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# Magnetically separable carbon nanocomposite catalysts for efficient nitroarene reduction and Suzuki reactions

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ABSTRACT

Novel magnetically recyclable carbon nanocomposites were synthesized to support various nanocatalysts using a simple, economical and scalable method. The designed nanocomposites, which are composed of porous carbon and $Fe_3O_4$ nanocrystals, can be used as an expandable platform to load versatile nanoparticle catalysts such as Pd and Pt. These nanocomposites with high surface area and permeable porous structure can contain abundant and accessible small-sized catalyst nanoparticles. These characteristics led to efficient catalytic reactions and enhanced catalytic activity, which were verified in selective reduction of nitroarenes and Suzuki cross-coupling reactions. The nanocomposite catalysts provided excellent catalytic activities to yield the desired products in short reaction time and mild reaction conditions. The catalysts could be easily separated from the reaction mixture by a magnet, and recycled five consecutive cycles in reduction of nitrobenzene and Suzuki cross-coupling of bromobenzene without losing significant activities.

## 1. Introduction

Catalysts play important roles in various fields such as oil refining, fine chemicals and pharmaceutical productions, and energy conversions [1,2]. Catalysts are generally classified into two types: homogeneous and heterogeneous catalysts. Homogeneous catalysts have the advantages of being dissolved in reaction medium, thus providing mild reaction conditions, and higher activities and selectivities compared to their heterogeneous counterparts [3]. For example, homogeneous palladium catalysts have been widely used in various catalytic transformations such as Buchwald–Hartwig amination, hydrogenation, Heck, Sonogashira, and Suzuki reactions [4–9]. These catalysts, however, are of somewhat limited use in the industry due to the difficulties in separating the products contaminated with residual unstable complexes and recycling the expensive catalysts [10,11]. These catalytic reactions need typical work-up steps to isolate the product from the mixture, and the reusability of the catalyst becomes complicated [12–14]. Consequently, typical industrial heterogeneous catalysts are composed of supported metal nanoparticles (NPs) owing to their advantages of recovering and reusing of the catalysts [15–17]. However traditional micrometer-sized heterogeneous catalysts generally suffer from low catalytic activities due to the slow diffusion of reactants [18,19]. Accordingly, heterogeneous catalytic reactions generally require more severe conditions than those of homogeneous catalysts [20,21]. Recent advancements in the synthesis of uniformly sized NPs offer numerous opportunities to improve the catalytic performance [22–24]. Although nanoparticle-based catalysts (nanocatalysts), which are often considered as a bridge between homogeneous and heterogeneous catalysts, have high catalytic activities because of their high surface-to-volume ratio, they suffer from several drawbacks such as recovery and instability at high reaction temperatures. Furthermore nanocatalysts without any support are usually unstable, and coagulation is inevitable [25,26]. These facts have motivated continuous research efforts for the developments of highly active and sustainable nanocomposite catalysts [27,28].

Of the wide range of catalyst supports, porous carbon materials have been extensively employed in heterogeneous catalysis because of their desirable properties including permeable pores,

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chemical inertness, and good mechanical stability [29–32]. Because the supports strongly affect the activity of catalyst NPs, numerous studies have been performed to modify the properties of carbon supports [33–36]. Nitrogen doping of carbon materials improves chemical/physical properties. In particular, the nitrogenated sites are known to enhance the interaction between nanocatalysts and support [37–40]. Furthermore, it is an important issue to develop economical and scalable approaches for preparing recyclable porous carbon nanocomposites.

Magnetic separation, among the various procedures for removing catalysts, obviates the requirement of catalyst filtration after the completion of reactions and provides an easy technique for recycling nanocatalysts by using a magnet [41–44]. This method minimizes the possibility of nanocatalyst aggregation during recovery and improves the durability of the catalysts [45–48]. The efficiency of the heterogeneous nanocatalysts also depends on the size, shape, composition and their interaction with supports [49–51]. Recently various NPs were immobilized in porous nanocomposite supports for fabrication easily recoverable and highly active catalysts [52–54]. Herein we report an economical scalable procedure to synthesize magnetically retrievable carbon nanocomposite catalysts by combining magnetic NPs, nitrogen-doped porous carbon support and ~ 3 nm-sized catalyst NPs of Pd or Pt. The designed carbon nanocomposite catalysts provide excellent catalytic activities for reduction of nitroarenes and Suzuki cross-coupling reactions.

