# ARTICLE IN PRESS

#### Tetrahedron xxx (2014) 1-5



# Tetrahedron



# Pd—Co bimetallic nanoparticles supported on graphene as a highly active catalyst for Suzuki—Miyaura and Sonogashira cross-coupling reactions

# Yi-Si Feng<sup>a,b</sup>, Xin-Yan Lin<sup>a,b</sup>, Jian Hao<sup>a,b</sup>, Hua-Jian Xu<sup>a,b,\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, School of Medical Engineering, Hefei University of Technology, Hefei 230009, PR China
<sup>b</sup> Key Laboratory of Advanced Functional Materials and Devices, Anhui Province, PR China

#### ARTICLE INFO

Article history: Received 26 February 2014 Received in revised form 17 May 2014 Accepted 22 May 2014 Available online xxx

Keywords: Pd—Co Graphene Graphene oxide Coupling reaction

#### 1. Introduction

During the past decades, homogeneous palladium(II) complexes are one of the most popular catalysts used to catalyze carbon--carbon coupling reactions such as Sonogashira-, Heck-, and Suzuki-type reactions.<sup>1–3</sup> However, the homogeneous catalysis owns numerous drawbacks, especially, high cost, and non-reusability.<sup>4</sup> Pd nanoparticles (NPs) with high catalytic activity seem to be one promising option to replace the homogeneous catalysis for these reactions.<sup>5</sup> To reduce the usage of noble material Pd, the hybrid structure alloyed by Pd and non-noble (e.g., Fe, Co, Cu) metals was designed and synthesized.<sup>4</sup> In many cases, the synthesized Pd/non-noblemetal catalysts not only show a combination of the properties associated with two different metals but also has an enhancement in specific properties due to synergistic effects.<sup>6</sup> Especially, if magnetic metals are alloyed into noble metals, such as Co metals, the nano-catalyst would have a magnetic nature, which could overcome the issue of catalyst separation and reusability.<sup>7,8</sup> In a previous paper,<sup>9</sup> Li, etc. successfully prepared Pd-Co bimetallic hollow nanospheres, which had been demonstrated to be a good catalyst for the Sonogashira reaction in aqueous media. However, very tiny nanoparticles usually add problems in catalyst separation<sup>10</sup> and also induce agglomeration due to high surface energy, leading to the decrease in catalytic efficiency.<sup>11</sup> The

#### ABSTRACT

Graphene (G) supported Pd–Co bimetallic nanoparticles (NPs) as a highly active catalyst was prepared by a chemical reduction method and used for coupling reactions. With the characterization of X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and Raman spectrum, the composition of resulting Pd–Co material was identified to be alloy structural. The Pd–Co (1:1)/G exhibited the highest catalytic activity for the Sonogashira-type coupling reactions and also exerted satisfied catalytic activity and recycle stability for Suzuki–Miyaura cross-coupling reactions. This Pd–Co/G material also possessed other advantages such as low-cost, easy recycled from reaction system by a magnet for their magnetic property, and easy experimental handling.

© 2014 Elsevier Ltd. All rights reserved.

problem may be solved by using proper substrate for supported bimetallic NPs.

As one of the members of the carbon family, G is a single atomic layer of sp<sup>2</sup> carbon atoms,<sup>12</sup> which has large specific surface area and high adsorption capacity. Hence, G and its derivatives can be used as the substrates to host metal nanoparticles.<sup>13,14</sup> In recent studies, Zhang's group<sup>15</sup> successfully modified G with palladium nanoparticles and demonstrated that the Pd–G hybrids can act as an efficient catalyst for the Suzuki reaction under aqueous and aerobic conditions, indicating that the enhanced catalytic activity due to the special nature of G. Therefore, G-supported Pd–Co bimetallic nanoparticles may be acted as an efficient catalyst to carbon–carbon bond coupling.

Herein we disclosed that Pd—Co bimetallic nanoparticles can be dispersed on G with controllable size of nanomaterial by a facile route. The catalytic performances are evaluated in Sonogashira-, Suzuki-type reactions. Furthermore, this efficient catalyst could be used repetitively by a magnet for five times, shows good potential in future industrial applications.

