectively [26]. The weak diffraction peaks identified by # symbol correspond to the (220), (311), (400), (422), (511) and (440) planes of Fe<sub>3</sub>O<sub>4</sub> lattice, respectively [6g]. r-GO shows a broad diffraction peak for C (002) at  $2\theta = 28^{\circ}$  similar to that of carbon black [27].



Figure 2. XRD pattern of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid.

Figure 3 shows the results for magnetization as function of applied field at room temperature obtained for dry powder of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid. Magnetic measurement indicates magnetic behavior at room temperature for Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid with no hesteresis and perfect Langevin behavior. For Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid, the saturation magnetization value (*Ms*) is 5.9 emu/g, which was lower than that of pure Fe<sub>3</sub>O<sub>4</sub> NPs. There are numerous routes that can explain the reduction of the *Ms* for coated magnetic NPs. In this case, the presence of nonmagnetic APTES and r-GO on the surface of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO lead to decrease of the *Ms*.



Figure 3. Room-temperature magnetization curve of magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid.

#### 3.1. Characterization of Suzuki-Miyaura reaction

Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid is used as an efficient recoverable catalyst in the Suzuki-Miyaura coupling reaction. As shown in Scheme 2, reaction of aryl halide and phenyl boronic acid in water was investigated in the presence of Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid as catalyst.



G = H, Me, CN, NO<sub>2</sub>

**Scheme 2**. Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid catalyzed Suzuki-Miyaura coupling reaction of aryl halides with phenyl boronic acid in water.

The experiments with different solvents were rather performed to find the best medium for the coupling in the presence of the Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid catalyst. According to the results shown in Table 1, biphenyl product was detected in 69-75% yield when the reaction was carried out in toluene, tetrahydrofuran (THF) and EtOH (Table 1, entries 1-3). The better conversion of biphenyl was observed for H<sub>2</sub>O/EtOH (92% yield for entry 4). When H<sub>2</sub>O was used as solvent, an excellent yield (97%) was detected (Table 1, entries 5 and 6). K<sub>2</sub>CO<sub>3</sub> was used as base for optimizing the conditions of reaction. Table 1 illustrates the effect of catalyst molar ratio on the conversion time of bromobenzene as typical substrate at 80 °C in water. The optimum amount of the catalyst was found to be 0.36 mol% of Pd in current conditions (Table 1, entries 5-7).





Entry	Solvent	Catalyst (mol%) <sup>a</sup>	Temp (°C)	Yields% <sup>b</sup>
1	EtOH	0.54	70	75
2	H <sub>2</sub> O/EtOH (1:1)	0.54	80	92
3	THF	0.54	60	74
4	toluene	0.54	80	69
5	H <sub>2</sub> O	0.54	80	97
6	$H_2O$	0.36	80	97
7	$H_2O$	0.18	80	90

<sup>a</sup> Mol% of Pd.

<sup>b</sup> Isolated yields.

As shown in Table 2, the Suzuki-Miyaura reaction of various aryl halides, even aryl chloride, was examined under optimal reaction conditions to show the high catalytic activity of magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid. Suzuki-Miyaura reactions of deactivated aryl chloride including chlorobenzene and 2-chloropyridine proceeded with high yields of 85% and 88%, respectively, (Table 2, entries 4 and 7). The Suzuki reaction of activated aryl chlorides with different substituents also gave good yields, (Table 2, entries 5 and 6). In addition, the Suzuki reaction of aryl iodide and bromides produced excellent yields, (Table 2, entries 1-3). Usually, aryl chloride is less reactive than aryl bromide and aryl iodide in cross-coupling reactions due to its stronger  $C(sp^2)$ -Cl bond than that of  $C(sp^2)$ -Br and  $C(sp^2)$ -I. Also, the electron-deficient aryl halide is generally more active than the electron-rich one [28]. This observed fact presumably is held for the reaction with the oxidative addition process as the rate-determining step.

**Table 2** Suzuki-Miyaura reaction between aryl halides and phenyl boronic acid in the presenceof  $Pd/Fe_3O_4/r$ -GO nanohybrid.

Entry	Substrate	Product	Time(h)	Yields <sup>a</sup> %	
1	C <sub>6</sub> H <sub>5</sub> I	<b>1</b> a	15min	>99	

2	$C_6H_5Br$	<b>1</b> a	25min	97	
3	4-MeC <sub>6</sub> H <sub>4</sub> Br	1b	1.5	85	
4	C <sub>6</sub> H <sub>5</sub> Cl	1a	2.5	85	
5	4-CNC <sub>6</sub> H <sub>4</sub> Cl	1c	1.5	82	
6	$4-NO_2C_6H_4Cl$	1d	1.5	78	
7	C <sub>5</sub> H <sub>4</sub> NCl	1e	20	88	

<sup>a</sup> Isolated yield.

