

# Palladium Complex Immobilized on Graphene Oxide as an Efficient and Recyclable Catalyst for Suzuki Coupling Reaction

Chan Bai · Qingshan Zhao · Yang Li ·  
Guoliang Zhang · Fengbao Zhang · Xiaobin Fan

Received: 18 March 2014 / Accepted: 6 June 2014 / Published online: 2 July 2014  
© Springer Science+Business Media New York 2014

**Abstract** A graphene supported palladium (Pd) catalyst for Suzuki coupling reaction has been successfully prepared by immobilizing Pd(II) onto graphene oxide surface through the in situ coordination interaction with aminosilane ligand spacers. This catalyst showed high catalytic activities in the Suzuki coupling of various aryl halides and phenylboronic acid. Moreover, it could be readily recycled and reused for several times without discernible loss of its catalytic activity.

**Keywords** Graphene oxide · Heterogeneous catalysis · Suzuki reaction · Immobilization · Palladium

## 1 Introduction

Palladium (Pd)-catalyzed reactions play a key role in the synthesis of many important chemicals [1–4]. As an efficient catalyst in organic reactions, it can offer the most beneficial combination of activity and selectivity [5]. Among these reactions, Suzuki coupling is the most powerful tool for constructing the biaryl structures that exist in many biologically active compounds and natural products [6, 7]. Usually, the Suzuki coupling reactions were catalyzed by Pd complex under homogeneous condition.

However, the high cost of the catalysts and their low efficiency in separation limit their applications on an industrial scale. Therefore, considerable efforts have been made to immobilize Pd complex on various separable organic, inorganic or hybrid supports for decades [8, 9]. Unfortunately, the supported Pd complex catalysts often suffer from reduced activity, inferior selectivity, and other problems such as metal leaching and high preparation complexity.

Recently, graphene [10] and graphene oxide (GO) [11, 12] have attracted extensive attention in heterocatalysis due to their unique two-dimensional structures, huge surface areas and other excellent properties [13, 14]. In fact, they have been demonstrated as promising supports for many metallic nanocatalysts, such as Pd [15–17], Au [18], Co<sub>3</sub>O<sub>4</sub> [19], Fe<sub>3</sub>O<sub>4</sub> [20], Au<sub>core</sub>Pt<sub>shell</sub> nanoparticles [21] and PdAg nanorings [22].

In this study, we report a facile and efficient method to immobilize Pd complexes on GO. The supported Pd catalyst was prepared by the in situ coordination between Pd(II) and aminosilane ligand that was covalently immobilized on GO via the one-pot silylation (Scheme 1). We found that this catalyst afforded high catalytic activities for the Suzuki coupling of various halogenobenzene and phenylboronic acids.

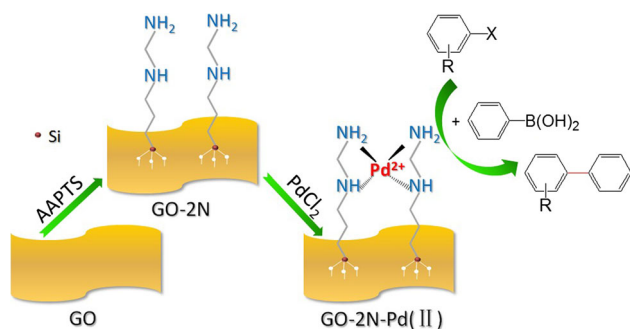
**Electronic supplementary material** The online version of this article (doi:10.1007/s10562-014-1299-0) contains supplementary material, which is available to authorized users.

C. Bai · Q. Zhao · Y. Li · G. Zhang · F. Zhang · X. Fan (✉)  
State Key Laboratory of Chemical Engineering, School of  
Chemical Engineering & Technology, Collaborative Innovation  
Center of Chemical Science and Engineering, Tianjin  
University, Tianjin 300072, China  
e-mail: xiaobinfan@tju.edu.cn

## 2 Experimental

### 2.1 Reagents and Materials

*N*-[3-(Trimethoxysilyl)propyl] ethylenediamine (AAPTS, 95 %), Pd(II) chloride and graphite powder were purchased from Sigma-Aldrich Chemical Company (USA). Various aryl halide, phenylboronic acid and ethanol (99.8 %) were



**Scheme 1** Illustration for synthetic methodology of GO-2N-Pd(II) and its catalytic application for the Suzuki coupling reaction

purchased from Aladdin Reagent Company (Shanghai, China). All other chemicals were of analytical grade and used as received without further purification.