#### 2. Results and discussion

#### 2.1. Structural characteristics

The crystalline structure of Pd–Co (x:y)/G catalysts with different Pd/Co nominal atomic ratios was characterized by XRD and



<sup>\*</sup> Corresponding author. E-mail address: hjxu@hfut.edu.cn (H.-J. Xu).

<sup>0040-4020/\$ -</sup> see front matter © 2014 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2014.05.083

2

Y.-S. Feng et al. / Tetrahedron xxx (2014) 1–5

shown in Fig. 1. The XRD patterns of Pd/G and Co/G that included in the figure were used as a comparison. The first diffraction peak at about 26° in all the XRD patterns was originated from the G support. The peaks at 2 $\theta$  values of 40.1°, 46.80°, 68.20°, and 82.16° are due to the (111), (200), (220), and (311) diffraction peaks of face centered cubic Pd (JCPD-46-1043). The XRD pattern of the pure Co sample exhibited two diffraction peaks around 2 $\theta$ =44.5°, 47.3°, which increased the lattice structure of the Co (JCPD-15-0806) species. As the cobalt content increases, the diffraction peak position was shifted to a higher angle. This confirms the alloy formation between Pd and Co, and which indicates a lattice contraction, which was caused by the incorporation of Co into the Pd face centered cubic structure.<sup>16</sup> But no significant diffraction peak characteristic was found when the content of Co decreased, which was likely due to their poor crystallinity.



Fig. 1. XRD patterns of Pd–Co/G with different Pd/Co atomic ratios (a) Co/G; (b) Pd–Co\_3(1:3)/G; (c) Pd–Co(1:1)/G; (d) Pd\_3–Co (3:1)/G; (e) Pd/G.

Raman spectra of GO and Pd–Co (1:1)/G were shown in Fig. 2. The band at about ~1355 cm<sup>-1</sup> corresponded to the disorderinduced D band may be due to disorder-induced features caused by lattice defect.<sup>17</sup> While the in-phase vibration of the G lattice (G band) at about ~1605 cm<sup>-1</sup> represented the first-order scattering of the  $E_{2g}$  vibrational mode within aromatic carbon rings.<sup>18</sup> The I(D)/I(G) intensity ratio of GO ( $I(D)/I(G)^{GO}$ =0.92) was slightly lower than that of Pd–Co (1:1)/G ( $I(D)/I(G)^{G}$ =1.41).<sup>19,20</sup> Such an enhancement therefore suggested after restored large number of



lamellae sp<sup>3</sup> hybridized carbon atoms re-converted to sp<sup>2</sup> hybridized carbon atoms, but the average of sp<sup>2</sup> carbon ribbons' area became smaller, making the D peak and G peak ratio increase. These results indicated that GO had been reduced and subsequently gave rise to the restoration of sp<sup>2</sup> network with small and isolated domains of aromatics within the sheets.<sup>21</sup>

Fig. 3 shows the morphology and structure of Pd–Co (1:1)/G catalyst determined by TEM and HRTEM. It can be seen that nanoparticles are well-dispersed on graphene. From Fig. 3b, it is clearly that the size distribution of Pd–Co (1:1)/G catalyst was 3–16 nm, with an average size of 8.96 ±0.4 nm, which is consistent with X-ray diffraction pattern. The elemental mapping images (Fig. 3d, e) reveal that a single alloy nanoparticle was built up by Pd (Fig. 3d) and Co (Fig. 3e). Furthermore, to confirm the Pd–Co alloy structure, the energy dispersive spectrometer (EDS) was texted (as shown in Fig. 3f), which reveals the presence of C, Pd, and Co on the surfaces of the G sheets (Si and Cu peaks from the TEM grid).



**Fig. 3.** (a, b) TEM image and the particle size distribution of Pd–Co (1:1)/G catalyst, (c) TEM image of a single Pd–Co (1:1)/G nanoparticle, (d) Pd and (e) EDS mapping profiles, (f) EDS of Pd–Co (1:1)/G catalyst.