The catalytic performance of different Pd-based catalysts in the coupling of chlorobenzene and phenyl boronic acid were shown in Table 3. Magnetic  $Pd/Fe_3O_4/r$ -GO nanohybrid as a heterogeneous catalyst shows the highest performance in comparison to other catalysts. Most of the other published procedures (Table 3) need long time and using toxic solvent with lower isolated yield. Regardless of the exact mechanism of the reaction, high surface area of Pd, magnetic Fe<sub>3</sub>O<sub>4</sub> NPs and r-GO as support is expected to increase the activity of a heterogeneous catalyst.

**Table 3** Catalytic performance of different Pd-based catalysts in the coupling of chlorobenzene and phenyl boronic acid.

Entry	Catalyst	Solvent	Base	Temp(°C)	Time(h)	Yields (%)	Ref
1	$Pd(OAc)_2(1f)_2^a$	H <sub>2</sub> O/EtOH=3:2	K <sub>2</sub> CO <sub>3</sub>	80	10	66	29
2	Pd (II)-MWCNTs <sup>b</sup>	H <sub>2</sub> O/DMF=1:1	$K_2CO_3$	65	7	53	30
3	Pd NPs-IL <sup>c</sup>	H <sub>2</sub> O	NBu <sub>4</sub> OH	90	3	92	31
4	Pd (II)-SBA-16 <sup>d</sup>	H <sub>2</sub> O/EtOH=1:9	K <sub>2</sub> CO <sub>3</sub>	80	12	28	32
5	Pd (OAc) <sub>2</sub> /DABCO <sup>e</sup>	DMF	Cs <sub>2</sub> CO <sub>3</sub>	110	19	65	33
6	Pd/r-GO <sup>f</sup>	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	3	80	19
7	$Pd(OAc)_2$ - $Fe_3O_4^g$	H <sub>2</sub> O/EtOH=1:1	K <sub>2</sub> CO <sub>3</sub>	80	8	45	34

8	Pd NPs/PS <sup>h</sup>	H <sub>2</sub> O/DMF=1:1	Na <sub>2</sub> CO <sub>3</sub>	100	12	48	35
9	Pd/Fe <sub>3</sub> O <sub>4</sub> /r-GO	H <sub>2</sub> O	$K_2CO_3$	80	2.5	85	This work

a: 2 mol% of Pd and TBAB as additive; b: Pd-Schiff base@MWCNTs (0.2 mol%); c: Pd NPs in tetraheptylammonium bromide (2.5 mol% of Pd); d: 0.5 mol% of Pd (II)-SBA-16; e: 3 mol% of Pd(OAc)<sub>2</sub>; f: 0.48 mol% of Pd; g:  $Fe_3O_4/SiO_2$ -metformin-Pd(OAc)<sub>2</sub> (0.14 mol% of Pd); h: Pd NPs on styrene-divinylbenzene polymer (0.5 mol% of Pd).

From industrial point of view, the reusability of the catalyst is important for the large scale operation. Therefore, the reusability of the catalyst was examined in the reaction of bromobenzene with phenyl boronic acid at 80  $^{\circ}$ C in water. Since the catalyst can be separated from reaction mixture using external magnetic field, therefore it recovered with a simple magnet after dilution of the reaction mixture with CH<sub>2</sub>Cl<sub>2</sub>. The results showed that the catalyst can be reused eighth consecutive times without noticeable losing activity (Figure 4). The recovered catalyst was dried and checked with XRD analysis. Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid catalyst showed no significant change in magnetic property and reactivity after using the catalyst for eight times. These results show that reaction of bromobenzene with phenyl boronic acid occurred on heterogeneous Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO nanohybrid. Furthermore, the amount of Pd NPs after eighth consecutive runs was determined (0.31 mol% of Pd).



**Figure 4.** Reusability of  $Pd/Fe_3O_4/r$ -GO nanohybride in the synthesis of biphenyl from bromobenzene and phenyl boronic acid.

#### 4. Conclusion

In conclusion, we have demonstrated that Palladium NPs supported on an efficient magnetic  $Fe_3O_4/GO$  nanohybrid by reduction of dichloropalladium complex (II) in water. The magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO as heterogeneous catalyst exhibits high catalytic activity in the Suzuki-Miyaura cross-coupling reaction in water. However, a series of biaryl derivatives were obtained in moderate to excellent yield in mild conditions from the reaction of phenyl boronic acid with aryl bromides or chlorides derivatives. Additionally, the unique catalyst can be easily separated from the reaction mixture by simple magnetic attraction.