## 2. Experimental

### 2.1. Characterization

The loading amount of palladium and platinum in the magnetically recyclable nanocomposite catalysts was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The intermediates and final nanocomposite catalyst materials were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), High resolution powder X-ray diffraction (HRXRD), X-ray fluorescence (XRF) spectrometry, attenuated total reflection infrared spectroscopy (ATR-IR) and CHN elemental analysis. TEM images were obtained using a JEOL JEM-2010 microscope. High resolution TEM (HRTEM) images were obtained using a JEOL JEM-3010 microscope equipped with energy-dispersive X-ray spectroscopy (EDX) detector at an acceleration voltage of 200 kV. Scanning transmission electron microscopy (STEM) and High resolution STEM (HRSTEM) images were acquired using a JEOL JEM-2100F. The mi-micromeritics 3 Flex-surface characterization analyzer was used to measure the physisorption isotherms and surface area of the magnetically recyclable nanocomposite catalysts. ICP-AES was used for the elemental analysis using a Shimadzu ICPS-7500 Japan instrument. XPS was performed to collect core level spectra of Pd (3d) and Pt (4f) scans using Al Kα source (Sigma probe, VG Scientifics). HRXRD was obtained by a Bruker D8 Advance instrument. XRF spectrometry was recorded by a Bruker AXS S4 pioneer. The IR spectra were recorded with an ATR-IR Perkin Elmer spectrometer frontier. The products of the catalytic reactions were analyzed by gas chromatography mass spectrometers (GC-MS) using an Agilent Technologies 5975C VL MSD with triple-axis detector and a Hewlett Packard 5973 mass selective detector GC-MS.

### 2.2. Synthesis of iron oxide NPs

Iron oxide NPs were synthesized using the previously reported methods [55,56]. In a typical synthesis of iron-oleate complex, 10.8 g of iron chloride ($FeCl_3 \cdot 6H_2O$, 40 mmol) and 36.5 g of sodium oleate (120 mmol) were dissolved in a mixture solvent composed of 80 ml ethanol, 60 ml distilled water and 140 ml hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 h. Then, the upper organic layer containing the iron-oleate complex was washed three times with distilled water in a separatory funnel. After washing, hexane was evaporated off resulting in iron-oleate complex in a waxy solid form. The synthesized iron-oleate complex (36 g, 40 mmol) and 5.7 g of oleic acid (20 mmol) were dissolved in 200 g of 1-octadecene at room temperature. The reaction mixture was heated to 300 °C with a constant heating rate of 3.3 °C $min^{-1}$ and then kept at that temperature for 1 h. The resulting solution containing the nanocrystals was then cooled to room temperature and 500 ml of ethanol was added to the solution to precipitate the nanocrystals. The nanocrystals were separated by centrifugation and dispersed in chloroform.

### 2.3. Synthesis of magnetically recyclable polymer and carbon nanocomposite catalysts

In a typical synthesis, 0.5 g of $Fe_3O_4$ NPs was dispersed in 400 ml of chloroform and stirred at room temperature for 15 min. To this solution 15 ml pyrrole was directly added. While stirring vigorously 400 mg of palladium(II) acetate dissolved in 30 ml of $CHCl_3$ was added dropwise and the mixture was stirred for 8 h at room temperature to yield the magnetically recyclable polymer nanocomposite catalyst. The product was isolated by centrifugation and washed several times with chloroform. Finally the product was carbonized at 400 °C for 4 h under hydrogen gas flow to produce the magnetically recyclable carbon nanocomposite catalyst.

### 2.4. Heterogeneous Suzuki cross-coupling reactions catalyzed by nanocomposite Pd catalyst

Nanocomposite Pd catalyst (1 mol%) was added to a round-bottom flask (25 ml) and dispersed in dimethylformamide (DMF)/$H_2O$ (2:1) mixture. Then, aryl halide (0.5 mmol), aryl boronic acid (0.6 mmol), $K_2CO_3$ (1.5 mmol), and a small stirring bar were added to the round-bottom flask. The flask containing reaction mixture was placed in an oil bath (100 °C) and stirred under air atmosphere. After completion of reaction, the mixture was cooled to room temperature and the nanocomposite Pd catalyst was separated using a magnet. The separated catalysts were washed several times with DMF. Finally the products were analyzed by a GC-MS.

### 2.5. Heterogeneous reduction of nitroarenes catalyzed by nanocomposite Pt catalyst

The reduction of nitroarenes was carried out in a 25 round-bottom flask. In a typical procedure, 1 mol% of nanocomposite Pt catalyst was dispersed in EtOH. Then, nitrobenzene (0.5 mmol), hydrazine (2 equiv.), and a small stirring bar were added to the flask. The flask containing reaction mixture was placed in an oil bath (80 °C) and stirred under air atmosphere. After completion of reaction, the mixture was cooled to room temperature and the nanocomposite Pt catalyst was separated using a magnet. The separated catalysts were washed several times with EtOH. The products were analyzed by a GC-MS.