As shown in Fig. 4, the surface composition of GO and Pd–Co/G was further analyzed by X-ray photoelectron spectroscopy (XPS). The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s signal to 284.70 eV.<sup>25</sup> The survey spectra of GO and Pd–Co/G were shown in Fig. 4a. Compared to that of GO, the XPS spectrum of Pd-Co/G not only exhibits O 1s and C 1s but also exhibits two additional peaks, which correspond to the Pd 3d and Co 2p states. The higher resolution XPS data of C 1s peaks of GO and Pd-Co/G are shown in the Fig 4b and c, respectively. From the C 1s XPS spectrum of GO (Fig. 4b), the most resolved peak, located at 284.7 eV, corresponds to C–C bonds of the G such as C–C, C=C, C–H bonds.<sup>17,25,27</sup> The weak peak centered at 285.08 eV was attributed to C-O, and the other two peaks at 286.8 eV and 288.2 eV were attributed to epoxy carbon and carbonyl carbon. The C 1s XPS spectrum of the Pd–Co/ G also exhibits the same functionalities, and their peak intensities are a litter smaller than those in GO, revealing that most of the epoxide and hydroxy functional groups were successfully removed. In addition, the O 1s XPS spectra of GO and Pd-Co/G are presented in Fig. 4d, which exhibit different peak shape. The O 1s peak of GO at 532.38 eV is closely related to the significant hydroxyl groups on the surface of GO, whereas, the O 1s peak of Pd-Co/G is at around 530.5 eV. All these results further confirm GO reduction to G, the successful integration between Pd-Co

Please cite this article in press as: Feng, Y.-S.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.05.083

### **ARTICLE IN PRESS**



**Fig. 4.** XPS of Pd–Co/G and GO. (a) The survey XPS spectra of the GO and Pd–Co/G; C1s XPS spectra of GO (b) and Pd–Co/G (c); O 1s XPS spectra of GO and Pd–Co/G (d); XPS spectra showing the (e)  $Pd_{3d}$  and (f) Co  $_{2p}$  peaks.

bimetallic alloy and G.<sup>26</sup> The Pd 3d XPS spectra (Fig 4e) show two major peaks with binding energy at 335.6 eV and 340.91 eV, corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>, and the binding energy separation between them is 5.31 eV. The peak at 335.6 eV is corresponding to the Pd<sup>0</sup> state, which shifted by 0.9 eV toward higher binding energy with respect to Pd/C,<sup>22–24</sup> suggesting that their alloy structure. The peak at 336.28 eV for Pd–Co/G can be owed to Pd<sup>2+</sup> states.<sup>16</sup> The XPS for Co 2p core level region is shown in Fig 4f, there were two major peaks with binding energies at 780.59 and 796.22 eV, corresponding to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>,<sup>28</sup> revealing that it is in good agreement with the literature value for the Pd–Co alloy, which also matches well with literature reports for cobalt metallic.<sup>16</sup>

#### 2.2. Catalytic performances

The Pd–Co bimetallic alloy supported on the G is very stable and has little influence on the diffusion of reaction molecules in liquid-phase reaction. More importantly, these nanospheres can be readily dispersed in liquid-phase solution due to their low density and cycling performance from reaction system by a magnet for their magnetic property. All these properties present the opportunities for this material to be used as a highly efficient catalyst in liquid-phase reaction. The synthesized Pd–Co (x:y)/G catalysts was subjected to Sonogashira-type coupling reactions between aryl iodide and terminal alkyne in water and THF. The general procedure for the Sonogashira cross-coupling reactions was shown in Supplementary data. All the Pd-based catalysts displayed nearly 100% selectivity to diphenylacetylene. From Table 1, it could be clearly found that Pd–Co (1:1)/G was more active than other ratio of Pd–Co/G samples. Pd–Co/G exhibited high selectivity, which may be related to the presence of Co species. The enhanced reactivity was attributed to both the large surface area of G and the promotional effect of Co-dopants, which provided more Pd active sites for the reactants. The position of substituted group of aryl iodide showed obvious effect on reactivity (entries 2 and 3).



R <sub>1</sub>	≻× +			x:y)/G	
Entry	Х	R <sub>1</sub>	Time/h	Conversion/%	Selectivity/%
1	Ι	H	12	98	100
2	Ι	2-NO <sub>2</sub>	12	Trace	100
3	Ι	4-NO <sub>2</sub>	12	99	100
4	Ι	4-Me	12	90	100
5	Br	Н	12	37	100
6	Br	4-NO <sub>2</sub>	12	56	100
7 <sup>b</sup>	Ι	Н	12	84	100
8 <sup>c</sup>	Ι	Н	12	87	100
9 <sup>d</sup>	Ι	Н	12	80	100
10 <sup>e</sup>	Ι	Н	12	Trace	_

<sup>a</sup> Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.2 mmol), a catalyst amount containing 0.02 mmol Pd (Pd–Co(1:1)/G), PPh<sub>3</sub> (0.020 mmol), CuI (0.0030 mmol), and Et<sub>3</sub>N (1.2 mmol), THF (1 mL), water (1 mL), T=80 °C.

