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One-pot hydrothermal synthesis of Pd/Fe_3O_4 nanocomposite in HEPES buffer solution and catalytic activity for Suzuki reaction

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Graphical abstract

Highlights

- Pd/Fe_3O_4 nanocomposite was made by a facile one-pot hydrothermal method.
- In-situ formed Pd/Fe_3O_4 had excellent activity for various Suzuki reactions.
- In-situ formed Pd/Fe_3O_4 was magnetically recoverable and recycled for ten runs.

Abstract: The Pd/Fe_3O_4 nanocomposite integrates versatile Pd nanocatalysts with magnetic separation, and has great potential in fine chemical and pharmaceutical synthesis. Its preparation usually involves multi-steps. Herein it was prepared via a facile one-pot hydrothermal synthesis in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer solution with the assistant of polyvinylpyrrolidone (PVP). HEPES plays multi-functions, particularly as a ligand to enhance the oxidation of Fe^{2+} to Fe^{3+} and as a buffer to control the pH value at slightly basic conditions (ca. 7.4) for the formation of crystalline Fe_3O_4 phase via Fe^{2+}/Fe^{3+} co-precipitation. PVP works as a dispersant to prevent the particle from aggregation. The obtained Pd/Fe_3O_4 nanocomposite comprised uniform Pd nanoparticles (ca. 5 nm) deposited on Fe_3O_4 nanocrystals (ca. 15 nm). It exhibited excellent catalytic activity and stability for various Suzuki coupling reactions, and could be efficiently recovered with a magnet and recycled for at least 10 cycles without losing catalytic activity.

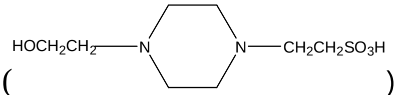
KEYWORDS:

A. magnetic materials; B. chemical synthesis; C. X-ray diffraction; D. catalytic properties

1. Introduction

Palladium (Pd) nanoparticles exhibit remarkable catalytic activities for carbon-carbon cross-coupling reactions (e.g. Suzuki, Heck and Sonogashira) [1-3], and have great potential in the synthesis of drugs and fine chemicals. However, they face inherent problems in catalyst agglomeration and separation, which usually result in the decrease in catalytic activity and life time. In order to overcome these drawbacks, many efforts have been devoted to magnetically recoverable Pd nanocatalysts [4-6], which combine the advantages of high catalytic activity of Pd nanocatalysts and easy separation of magnetic materials.

Magnetite (Fe_3O_4) is often used as support to make magnetic nanocatalysts due to its intrinsic magnetic property, good chemical stability and low toxicity. In the literature, synthesis of Pd/Fe_3O_4 nanocatalysts usually involves hazardous organic solvents and chemicals, harsh reaction conditions and multi-steps, e.g., deposit the Pd source onto the pre-formed Fe_3O_4 support followed by decomposition or reduction of Pd precursors [7-13]. Therefore, it remains a great challenge to develop facile and rapid methods for the synthesis of Pd/Fe_3O_4 nanocatalysts [14].

In the present work, the Pd/Fe_3O_4 nanocomposite was prepared via a facile one-pot hydrothermal synthesis in HEPES buffer solution. HEPES represents 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (), which is low-toxic and widely used as a buffer in cell culture. The obtained Pd/Fe_3O_4 nanocomposite exhibited excellent catalytic performance for various Suzuki coupling reactions, and could be efficiently recovered with a magnet and recycled for at least 10 cycles without losing its catalytic activity.

2. Experimental

The Pd/Fe_3O_4 nanocomposite was prepared via one-pot hydrothermal synthesis as follows: 0.0133 g of $PdCl_2 \cdot 2H_2O$ (0.075 mmol), 0.16 g of polyvinylpyrrolidone (PVP, M.W. =55,000) and 0.0149 g $FeCl_2 \cdot 4H_2O$ (0.075 mmol) were added into the solution of 10 mL of HEPES buffer solution (200 mmol/L, pH 7.40) in 2 mL of deionized water. After sonication for 2 min, the whole mixture was transferred to a 30 mL Teflon-lined stainless-steel autoclave and heated at 100 ^{o}C for 8 h. After cooling down to room temperature (r.t.), black particles were collected with a magnet, washed with deionized water and ethanol, and dried in a desiccator at r.t. All chemicals were of analytical grade from Sigma-Aldrich.

To investigate the influence of halide ions on the synthesis of Pd/Fe_3O_4 composites, the same experimental procedure as described above was used except that 2 mL of deionized water was replaced with 2 mL of NaX (X = Cl, Br and I) aqueous solution (1 mol/L).

Suzuki reaction was carried out as follows: aryl halide (ArX, X=Br, I) (1.0 mmol), phenylboronic acid (1.5 mmol), tetrabutylammonium bromide (TBAB, 1 mmol), K_2CO_3 (2 mmol), and Pd/Fe_3O_4 nanocatalyst (1.5 mg, containing 0.5 mmol % Pd with regard to ArX) were added into 9 mL of ethanol/H_2O (v/v=1:2) solution. The whole mixture was refluxed at 86 ^{o}C for 0.5-1.5 h, and then cooled down to r.t. The product was extracted with diethyl ether for three times, and then dried with anhydrous Na_2SO_4. After being concentrated in a rotary evaporator, the product was finally purified by column chromatography using diethyl ether/petroleum ether as eluent, and identified by comparing their ^{1}H NMR spectra with standard data. For comparison, carbon-supported Pd nanoparticles (Pd/C) with 10 % of Pd content purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were also used as catalysts for Suzuki reaction.