## 3. Results and discussion

The overall synthetic procedure to prepare magnetically recyclable carbon nanocomposite catalysts is illustrated in Fig. 1. Polymer nanocomposite was first prepared via a redox reaction between pyrrole and $Pd(OAc)_2$ in the presence of iron oxide NPs. Pyrrole monomers can be chemically polymerized using palladium(II) acetate as an oxidizing agent. Subsequently the magnetic

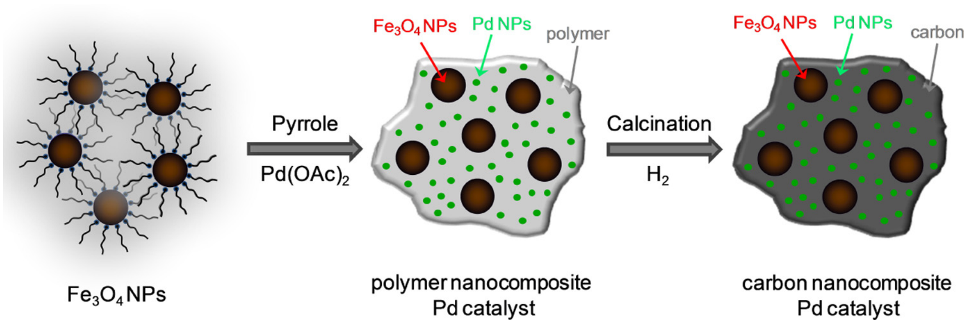


**Fig. 1.** Synthetic procedure of the magnetically recyclable carbon nanocomposite Pd catalyst.

carbon nanocomposite Pd catalyst was prepared via carbonization of the synthesized polymer nanocomposite. This procedure provides direct chemical reduction of palladium ions during pyrrole oxidation so that it incorporates the Pd NPs inside the polymer matrix and subsequently the carbon nanocomposite. Consequently relatively uniform 3 nm-sized Pd nanocatalysts are embedded and stabilized in an *N*-doped carbon framework.

Developing a simple method to produce a large amount of hybrid nanocomposites is very challenging because each constituent material has different physicochemical properties and requires different reaction conditions. We conducted several control experiments to optimize the synthetic conditions. The iron oxide NPs for magnetic separation are generally dispersible in organic solvents such as $CHCl_3$. After performing several control reactions, we found that among various palladium(II) precursors, only $Pd(OAc)_2$ is soluble in chloroform, enabling a one-phase reaction without agglomeration.

TEM images (Fig. 2a) of the magnetic iron oxide NPs showed that they were relatively uniform and spherical with an average diameter of 18 nm. TEM images of the polymer (Fig. 2b) and carbon (Fig. 2c) nanocomposite Pd catalysts revealed that Pd NPs were crystallized with an average distribution size of 3 nm. STEM images of the carbon nanocomposite Pd catalyst (Fig. 2d) indicated a distinct contrast of Pd and $Fe_3O_4$ NPs incorporated in the carbon matrix. HRTEM images clearly showed the porous carbon matrix which is an important parameter for accessibility of reactants to the nanocatalysts (Fig. S1). The ATR-IR spectrum of the polypyrrole nanocomposite catalyst exhibited strong characteristic vibration peaks of ring, C—N, and C—H stretching at 1557, 1417, and 930 $cm^{-1}$, respectively (Fig. S2). The EDX (Fig. 3a) and XRF (Fig. S3) spectra revealed that the nanocomposite Pd catalyst is composed of carbon, iron and palladium. The presence of palladium NPs in the carbon nanocomposite catalyst was verified by XPS analysis (Fig. 3c). The magnetic property of the carbon nanocomposite Pd catalyst was investigated using a superconducting quantum interference device (SQUID) magnetometer. The field-dependent magnetization curve at 300 K revealed superparamagnetic behavior (Fig. 3b). The HRXRD pattern revealed that the nanocomposite Pd catalyst is composed of $Fe_3O_4$ and Pd NPs (Fig. 3d). In addition, CHN elemental analysis showed the composition of C (38.4%) and N (7.5%).

The catalytic performance of the magnetically recyclable carbon nanocomposite Pd catalyst was investigated in Suzuki cross-coupling reactions. To make the reaction conditions greener we screened various organic/water mixtures as the solvent in the cross-coupling of iodobenzene with phenylboronic acid with 1 mol% of the catalyst. The yield of this heterogeneous catalytic reactions was found to be solvent-dependent with 2:1 volume ratio of DMF/$H_2O$ giving the highest yield (Table S1). We next tested the coupling of iodobenzene with phenylboronic acid in the presence of various bases, and the best performance was obtained with $K_2CO_3$ (Table S2).