<sup>b</sup> Catalyst: Pd–Co<sub>3</sub> (1:3)/G.

<sup>c</sup> Catalyst: Pd/G.

<sup>d</sup> Catalyst: Pd<sub>3</sub>Co (3:1)/G.

<sup>e</sup> Catalyst: Co/G.

To extend the scope of coupling reaction, we examined the Suzuki reaction of phenylboronic acid with iodobenzene (Table 2). All the Pd-based catalysts displayed nearly 100% selectivity to diphenyl. As the similar result with Sonogashira reaction, the result meant that the reaction is relatively insensitive to the electronic characteristics of the substituent groups. Pd–Co/G could be easily separated from the reaction solution by a magnet and used at least five times for the aqueous coupling reaction between iodobenzene and boronic acid. The recyclability and reusability showed its superiority over the homogeneous Pd catalyst (Fig. 5: reaction conditions are listed in Table 2). No significant decrease in the selectivity to diphenyl was observed in the catalyst recycling study. This suggested that the nature of Pd active sites did not change after five runs. Because the weight of catalyst decreased

 Table 2

 Pd-Co/G catalyzed Suzuki coupling reactions<sup>a</sup>

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

 Q

B(OH) <sub>2</sub> + R-X			Pd-Co	⟨	
Entry	R	Х	Time/h	Conversion/%	Selectivity/%
1	Ph	I	2	96	100
2	$4 - NO_2 - C_6H_4$	Ι	2	97	100
3	4-Me-C <sub>6</sub> H <sub>4</sub>	I	2	95	100
4	4-OMe-C <sub>6</sub> H <sub>4</sub>	Ι	2	94	100
5	2-Pyridine	Ι	2	84.5	100
6	Ph-	Br	4	76	100
7	$4-NO_2-C_6H_4$	Br	4	82	100
8	$2-NO_2-C_6H_4$	Ι	4	90	100

<sup>a</sup> Reaction conditions: boronic acid (0.55 mmol), aryl halide (0.5 mmol), a catalyst amount containing 0.02 mmol Pd (Pd–Co(1:1)/G),  $Na_2CO_3$  (2 mmol), ethanol (1 mL), water (1 mL), T=80 °C.

Please cite this article in press as: Feng, Y.-S.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.05.083

#### 4

## **ARTICLE IN PRESS**

Y.-S. Feng et al. / Tetrahedron xxx (2014) 1-5



Fig. 5. Recyling test of Pd–Co/G catalyzed coupling reaction of iodobenzene and phenylboronic acid.

slightly after five consecutive runs while no significant change in the composition of Pd–Co/G, we assumed that the loss of catalyst during the separation process, rather than the leaching of Pd species from Pd–Co/G, was the main factor responsible for the slightly decrease of the conversion of iodobenzene during the recycling tests.

#### 3. Conclusions

The results in the present study supplied a facile way to synthesize a series of Pd–Co nanoparticles with different compositions on G sheets and characterized by XRD, Raman, TEM, and XPS techniques. The catalytic efficiencies of these Pd-Co/G were tested in various Sonogashira-type reactions. Among these different kinds of Pd–Co/G NPs tested, the Pd–Co (1:1) NPs were found to be the most active catalyst for the coupling between phenylacetylene and aryl halide in a tetrahydrofuran/water mixture by using triethylamine as a base at 80 °C. The as-prepared Pd-Co/G had also satisfied catalytic activity and recycle stability for Suzuki-Miyaura cross-coupling reactions due to their magnetic nature, providing 86% conversion after five successive catalytic runs. The enhanced reactivity was attributed to both the large surface area of G and the promotional effect of Co-dopants, which provided more Pd active sites for the reactants. Combined both efficiency of a homogeneous catalyst and the durability of a heterogeneous catalyst, the Pd-Co/G composites provide great potential for G to support other bimetallic nanoparticles, which offer more opportunities for designing new catalysts.