## 2.2 Synthesis of GO and Ethylenediamine-Functionalized GO (GO-2N)

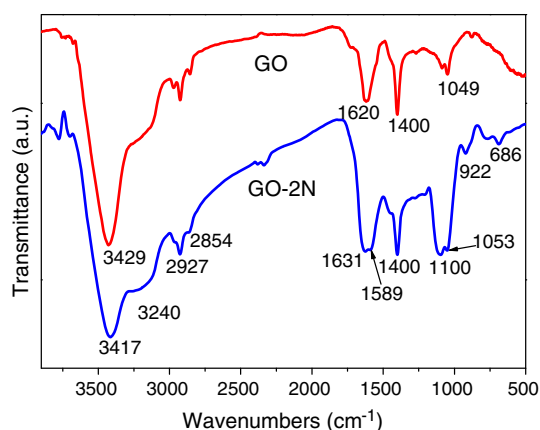
GO was prepared and purified by modified Hummers Method [23]. A suspension was obtained by dispersing GO ( $12.0 \text{ mg mL}^{-1}$ , 20.0 mL) in 120 mL ethanol with the aid of intensive sonication (100 W, 40 kHz, 0.5 h). Ethylenediamine-functionalized GO was processed by stirring the obtained GO suspension with excess AAPTSS (373.6 mg, 1.68 mmol) and refluxed for 6 h. The suspension was filtrated and intensively washed with water, ethanol and methanol twice, respectively, followed by freeze-drying.

## 2.3 Synthesis of Ethylenediamine-Functionalized GO Immobilized Pd Complex [GO-2N-Pd(II)]

200 mg of the as-prepared GO-2N was added to a methanol solution of Pd(II) chloride (177 mg, 1 mmol). After the mixed system was stirred at room temperature for 24 h, the resulting precipitates were then thoroughly filtrated and washed with methanol, ethanol and water, twice, respectively. A black solid was obtained after a freeze-drying procedure.

## 2.4 Typical Procedures for the Suzuki Reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1.5 mmol),  $\text{K}_2\text{CO}_3$  (2 mmol), ethanol (15 mL) and GO-2N-Pd(II) (10 mg, 0.5 mol%) were stirred at  $80^\circ\text{C}$  in a 25 mL round bottom flask. Thereafter, the catalyst was simply separated from the mixture by simple centrifugation and could be reused after washed with ethanol three times. For the control experiments, samples containing the same amount of Pd species (0.005 mmol) were used as the catalyst. The resulting solution was analyzed by gas chromatography (GC) using a capillary column.



**Fig. 1** FTIR spectra of GO and GO-2N

## 2.5 Instrumentations

The samples were characterized by Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet Nexus FTIR), X-ray photoelectron spectroscopy (XPS, PerkinElmer, PHI 1600 spectrometer), Raman spectroscopy (NT-MDT NTEGRA Spectra), scanning electron microscopy (SEM, Hitachi S4800), energy dispersive X-ray spectroscopy (EDS, Hitachi S4800), transmission electron microscopy (TEM, Philips Tecnai G2 F20), thermogravimetric analysis (TGA, Shimadzu TGA-50),  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Varian-INOVA, 500 MHz) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista-MPX). The catalytic results were measured by Agilent 6890N GC using the standard curve method.