To extend the scope of this magnetically recyclable carbon nanocomposite Pd catalyst, we carried out the coupling of several aryl iodides with phenylboronic acid under the optimized reaction conditions. In all presented aryl iodide substrates (Table 1, entries 1–6) almost quantitative yields of products were obtained in 1.5 h. Furthermore, in an attempt to extend the application of the designed catalyst, we screened the Suzuki cross-coupling reactions of representative aryl bromides with phenylboronic acid. The reaction of these aryl bromides gave excellent yields in 3 h (Table 1, entries 7–12). More interestingly, Suzuki coupling of arylchlorides with phenylboronic acid, which are known to be very difficult to be catalyzed by heterogeneous catalytic systems were also converted to the coupled products in 15 h with high yields using 1.5 mol% of the Pd catalyst (Table 1, entries 13 and 14).

The hydrolysis of arylboronic acids generally occurs in Suzuki cross-coupling reactions and causes decrease in the product yields [57,58]. Therefore we investigated the reaction of various arylboronic acids with iodobenzene in DMF/$H_2O$ (2:1). As shown in Table 2, the Suzuki cross-coupling reactions of the arylboronic acids with iodobenzene using the magnetically recyclable carbon nanocomposite Pd catalyst (1 mol%) were achieved successfully in DMF/$H_2O$. The reactions were accomplished to produce the respective biaryls with high yields within 1.5 h.

To compare the catalytic activity differences between the polymer nanocomposite Pd catalyst and the carbon nanocomposite Pd catalyst, we performed the Suzuki coupling reaction of iodobenzene with phenyl boronic acid using both kinds of catalysts. The carbon nanocomposite catalyst gave much higher conversion (97%) than the polymer nanocomposite catalyst (31%) under the same reaction conditions in 1.5 h. We ran the catalytic reactions using the polymer and carbon nanocomposite Pd catalysts (1 mol%) under identical reaction conditions, and aliquots were drawn from the reaction mixtures at 15 min intervals. The yield of products in each reaction was measured and the results are shown in Fig. 4. The reaction was completed within 1.5 h with the carbon nanocomposite Pd catalyst while the reaction catalyzed by the polymer nanocomposite took more than 7 h for the completion. The outstanding increase of reaction rate for the carbon nanocomposite catalyst can be explained by pore diffusion [59–61].

These results demonstrate the porous carbon nanocomposite catalyst with a high surface area of 74 $m^2 g^{-1}$ (Fig. 5) is a more efficient catalyst than polymer nanocomposite with a low surface area of 6 $m^2 g^{-1}$ (Fig. S7). The Pd NPs in polymer nanocomposites cannot be reactive because they are thoroughly coated and immersed in the polymer matrix. Unlike the polymer matrix, the porous carbon nanocomposite support is permeable to organic reagents and improves the accessibility of the nanocatalysts and diffusion of reactants and products. The well-defined