#### 4. Experimental section

#### 4.1. Preparation of catalyst lists

The chemicals used in this experiment were analytical grade and graphene oxide (GO) was prepared by the oxidation of graphite powder (Aldrich) according to an improved Hummers' method.<sup>29</sup> The G-supported Pd-Co bimetallic nanoparticles catalysts involved two metal precursors, palladium(II) chloride and cobalt acetate anhydrous (Pd<sup>II</sup>Cl<sub>2</sub> and Co(OAc)<sub>2</sub>·4H<sub>2</sub>O), with varying atomic ratios of Pd to Co, 1:11:3 and 3:1, at the same time Pd/G and Co/G were also prepared for compassion. The graphene supported 20 wt % Pd–Co bimetallic nanoparticles catalysts were prepared as follows: first the solution was prepared by dissolving a given amount of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and 0.02 M of deep-brown PdCl<sub>2</sub> powder in 10 mL deionized water, and then 0.3 g GO, which was already sonicated for 4 h in 20 mL deionized water was dispersed in it. After magnetic stirring for 60 min, a solution of 0.1 M N<sub>2</sub>H<sub>4</sub> with 0.2 M NH<sub>3</sub>·H<sub>2</sub>O was added into the suspension. Under vigorous stirring at 80 °C and reacted for 4 h, the nanoparticle product was isolated by centrifugation with deionized water until a pH  $\sim$ 7, and then the prepared nanoparticle was achieved and dried overnight. The obtained dark powder was heated in a tube furnace at 300 °C under constant flow of a mixture of nitrogen and hydrogen (3:1 ratio) for 2 h, the subsequently cooled to room temperature under nitrogen. Finally, the powder was annealed at 500 °C under constant flow of a mixture of nitrogen and hydrogen (3:1 ratio) for another 2 h, thus forming a G-supported Pd–Co bimetallic nanoparticles catalyst as shown in Fig. 6.



Fig. 6. Illustration of the synthesis procedure for Pd-Co(x:y)/G.

#### 4.2. Physical characterization

X-ray photoelectron spectroscopy (XPS) were recorded on Thermo Fisher Scientific ESCALAB 250. X-ray source was Al KR at 12 kV and all the binding energies reported were corrected using the signal for the carbon peak (C 1 s) at 284.5 eV. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectrometer (EDS) patterns were observed by JEOL JEM-2100F electron microscope performed at an accelerating voltage of 120 kV. X-ray diffraction (XRD) patterns were carried out on a D/MAX 2500 V diffractometer using Cu K $\alpha$  radiation ( $\lambda$ =1.5406 Å) between 10° and 90°. Raman spectra were collected at room temperature on LABRAM-HR, using an Ar-ion laser operating at 514.5 nm. For the structural determination of the Sonogashira and Suzuki reaction products, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were determined on a BrukerAV 300with TMS as internal standard.

# 4.3. General procedure for the Sonogashira cross-coupling reactions

For the cross-coupling catalysis experiments, a typical experiment was carried out as follows. Aryl halide (1.0 mmol) and phenylacetylene (1.2 mmol) were dissolved in a mixture of 2 mL of H<sub>2</sub>O/THF (1:1), then the catalyst (containing 0.020 mmol Pd), PPh<sub>3</sub> (0.020 mmol), Cul (0.003 mmol), and Et<sub>3</sub>N (1.2 mmol) were added into it. Under argon, the mixture was stirred in 80 °C oil bath for the appropriate time. After the reaction completed, the mixture was extracted with ether, and then centrifuged. The product was analyzed by TLC.

Please cite this article in press as: Feng, Y.-S.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.05.083

4.3.1. Diphenylacetylene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56–7.50 (m, 4H), 7.40–7.29 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  131.60, 128.29 (d, *J*=8.9 Hz), 123.25, 89.36, 77.33, 77.02, 76.70.

4.3.2. 1-Methyl-4-(phenylethynyl)benzene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56–7.48 (m, 2H), 7.43 (d, J=8.1 Hz, 2H), 7.33 (d, J=7.3 Hz, 3H), 7.15 (d, J=7.9 Hz, 2H), 2.36 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.42, 132.54, 131.56 (d, J=4.9 Hz), 129.16, 128.36, 128.11, 123.50, 120.21, 89.60, 88.76, 77.38, 77.07, 76.75, 21.56.