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#### **Graphical Abstract**

## Magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/reduced-graphene oxide nanohybrid as an efficient and recoverable catalyst for Suzuki-Miyaura coupling reaction in water

S. Jafar Hoseini, Vahid Heidari and Hasan Nasrabadi

Palladium nanoparticles supported successfully on an efficient magnetic Fe<sub>3</sub>O<sub>4</sub>/graphene oxide nanohybrid by reduction of dichloropalladium complex in water. Pd/Fe<sub>3</sub>O<sub>4</sub>/reduced-graphene oxide nanohybrid was suitable for Suzuki-Miyaura carbon-carbon coupling reaction.



#### Highlights

- Palladium NPs supported on an efficient magnetic Fe<sub>3</sub>O<sub>4</sub>/GO nanohybrid.
- Magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/r-GO shows high catalytic activity in the Suzuki-Miyaura reaction.
- Catalyst can be separated from the reaction mixture by simple magnetic attraction.

#### Supplementary Data

Magnetic Pd/Fe<sub>3</sub>O<sub>4</sub>/reduced-graphene oxide nanohybrid as an efficient and recoverable catalyst for Suzuki-Miyaura coupling reaction in water

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#### Analytical data for compounds



Figure S1. FTIR spectra of (a) GO, (b) Fe<sub>3</sub>O<sub>4</sub>/APTES and (c) Fe<sub>3</sub>O<sub>4</sub>/APTES/GO.

Biphenyl (**1a**) [1], White solid, mp: 66-69 °C (lit. mp 69-71 °C); FT-IR (KBr/cm<sup>-1</sup>): 3058, 3032, 1568, 1479, 1424, 1344, 1168, 1090, 1040, 1005, 725, 696; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.46$  (m, 2H), 7.55 (m, 4H), 7.71 (m, 4H).



Figure S2. <sup>1</sup>H NMR spectrum of biphenyl (1a) in CDCl<sub>3</sub>

4-Methylbiphenyl (**1b**) [2], White solid, mp: 43-44  $^{\circ}$ C (lit. mp 44-46  $^{\circ}$ C); FT-IR (KBr/cm<sup>-1</sup>): 3060, 2959, 2928, 1600, 1463, 1380, 1273, 1122, 1072, 1039; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.45 (s, 3H, CH<sub>3</sub>),  $\delta$  = 7.33 (m, 2H), 7.37 (m 1H), 7.59 (m, 2H), 7.76 (m, 2H), 7.88 (2H).



Figure S3. <sup>1</sup>H NMR spectrum of 4-methylbiphenyl (1b) in CDCl<sub>3</sub>

4-phenylbenzonitrile (**1c**) [3], White solid, mp: 84-86 °C (lit. mp 84-88 °C); FT-IR (KBr/cm<sup>-1</sup>): 3076, 3023, 2930, 2924, 2250, 1660, 1493, 1441, 1179, 1024, 845, 700; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53 (m, 3H), 7.63 (m 2H), 7.83 (m, 2H), 8.23 (m, 2H).



Figure S4. <sup>1</sup>H NMR spectrum of 4-phenylbenzonitrile (1c) in CDCl<sub>3</sub>

4-nitrobiphenyl (**1d**) [4], Yellow solid, mp: 111-113 °C (lit. mp 113-115 °C); FT-IR (KBr/cm<sup>-1</sup>): 3053, 2922, 1602, 1522, 1476, 1446, 1341, 1307, 1087, 1012, 846, 743; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47 (m, 3H), 7.67 (m 2H), 7.77 (m, 2H), 8.46 (m, 2H).



Figure S5. <sup>1</sup>H NMR spectrum of 4-nitrobiphenyl (1d) in CDCl<sub>3</sub>

2-phenylpyridine (**1e**) [4], Colorless oil, FT-IR (KBr/cm<sup>-1</sup>): 3061, 3033, 1740, 1586, 1476, 1449, 1260, 1151, 1094, 1020,799, 745, 687; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.89 (m, 1H), 7.28 (m, 1H), 7.32 (m, 2H), 7.37 (m, 1H), 7.45 (m, 1H), 7.96 (m, 2H), 8.56 (m, 1H).



Figure S6. <sup>1</sup>H NMR spectrum of 2-phenylpyridine (1e) in CDCl<sub>3</sub>

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