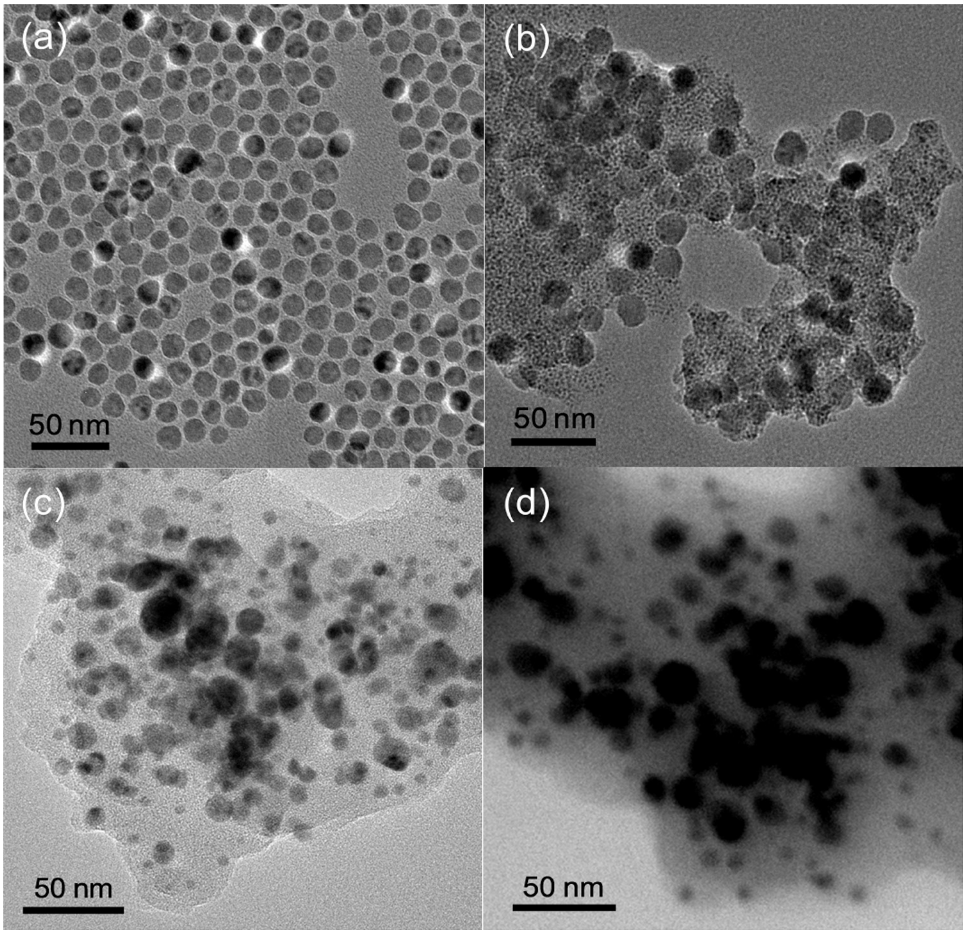


**Fig. 2.** (a) TEM image of $Fe_3O_4$ NPs. (b) TEM image of polymer nanocomposite Pd catalyst. (c) TEM image of carbon nanocomposite Pd catalyst. (d) STEM image of carbon nanocomposite Pd catalyst.

nitrogen-containing carbon increases the interaction between the nanocatalysts and carbon matrix, enabling to maintain their activities in harsh reaction conditions such as temperature alteration, stirring and shaking. The designed carbon nanocomposite provides a high surface area and accommodates a large amount of small sized nanocatalysts, leading to the high catalytic activity. In addition, magnetic separation of the carbon nanocomposite catalyst is much more convenient for the catalyst recycling than that required by the polymer nanocomposite (Fig. S8). These attractive features exhibited by the designed magnetically recyclable carbon nanocomposite enabled to have high catalytic activity for Suzuki reactions in milder reaction conditions and shorter reaction time compared to those required by our previously reported heterogeneous catalysts [24,62,63]. The magnetically recyclable carbon nanocomposite Pd catalyst also presented higher catalytic activity than the commercially available Pd/C catalyst. TEM images of the commercial Pd/C catalyst shows Pd NPs are polydisperse with a size distribution of 5 to 25 nm (Fig. S9). When 1 mol% of commercial Pd/C catalyst was used in the Suzuki coupling reaction of iodobenzene with phenyl boronic acid under the identical reaction conditions, it provided a much lower yield (39%) in 1.5 h. These advantages, including excellent product yield and sustainable catalytic activity, make this nanocomposite catalyst a potential candidate for industrial considerations.

The designed magnetically recyclable carbon nanocomposite can be readily used as general framework supports for loading other noble metal NPs, such as platinum, which can be utilized for catalytic reduction of nitro compounds to amines. The reduction of nitro aromatics is an important chemical reaction because organic amines are intermediate materials for the production of agrochemicals, pharmaceuticals, polymers and pigments [64–67]. Magnetically recyclable nanocomposite Pt catalyst can be prepared using a similar procedure for the nanocomposite Pd catalyst. We first prepared the polymer nanocomposite Pt catalyst via a direct redox reaction between pyrrole and a Pt precursor ($PtCl_2$) as an oxidizing agent in the presence of iron oxide NPs. Then the magnetically retrievable carbon nanocomposite Pt catalyst was prepared via carbonization of the synthesized polymer nanocomposite.

TEM images of this nanocomposite showed the Pt NPs were uniform with an average size of 3 nm (Fig. S4). EDX of the nanocomposite Pt catalyst showed that the Pt species were successfully immobilized in the nanocomposite (Fig. S5). The existence of Pt NPs on the nanocomposite was also confirmed by XPS analysis (Fig. S6). In a continuation of our research toward the development of sustainable organic transformations, we investigated the catalytic activity of the nanocomposite Pt catalyst for the reduction of structurally diverse nitro compounds. When we tested the catalytic performance of the nanocomposite Pt catalyst for the reduction of nitrobenzene using hydrazine, the reaction was completed in 3 h yielding quantitative aniline (Table 3, entry 1). In an attempt to extend the application of this catalyst, we studied the reduction of structurally diverse nitro compounds. Table 3 confirmed that the nanocomposite Pt catalyst exhibited excellent activities for the reduction of nitrobenzenes. The selective reduction of nitro group in organic compounds containing other reducible functional