4.3.3. *1-Nitro-4-(phenylethynyl)benzene*. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J*=8.6 Hz, 2H), 7.67 (dd, *J*=14.0, 8.7 Hz, 2H), 7.56 (dd, *J*=7.3, 2.2 Hz, 2H), 7.43–7.34 (m, 3H).

#### 4.4. General procedure for the Suzuki–Miyaura crosscoupling reactions

A typical experiment was carried out as follows: boronic acid (0.55 mmol) and aryl bromide (0.5 mmol) were dissolved in a mixture of 3 mL of ethanol (1 mL) and water (2 mL), then the catalyst (containing 0.020 mmol Pd) and sodium carbonate (2 mmol) were added into it. Under argon, the mixture was stirred in 80 °C oil bath for the appropriate time. After the reaction completed, the mixture was extracted with ether, and then centrifuged. The product was analyzed by TLC.

4.4.1. Biphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63–7.55 (m, 4H), 7.43 (dd, *J*=10.3, 4.8 Hz, 4H), 7.38–7.30 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.21, 128.74, 127.19 (d, *J*=8.3 Hz), 77.33, 77.01, 76.69.

4.4.2. 4-Nitrobiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.26–8.18 (m, 2H), 7.70–7.63 (m, 2H), 7.59–7.52 (m, 2H), 7.48–7.34 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.63, 147.07, 138.77, 129.16, 128.92, 127.80, 127.39, 124.11, 77.35, 77.03, 76.71.

4.4.3. 4-Methoxybiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (t, *J*=8.4 Hz, 4H), 7.41 (t, *J*=7.3 Hz, 2H), 7.29 (t, *J*=7.0 Hz, 1H), 6.97 (d, *J*=8.3 Hz, 2H), 3.83 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.17, 140.86, 133.80, 128.77, 128.20, 126.74 (d, *J*=7.8 Hz), 114.23, 77.40, 77.08, 76.76, 55.38.

4.4.4. 4-Methylbiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (dd, J=8.2, 1.2 Hz, 2H), 7.52–7.45 (m, 2H), 7.45–7.36 (m, 2H), 7.34–7.27 (m, 1H), 7.26–7.19 (m, 2H), 2.39 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.21, 138.40, 137.07, 129.53, 128.77, 127.04 (d, J=2.1 Hz), 77.40, 77.08, 76.76, 21.16.

4.4.5. 2-Phenylpyridine. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.78–8.62 (m, 1H), 8.09–7.91 (m, 2H), 7.83–7.66 (m, 2H), 7.58–7.44 (m, 2H), 7.44–7.37 (m, 1H), 7.22 (ddd, *J*=6.1, 4.8, 2.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.48, 149.69, 139.41, 136.79, 128.98, 128.78, 126.94, 122.13, 120.60, 77.40, 77.08, 76.76.

4.4.6. 2-Nitrobiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (dd, *J*=8.1, 1.2 Hz, 1H), 7.62 (td, *J*=7.6, 1.3 Hz, 1H), 7.51–7.40 (m, 5H), 7.35–7.30

(m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.32, 137.40, 136.36, 132.31, 131.98, 128.72, 128.26, 128.19, 127.91, 124.10, 77.38, 77.06, 76.74.

#### Acknowledgements

We gratefully acknowledge financial assistance from the National Natural Science Foundation of China (Nos. 21272050, 21371044) and the Program for New Century Excellent Talents in University of the Chinese Ministry of Education (NCET-11-0627).

#### Supplementary data

Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra for the products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.05.083. These data include MOL files and InChiKeys of the most important compounds described in this article.