## 3 Results and Discussion

### 3.1 Characterization of GO-2N and GO-2N-Pd(II)

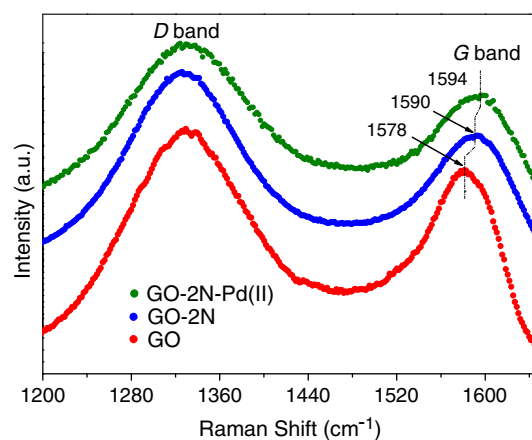
The typical FTIR absorption peaks of GO could be observed in Fig. 1. Comparison studies on the spectra of GO and GO-2N identified the incorporation of ethylenediamine group silanes onto the GO surface. Note that bands at around  $3,400 \text{ cm}^{-1}$  of both GO and GO-2N ascribed to the absorbed water. The doublet at 2,927 and  $2,854 \text{ cm}^{-1}$  were assigned to the stretching vibrations of  $\text{CH}_2$  that existed on the long silane chains which were obviously strengthened compared to GO. The obvious band at  $1,400 \text{ cm}^{-1}$  was assigned to C-H deformation vibrations of alkyl groups which could also verify the presence of long silane chains. The prominent bands at 3,240 and  $1,589 \text{ cm}^{-1}$  were ascribed to the stretching and bending vibrations of N-H which testified the successful introduction of amines group [24]. Stretching vibrations of C-N at around  $1,631 \text{ cm}^{-1}$  could also be observed. In addition, the

strong absorption of Si–O (at 1,100 and 1,053  $\text{cm}^{-1}$ ) and stretching vibrations of Si–O–C at 686  $\text{cm}^{-1}$  provided direct evidences for the successful silylation of GO [25]. Similar characteristic bands could be found in the FTIR of free AAPTS (Fig. S1).

These results were further confirmed by XPS analysis. Additional signals of Si and N were clearly observed in the XPS spectrum of GO–2N (Fig. S3b). C 1s XPS spectrum of GO–2N showed a significant decrease in the C–O–C and C–OH peaks at around 286.5 eV after the silylation reaction (Fig. S3d), which suggested a structure deprived of parts of hydroxy groups [26]. A pronounced peak at 101.7 eV corresponding to the binding energy of Si–O–C appeared at the same time (Fig. 2a), indicating that considerable amounts of C–OH were converted into Si–O–C through the silylation process [27]. Besides, compared with the N 1s XPS spectrum of GO–2N (Fig. 2b), the binding energy shifted from 399.36 to 399.52 eV after the coordination reaction, and this was attributed to the stronger coordination bond between the ethylenediamine group and the Pd centers [28]. The loading of the nitrogen atoms in GO–2N–Pd(II) was 3.94 wt% and the atom percentage of N–Pd is approximately 4.0, corresponding to the structure of the GO–2N–Pd(II) catalyst. Note that additional signals of Pd were clearly observed in the obtained GO–2N–Pd(II) (Fig. 2c) with the Pd weight percentage of 5.38 %, which was much higher than those on other supports [29, 30]. In addition, all the Pd species in the GO–2N–Pd(II) presented

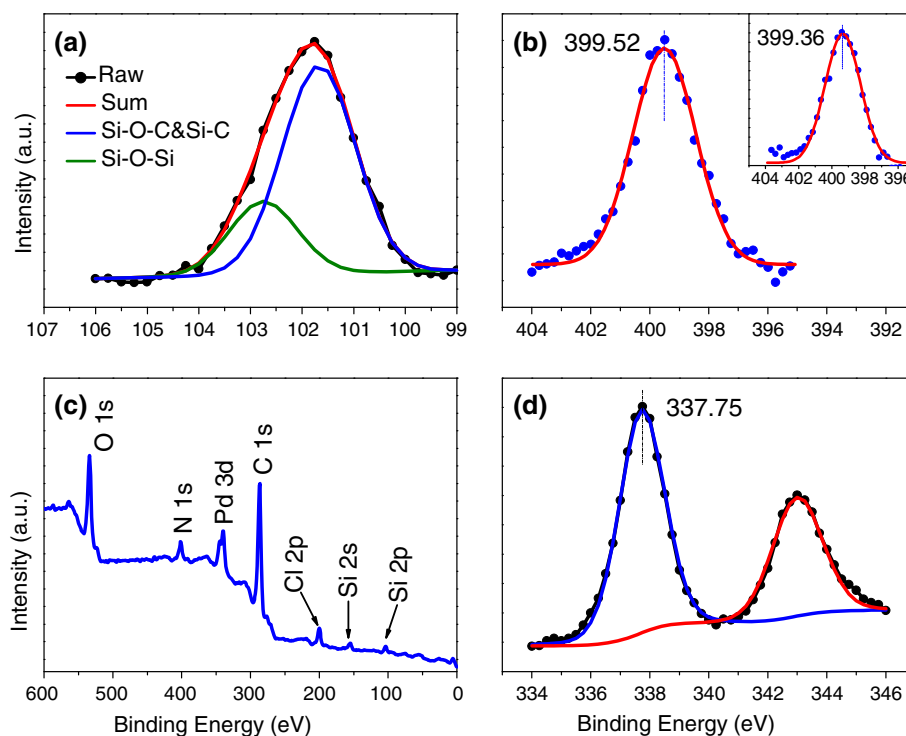
in +2 oxidation state, corresponding to the binding energy of 337.75 eV in Pd 3d<sub>5/2</sub> level (Fig. 2d) [31].