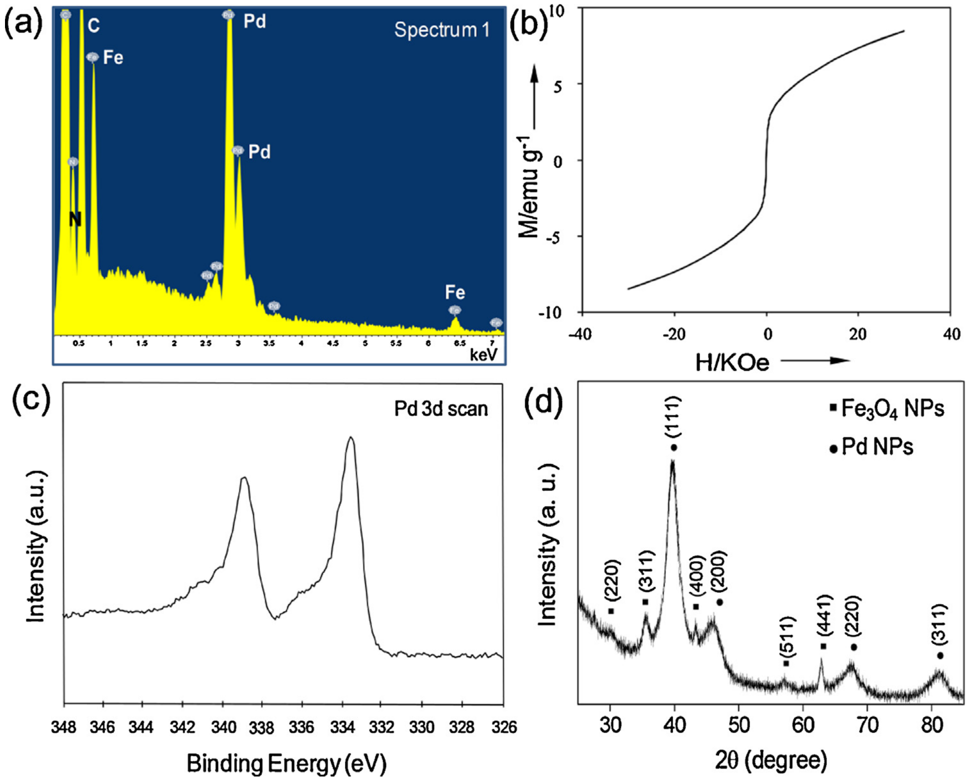


**Fig. 3.** (a) EDX spectrum of the carbon nanocomposite Pd catalyst. (b) Field-dependent magnetization of the carbon nanocomposite Pd catalyst. (c) XPS analysis of Pd 3d scan. (d) HRXRD pattern of magnetically recyclable carbon nanocomposite Pd catalyst.

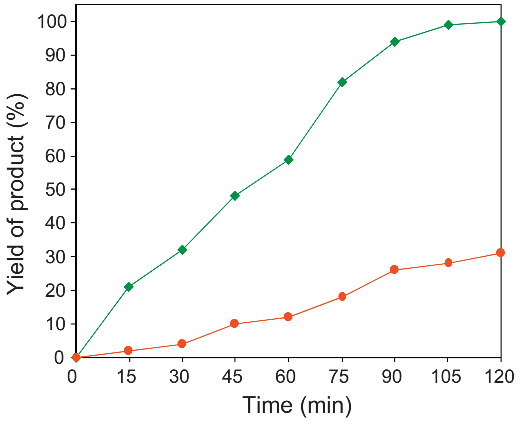


**Fig. 4.** Time-dependent product yields of the Suzuki cross-coupling reactions using polymer (red line) and carbon (green line) nanocomposite Pd catalysts. Reaction conditions: aryl iodide (0.5 mmol), phenylboronic acid (0.6 mmol), catalyst (1 mol%), $K_2CO_3$ (1.5 mmol), DMF/$H_2O$ (2:1), 100 °C.