#### **References and notes**

- 1. Rafael, C.; Carmen, N. Chem. Rev. 2007, 107, 874-922.
- 2. Akira, S. J. Organomet. Chem. 1999, 576, 147–168.
- Jwanro, H.; Marc, S.; Christel, G.; Emmanuelle, S.; Marc, L. Chem. Rev. 2002, 102, 1359–1469.
- 4. Wang, D.; Li, Y. Adv. Mater. 2011, 23, 1044–1060.
- 5. Angelica, B.; Cyril, G.; Carmen, C. Chem. Soc. Rev. 2011, 40, 4973-4985.
- Bao, J.; Chen, W.; Liu, T.; Zhu, Y.; Jin, P.; Wang, L.; Liu, J.; Wei, Y.; Li, Y. ACS Nano 2007, 1, 293–298.
- Sankaranarayanapillai, S.; Volker, S.; Werner, R. T. Angew. Chem., Int. Ed. 2010, 49, 3428–3459.
- 8. Didier, A.; Lu, F.; Jaime, R. A. Angew. Chem., Int. Ed. 2005, 44, 7852-7872.
- 9. Li, H.; Zhu, Z.; Liu, J.; Xie, S.; Li, H. J. Mater. Chem. 2010, 20, 4366-4370.
- Zhang, H.; Zhu, Q.; Zhang, Y.; Wang, Y.; Zhao, L.; Yu, B. Adv. Funct. Mater. 2007, 17, 2766–2771.
- 11. Robert, S.; Sharifah, B. A. H. Angew. Chem., Int. Ed. 2004, 43, 1628-1637.
- 12. Luo, J.; Jaemyung, K.; Huang, J. Acc. Chem. Res. 2013, 46, 2225-2234.
- 13. Bruno, F. M.; Philippe, S. Catal. Sci. Technol. 2012, 2, 54–75.
- 14. Bai, S.; Shen, X. RSC Adv. 2012, 2, 64–98.
- Li, Y.; Fan, X.; Wang, L.; Qi, J.; Ji, J.; Wang, S.; Zhang, G.; Zhang, F. Nano Res. 2010, 3, 429–437.
- Maheswari, S.; Karthikeyan, S.; Murugan, P.; Sridhar, P.; Pitchumani, S. Phys. Chem. Chem. Phys. 2012, 14, 9683–9695.
- Yang, D.; Aruna, V.; Gülay, B.; Sungjin, P.; Meryl, S.; Richard, D. P.; Sasha, S.; Inhwa, J.; Daniel, A. F.; Carl, A. V. J.; Rodney, S. R. *Carbon* **2009**, *47*, 145–152.
- Lin, Y.; Kent, A. W.; Michael, J. F.; Sayata, G.; Joseph, G. S.; Donavon, M. D.; Cao, W.; Roy, E. C.; John, W. C. ACS Nano 2009, 3, 871–884.
- 19. Kabeer, J.; Vikas, B. ACS Nano 2009, 3, 2358–2366.
- 20. Tong, L.; Li, Z.; Zhu, T.; Xu, H.; Liu, Z. J. Phys. Chem. C 2008, 112, 7119-7123.
- Konstantin, N. K.; Bulent, O.; Hannes, C. S.; Robert, K. P.; Ilhan, A. A.; Roberto, C. NanoLett 2008, 8, 36–41.
- 22. Weightman, P.; Andrews, P. T. J. Phys. C: Solid State Phys. 1980, 13, 815-819.
- Brun, M.; Berthet, A.; Bertolini, J. C. J. Electron. Spectrosc. Relat.Phenom. 1999, 104, 55–60.
- Andrzej, G.; Anna, M. T.; Józef, J. Z.; Leszek, K.; Józef, W.; Włodzimierz, T. J. Catal. 2005, 229, 332–343.
- Lu, Y.; Wang, X.; Mai, Y.; Xiang, J.; Zhang, H.; Li, L.; Gu, C.; Tu, J.; Mao, S. J. Phys. Chem. C 2012, 116, 22217–22225.
- Shukla, A. K.; Neergat, M.; Parthasarathi, B.; Jayaram, V.; Hegde, M. S. J. Electroanal. Chem. 2001, 504, 111–119.
- 27. Zhang, S.; Shao, Y.; Liao, H.; Mark, H. E.; Yin, G.; Lin, Y. ACS Nano 2001, 5, 1785–1791.
- Yi, L.; Liu, L.; Liu, X.; Wang, X.; Yi, W.; He, P.; Wang, X. Int. J. Hydrogen Energy 2012, 37, 12650–12658.
- Daniela, C. M.; Dmitry, V. K.; Jacob, M. B.; Alexander, S.; Sun, Z.; Alexander, S.; Lawrence, B. A.; Lu, W.; James, M. T. ACS Nano 2010, 4, 4806–4814.