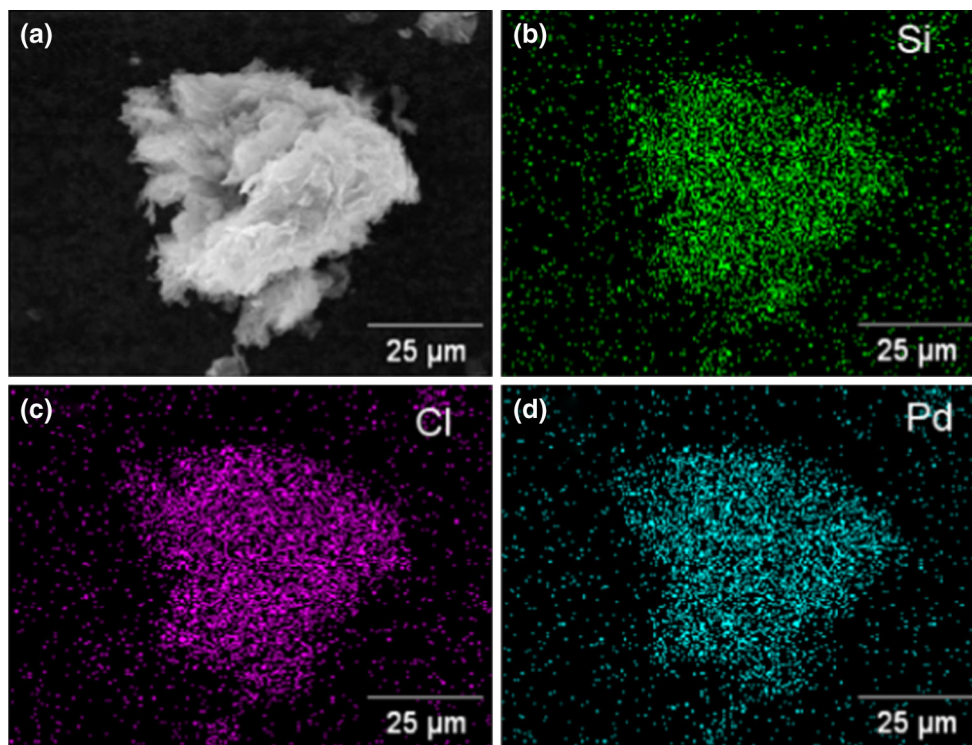
Raman spectra of GO, GO–2N and GO–2N–Pd(II) (Fig. 3) showed an obvious and step-by-step blue shift of the G band from 1,578 to 1,590 and 1,594  $\text{cm}^{-1}$ , probably due to the gradually increased compressive local stress caused by molecule intercalation. Besides, the intensity ratio of D and G bands ( $I_D/I_G$ ) that related to the extent of disorder also increased [1.78, 1.96 and 2.35 for the GO, GO–2N and GO–2N–Pd(II), respectively], reflecting the



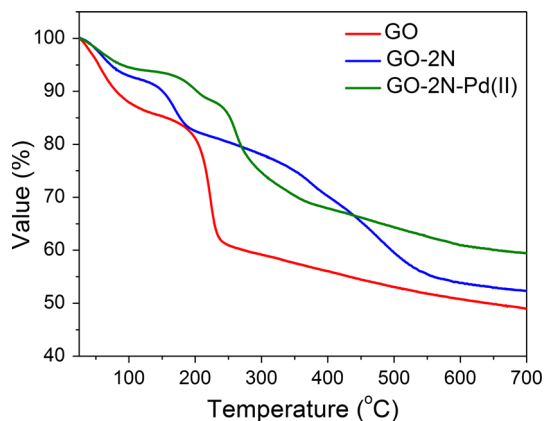
**Fig. 3** Raman spectra of GO, GO–2N and GO–2N–Pd(II)

**Fig. 2** **a** Si 2p XPS spectrum of GO–2N, **b** N 1s XPS spectra of GO–2N–Pd(II) and **b**, inset GO–2N, **c** XPS spectrum of GO–2N–Pd(II) and **d** Pd 3d XPS spectrum of GO–2N–Pd(II)





**Fig. 4** a SEM image of GO-2N-Pd(II), and corresponding quantitative EDS mapping of **b** Si, **c** Cl and **d** Pd



**Fig. 5** TGA graphs of GO, GO-2N and GO-2N-Pd(II)

formation of more edges and defects during the reaction processes [32].