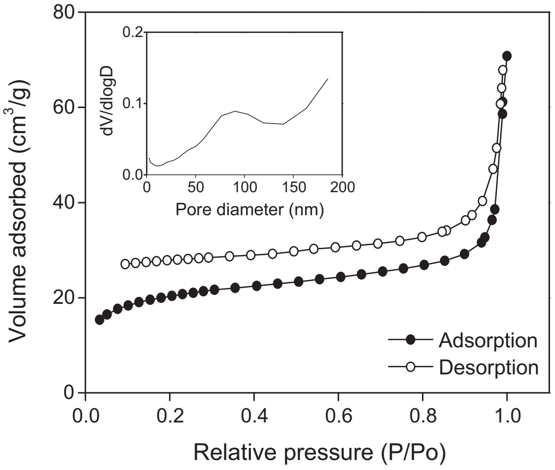


**Fig. 5.** $N_2$ adsorption/desorption isotherms of the magnetically recyclable carbon nanocomposite catalyst. The inset shows the corresponding pore size distribution.

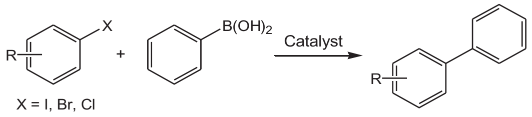
groups is a very challenging issue in organic synthesis [68–70]. However, the nitro group of nitroarenes with different functional groups using the magnetically recyclable nanocomposite catalyst was selectively reduced to the amino moiety (Table 3, entries 2–4). The halogen functional groups remained intact under the reaction conditions. In all cases examined in Table 3, the excellent yields of amine products were obtained as exclusive products.

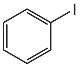
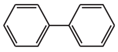
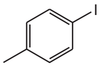
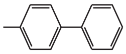
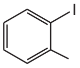
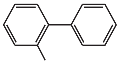
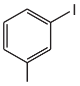
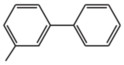
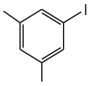
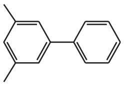
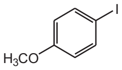
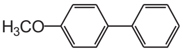
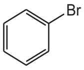
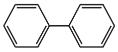
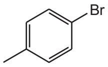
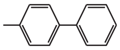
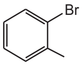
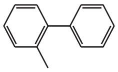
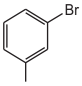
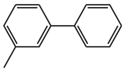
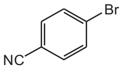
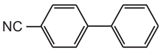
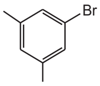
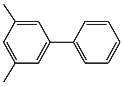
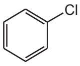
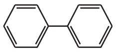
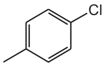
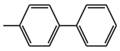
**Fig. 6.** Magnetic separation and recycling of the carbon nanocomposite Pt catalyst.

Reusability and durability of the catalysts are important factors for practical applications. To verify these issues, we investigated magnetic separation and recycling of the magnetically recyclable nanocomposite Pt catalyst (Fig. 6), which was successfully recycled and reused for five consecutive cycles of the reduction of nitrobenzene with no significant loss of activity (Table 4). Upon completion of the reaction the catalyst was easily separated using a magnet, washed with EtOH and reused in the next reaction.

When we examined the magnetic separation and durability of the nanocomposite Pd catalyst in the Suzuki coupling reaction

**Table 1**
Heterogeneous Suzuki cross-coupling reaction of aryl halides with phenylboronic acid[a].



| Entry | Aryl halide | Product | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  |  | 1.5 | 97 |
| 2 |  |  | 1.5 | 94 |
| 3 |  |  | 1.5 | 93 |
| 4 |  |  | 1.5 | 95 |
| 5 |  |  | 1.5 | 91 |
| 6 |  |  | 1.5 | 92 |
| 7 |  |  | 3 | 95 |
| 8 |  |  | 3 | 93 |
| 9 |  |  | 3 | 91 |
| 10 |  |  | 3 | 92 |
| 11 |  |  | 3 | 94 |
| 12 |  |  | 3 | 91 |
| 13 |  |  | 15 | 91[c] |
| 14 |  |  | 15 | 81[c] |

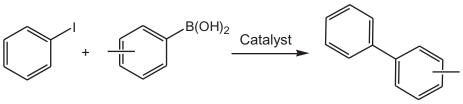
[a] Aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), carbon nanocomposite Pd catalyst (1 mol%), $K_2CO_3$ (1.5 mmol), DMF/$H_2O$ (2:1), 100 °C.

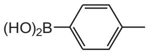
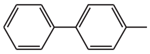
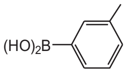
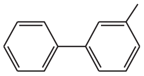
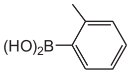
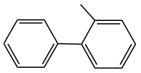
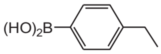
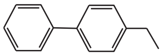
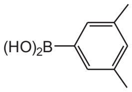
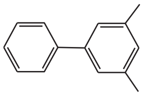
[b] Yields (average of at least two runs) were determined by gas chromatography mass spectrometry (GC-MS) analysis using internal standard (decane).