SEMs and corresponding quantitative EDS mapping were employed to determine the morphology of the obtained GO-2N-Pd(II). Figure 4a presented the typical planar structure of GO-2N-Pd(II) maintaining the two-dimensional structures with heavy crumpling features. Element distribution analysis displayed a homogeneous distribution of element Si, Cl and Pd (Fig. 4b–d) on the whole surface of GO, implying the consistent attachments of the silylation of GO and a desirable anchoring of the Pd complexes.

**Table 1** The Suzuki coupling reaction of iodobenzene and phenylboronic acid under different conditions

Entries	Pd (mol%)	Time (h)	Temperature (°C)	Yield <sup>a</sup> (%)
1	0.5	1	40	87
2	0.5	0.5	60	93
3	0.5	0.5	80	100
4	0.5	0.5	100	100
5	1	0.5	80	99
6	2	0.5	80	99
7	0.1	0.5	80	76
8	0.1	1	80	88

The reaction was carried out with 1 mmol of iodobenzene, 1.5 mmol phenylboronic acid, 2 mmol  $K_2CO_3$ , 0.5 mol% Pd with respect to halide, 15 mL ethanol in air

<sup>a</sup> The yield was determined by GC

TGA analysis of the samples were also used to investigate the thermal stability of GO, GO-2N and GO-2N-Pd(II) (Fig. 5). For GO, the weight loss was about 38 % at the temperature under 240 °C. This major weight loss was due to pyrolysis of the labile oxidation functional groups on GO. By comparison, GO-2N and GO-2N-Pd(II) showed slighter decrease in this region because some of the hydroxyl groups have been treated with silylation. In

**Table 2** Suzuki reaction catalyzed by various catalysts

Entries	Catalysts	Yield (%) <sup>a</sup>	Recycling times
1	None	0	–
2	GO–2N	0	–
3	GO + <i>N</i> -[3-(trimethoxysilyl)propyl] ethylenediamine + PdCl <sub>2</sub>	20.3	0
4	C + <i>N</i> -[3-(trimethoxysilyl)propyl] ethylenediamine + PdCl <sub>2</sub>	9.2	0
5	GO–2N–Pd(II)	100	6

The reaction was carried out with 1 mmol of halide, 1.5 mmol phenylboronic acid, 2 mmol K<sub>2</sub>CO<sub>3</sub>, catalyst (Pd 0.005 mmol), 15 mL ethanol at 80 °C in air for 0.5 h

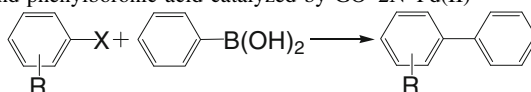
<sup>a</sup> The yield was determined by GC

addition, GO–2N and GO–2N–Pd(II) showed weight loss from 240 to 550 °C which was attributed to the oxidation of ethylenediamine groups. At the same time, there was no

obvious weight loss above 600 °C. The results indicated that the ethylenediamine groups were chemically bonded to the surface of GO and the coordination between the Pd and ethylenediamine groups exhibited a relatively high stability.

### 3.2 GO–2N–Pd(II) Catalyzing Suzuki Reaction

The catalytic performance of the prepared catalyst was systematically examined through Suzuki coupling reaction. We used ethanol as a medium because it was not only safe, cost-effective but also efficiently promoted the Suzuki reaction. The Suzuki reaction of iodobenzene and phenylboronic acid was chosen as the first model reaction, and the results were summarized in Table 1. We found that GO–2N–Pd(II) at a loading of 0.5 mol% Pd (with respect to iodobenzene) afforded biphenyl in 100 % within only 0.5 h at 80 °C (Table 1, Entry 3). The yield went down when the catalyst loading was reduced to 0.1 mol%. Otherwise, the

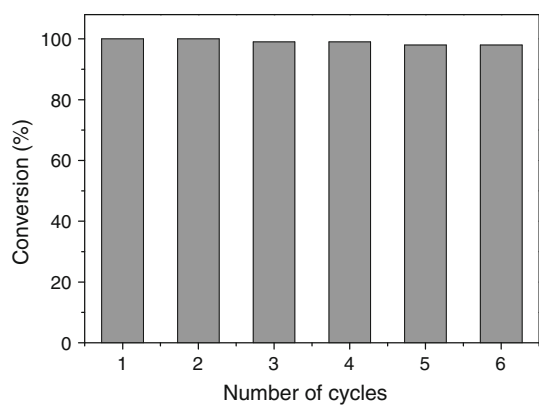
**Table 3** Suzuki coupling of aryl halides and phenylboronic acid catalyzed by GO–2N–Pd(II)

Entries	Substrates	Products	Time (h)	Yield <sup>a</sup> (%)	Final TOF (h <sup>-1</sup> )
1			0.5	100	400
2			0.5	99	396
3			0.5	100	400
4			4	82	41
5			4	77	38.5
6			4	87	43.5
7			4	88	44
8			4	53	26.5
9			8	78	19.5
10			8	75	18.75
11			20	87	8.7
12			20	78	7.8

The reaction was carried out with 1 mmol of halide, 1.5 mmol phenylboronic acid, 2 mmol K<sub>2</sub>CO<sub>3</sub>, 0.5 mol% Pd with respect to halide, 15 mL ethanol at 80 °C in air

<sup>a</sup> The yield was determined by GC





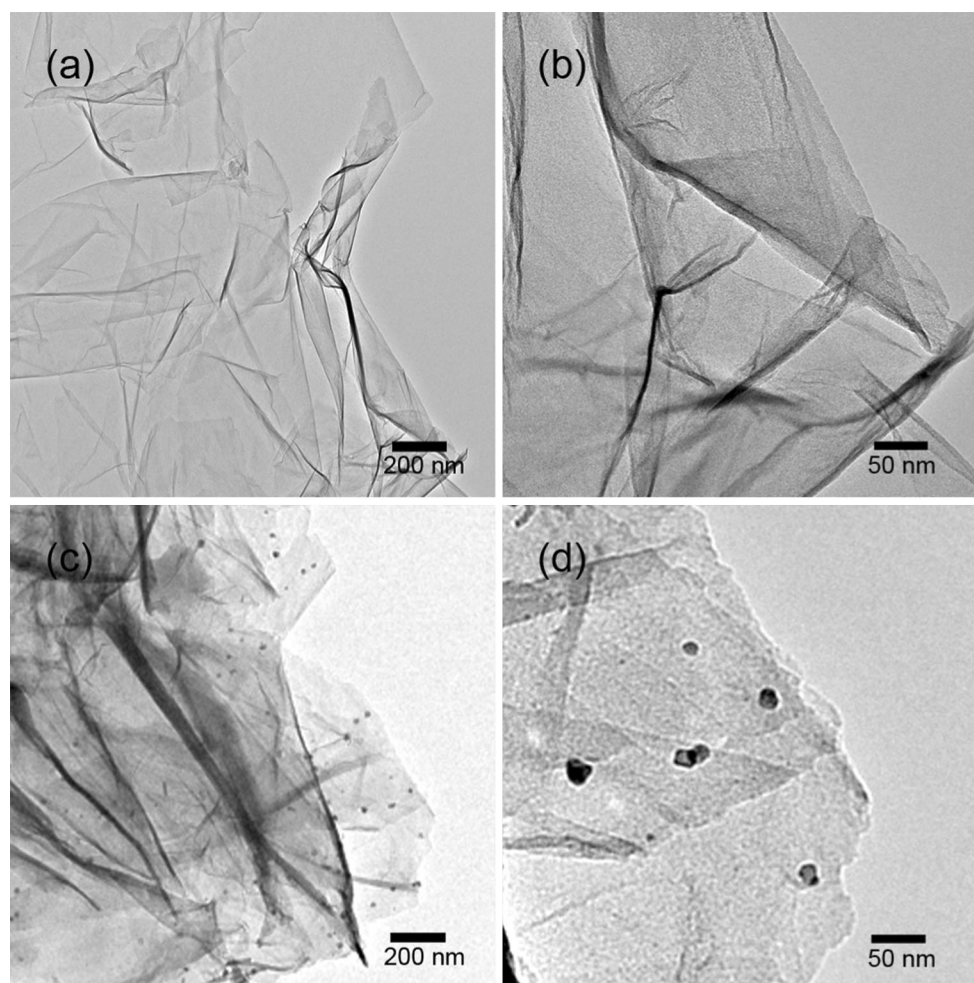
**Fig. 6** Recycle efficiency of GO-2N-Pd(II) in Suzuki coupling reaction between iodobenzene and phenylboronic acid