[c] 1.5 mol% Pd catalyst was used. Isolated yield was confirmed by GC-MS.

of bromobenzene with phenylboronic acid (Table S3), there was a small decrease of the activity after each recycling of the catalyst. The amount of palladium in the nanocomposite catalyst was analyzed after recovering the catalyst after the five cycles of the Suzuki coupling reactions of bromobenzene. The ICP-AES analysis indicated 1.4% of the palladium species remained in the reaction solution. TEM images of the recycled carbon nanocomposite Pd catalyst showed that the nanocomposite catalyst was stable after the recycling (Fig. S10). Therefore, the small decline of catalytic activity seems to result from incomplete magnetic separation of the catalyst during consecutive recycling because the viscosity of DMF is lower than EtOH.

**Table 2**
Heterogeneous Suzuki cross-coupling reaction of aryl iodide with arylboronic acids[a].

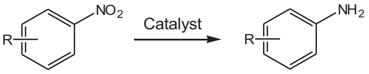


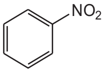
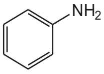
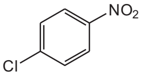
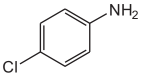
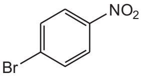
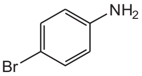
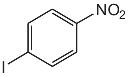
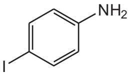
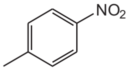
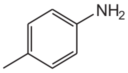
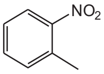
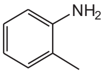
| Entry | Arylboronic acid | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 97 |
| 2 |  |  | 95 |
| 3 |  |  | 94 |
| 4 |  |  | 93 |
| 5 |  |  | 95 |

[a] Aryl iodide (0.5 mmol), aryl boronic acid (0.6 mmol), carbon nanocomposite Pd catalyst (1 mol%), $K_2CO_3$ (1.5 mmol), DMF/$H_2O$ (2:1), 100 °C, 1.5 h.

[b] Yields (average of at least two runs) were determined by GC-MS analysis using internal standard (decane).

**Table 3**
Heterogeneous reduction of substituted nitrobenzene with hydrazine[a].



| Entry | Substrate | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 99 |
| 2 |  |  | 98 |
| 3 |  |  | 95 |
| 4 |  |  | 97 |
| 5 |  |  | 95 |
| 6 |  |  | 94 |

[a] Substituted nitrobenzene (0.5 mmol), hydrazine (2 equiv.), carbon nanocomposite Pt catalyst (1 mol%), EtOH, 80 °C, 3 h.

[b] Yields (average of at least two runs) were determined by GC-MS with respect to an internal standard (decane).

**Table 4**
Magnetic separation and recycling of the nanocomposite Pt catalyst in heterogeneous reduction of nitrobenzene with hydrazine[a].

| Cycle | 1st | 2nd | 3rd | 4th | 5th |
|---|---|---|---|---|---|
| Yield of product[b] | 99 | 99 | 98 | 97 | 96 |

[a] Nitrobenzene (0.5 mmol), hydrazine (2 equiv.), carbon nanocomposite Pt catalyst (1 mol%), EtOH, 80 °C, 3 h.

[b] Yields were determined by GC-MS with respect to an internal standard (decane).

Magnetically recyclable carbon nanocomposite catalyst can be readily synthesized in large scale using a simple and economical process. For example, when we used 10 times more reagents, ∼5.6 g of the magnetically recyclable carbon nanocomposite catalyst could be obtained in one batch synthesis (Fig. S11).

## 4. Conclusions

In conclusion, we have demonstrated new sustainable and magnetically separable carbon nanocomposite catalysts for the selective reduction of nitroarenes and various Suzuki cross-coupling reactions. The designed nanocomposites with a well-defined porous carbon matrix and high surface area accommodate abundant 3 nm-sized NPs of Pd and Pt providing excellent catalytic activities in short reaction time. Furthermore the nanocomposites could be readily synthesized in a large scale by a simple and inexpensive process and used as general platform to load various catalytic NPs for different catalytic reactions. Magnetic recovery could eliminate tedious work-up and catalyst filtration procedures after completion of the reactions, which is an additional sustainable attribute of these carbon nanocomposite catalysts. Of particular note is the catalysts could be reused for five consecutive cycles in the reduction of nitrobenzenes and Suzuki cross-coupling of bromobenzenes. The aforementioned advantages presented by these nanocomposite catalysts are very important for their future industrial applications in numerous important catalytic processes.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.02.029.

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