yield remained unchanged when the catalyst loading rose to 1 mol%. As for the influence of temperature, 80 °C was found to be the optimal choice. The yield went down with the drop of temperature while the reaction effectively

occurred at 80 °C as the same as 100 °C. Therefore, the optimized reaction conditions were also employed in later Suzuki coupling reactions with variation of different substituents.

To investigate the effective component of the catalyst, a series of control experiments were conducted. The results were summarized in Table 2. When no catalyst was used or GO-2N was used as a control, hardly any reaction occurred (Entries 1 and 2). The results indicated that the Suzuki reaction could not proceed with the absence of Pd. When a physical mix of GO, APTS and PdCl<sub>2</sub> or a mix of charcoal, APTS and PdCl<sub>2</sub> was used to catalyze the reaction, poor yield was obtained and this might be due to the absence of coordinating ligands (Entries 3 and 4). When the supported catalyst GO-2N-Pd(II) was used, the yield was found to be 100 % (Entry 5). It seemed that the linkage ligand between GO and the Pd complex promoted the reaction and made the catalyst achieve excellent catalytic performance.

As shown in Table 3, GO-2N-Pd(II) was also found to be highly effective for different substituents. Various



**Fig. 7** TEM images of GO-2N-Pd(II) **a, b** before and **c, d** after repeated experiments

electron-donating and electron-withdrawing groups, such as  $-\text{OCH}_3$  and  $-\text{CH}_3$  on the aryl iodide were well tolerated (Entries 1–3), and a satisfactory yield for bromides containing  $-\text{CH}_3$ ,  $-\text{NH}_2$ , and  $-\text{OH}$  (Entries 4–7) was achieved. Biphenyl-4-carbaldehyde gave 53 % in yield when 4-bromo-benzaldehyde was coupled with phenylboronic acid (Entry 8). Note that aryl bromide containing electron-withdrawing substituents reacted faster than those with electron-donating substituents which is due to the electronic effects of the substituent (Entry 5 vs. 6). Further functional group tolerance of the catalyst was tested with the heteroaryl halides delivering good yield of 78 and 75 %, respectively (Entries 9 and 10). Additionally, the catalyst showed high activity towards aryl chlorides but with much longer time compared with aryl iodides and aryl bromides (Entries 11 and 12). This result could be attributed to the different strengths of the C–I, C–Br and C–Cl bonds, as well as the different electron-withdrawing abilities of the halogen substituents [33].

The reusability of GO–2N–Pd(II) was evaluated between iodobenzene and phenylboronic acid by repeating the same procedure. The solid catalyst was readily recovered from the reaction mixture by direct filtration and reused in sequential runs. As shown in Fig. 6, the catalytic activity almost did not reduce after reuse of six times. Comparison TEM study of GO–2N–Pd(II) before and after repeated experiments were shown in Fig. 7. Compared to the fresh one, Pd nanoparticles dispersed on the GO sheets could be observed after several runs. This was in agreement with the previously reported results that the formation of Pd nanoparticles as an active species were evolved during the catalytic reaction. To further investigate the stability of the used catalyst, ICP-OES analysis was also employed. We found that only about 0.5 % of the Pd species leached off after six cycles, suggesting that the loss of the active Pd(II) sites could be neglected. The high stability and excellent reusability of the catalyst should be attributed to the strong coordination bonds.

#### 4 Conclusions

In summary, we successfully developed a novel, practical and economic GO supported Pd complex catalyst. The GO–2N–Pd(II) catalyst showed extraordinary performances in the Suzuki coupling reaction and could be readily recycled and reused without discernible loss of its catalytic activity. This strategy could be used to prepare other GO supported metal complexes which may offer more opportunities for developing powerful and reusable catalysts for green organic synthesis.

**Acknowledgments** This study was supported by the National Natural Science Funds for Excellent Young Scholars (No. 21222608),

Program for New Century Excellent Talents in University (No. NCET-12-0392), Research Fund of the National Natural Science Foundation of China (No. 21106099), Foundation for the Author of National Excellent Doctoral Dissertation of China (No. 201251), the Tianjin Natural Science Foundation (No. 11JCYBJC01700) and the Programme of Introducing Talents of Discipline to Universities (No. B06006).

#### References

1. Chen Q-A, Ye Z-S, Duan Y, Zhou Y-G (2013) *Chem Soc Rev* 42:497
2. Santra S, Ranjan P, Bera P, Ghosh P, Mandal SK (2012) *RSC Adv* 2:7523
3. Sore HF, Galloway WRJD, Spring DR (2012) *Chem Soc Rev* 41:1845
4. Szóri K, Puskás R, Szóllósi G, Bertóti I, Szépvölgyi J, Bartók M (2013) *Catal Lett* 143:539
5. Jie X, Shang Y, Hu P, Su W (2013) *Angew Chem Int Ed* 52:3630
6. Han F-S (2013) *Chem Soc Rev* 42:5270
7. Shang N, Gao S, Feng C, Zhang H, Wang C, Wang Z (2013) *RSC Adv* 3:21863
8. Borah BJ, Dutta DK (2013) *J Mol Catal A* 366:202
9. Fang M, Fan G, Li F (2014) *Catal Lett* 144:142
10. Liu K, Chen T, Hou Z, Wang Y, Dai L (2014) *Catal Lett* 144:314
11. Chua CK, Pumera M (2014) *Chem Soc Rev* 43:291
12. Meyer JC, Geim AK, Katsnelson MI, Novoselov KS, Booth TJ, Roth S (2007) *Nature* 446:60
13. Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010) *Chem Soc Rev* 39:228
14. Tan R, Li C, Luo J, Kong Y, Zheng W, Yin D (2013) *J Catal* 298:138
15. Morimoto N, Yamamoto S-i, Takeuchi Y, Nishina Y (2013) *RSC Adv* 3:15608
16. Santra S, Hota PK, Bhattacharyya R, Bera P, Ghosh P, Mandal SK (2013) *ACS Catal* 3:2776
17. Shang N, Feng C, Zhang H, Gao S, Tang R, Wang C, Wang Z (2013) *Catal Commun* 40:111
18. Qin Y, Li J, Kong Y, Li X, Tao Y, Li S, Wang Y (2014) *Nanoscale* 6:1281
19. Yao Y, Yang Z, Sun H, Wang S (2012) *Ind Eng Chem Res* 51:14958
20. Feng C, Zhang H-Y, Shang N-Z, Gao S-T, Wang C (2013) *Chin Chem Lett* 24:539
21. Qi J, Lv W, Zhang G, Li Y, Zhang G, Zhang F, Fan X (2013) *Nanoscale* 5:6275
22. Liu M, Lu Y, Chen W (2013) *Adv Funct Mater* 23:1289
23. Hummers WS, Offeman RE (1958) *J Am Chem Soc* 80:1339
24. Ou X, Jiang L, Chen P, Zhu M, Hu W, Liu M, Zhu J, Ju H (2013) *Adv Funct Mater* 23:2422
25. Zhao Q, Li Y, Liu R, Chen A, Zhang G, Zhang F, Fan X (2013) *J Mater Chem A* 1:15039
26. Kim S, Zhou S, Hu Y, Acik M, Chabal YJ, Berger C, de Heer W, Bongiorno A, Riedo E (2012) *Nat Mater* 11:544
27. Ma PC, Kim J-K, Tang BZ (2006) *Carbon* 44:3232
28. Kannari N, Ozaki J-i (2012) *Carbon* 50:2941
29. Zhang Q, Su H, Luo J, Wei Y (2013) *Tetrahedron* 69:447
30. Wei SY, Ma ZY, Wang P, Dong ZP, Ma JT (2013) *J Mol Catal A* 370:175
31. Bera P, Patil KC, Jayaram V, Subbanna GN, Hegde MS (2000) *J Catal* 196:293
32. Fang M, Wang K, Lu H, Yang Y, Nutt S (2009) *J Mater Chem* 19:7098
33. Alonso F, Beletskaya IP, Yus M (2008) *Tetrahedron* 64:3047