Powder X-ray diffraction (XRD) was carried out on a Bruker AXS D8 Discover (Cu Kα = 1.5406 Å). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were recorded on a Philips Tecnai G2 20 electron microscope operating at 200 kV. The energy-dispersive X-ray (EDX) analysis was performed on an Oxford Instruments INCA with a scanning range from 0 to 20 keV. The Pd content in Pd/Fe_3O_4 nanocatalyst was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent ICP-MS 7500ce). Magnetic properties were investigated on a SQUID magnetometer (Quantum Design MPMS) at 298 K.

3. Results and discussion

3.1. Characterization of Pd/Fe_3O_4 nanocomposite

The XRD pattern of Pd/Fe_3O_4 nanocomposite showed diffraction peaks of both Pd (fcc) and magnetite crystals, which were well indexed in Fig. 1 according to standard diffraction data of Pd (JCPDS 05-0681) and Fe_3O_4 (JCPDS 75-0033). No other peak was observed, indicative of high purity of Pd/Fe_3O_4 nanocatalyst.

TEM images of Pd/Fe_3O_4 nanocomposite (Fig. 2) revealed that spherical Pd nanoparticles of ca. 5 nm were well-dispersed on the surface of Fe_3O_4 nanoparticles of ca. 15 nm. Its SAED pattern (Fig. 2a inset) featured many bright spots, indicating high crystallinity of the product. In consistent with the XRD result, the SAED pattern was features of both Pd (fcc) and Fe_3O_4 crystals. The elemental composition of selected areas in TEM images was also determined by EDX spectrum (Fig. S1 in supporting information), confirming the presence of palladium, iron and oxygen. The Pd content in the Pd/Fe_3O_4 nanocomposite was 33.8 wt%, as determined by ICP-MS analysis.

The room-temperature magnetization curve of the Pd/Fe_3O_4 nanocomposite (Fig. 3) showed typical superparamagnetic characteristics, i.e., zero coercivity and no remanence on hysteresis. The saturated magnetization value was 41.3 $emu \cdot g^{-1}$. These magnetic properties are ideal for magnetic separation and recycling of the Pd/Fe_3O_4 nanocomposite. It can be easily separated from the solution with a normal magnet (see Fig. 3 inset), while avoid aggregation after removing the external magnet.

3.2. Effects of reaction components on the synthesis of Pd/Fe_3O_4 nanocomposite

HEPES: The addition of HEPES is crucial for the one-pot formation of Pd/Fe_3O_4 nanocomposite via hydrothermal treatment of the reaction mixture of $FeCl_2$-$PdCl_2$-HEPES-PVP-H_2O. Under otherwise identical conditions except the absence of HEPES, no crystalline iron oxide phase except Pd crystals was formed (XRD shown in Fig. S2). The Pd crystals were formed via $2Fe^{2+} + Pd^{2+} \rightarrow 2Fe^{3+} + Pd$. HEPES may play multi-functions [15]: Firstly, it may reduce the redox potential of Fe^{3+}/Fe^{2+} by forming the iron-HEPES complex, thus enhancing the oxidation of Fe^{2+} to Fe^{3+} by Pd^{2+} ions in the solution along with the inadvertent air. Such enhancing effects have been reported in Fenton oxidation processes for degradation of organic pollutants in waste water treatment with the assistance of different organic ligands (e.g., EDTA [16, 17], 5-sulfosalicylic acid [18] and citrate [19]). For example, the formation of Fe-EDTA complex reduces the standard redox potential of Fe^{3+}/Fe^{2+} from the conventional level of 0.77 V to 0.17 V [16], which is much lower than the standard redox potential of Pd^{2+}/Pd (0.915 V). Secondly, HEPES is a buffer to control the pH value of the reaction mixture at ca. 7.4. Fe_3O_4 was formed by Fe^{2+}/Fe^{3+} co-precipitation under such slightly basic conditions, i.e., $Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$. Thirdly, HEPES acts as an anchoring agent for depositing Pd nanoparticles onto Fe_3O_4 by multiple functional groups (e.g., sulfonate, hydroxyl and amine groups or their derivatives). This is important for the formation of well-dispersed and stable Pd/Fe_3O_4 nanocomposites, similar to the preparation of Pd nanoparticles supported on Fe_3O_4/amino acid nanocomposite [13].

PVP: PVP works as a dispersant in our synthesis system. Without the addition of PVP, Pd/Fe_3O_4 composite with minor γ-Fe_2O_3 (PDF No. 4-755) impurity was produced, as shown by XRD in Fig. 4. However, the resulting particles were severely agglomerated, as shown by TEM images in Fig. 5.

Influence of halide ions: It has been reported that various Pd nanostructures (e.g., nanosheets, nanobars, nanorods, concave tetrahedra, and a series of single-crystalline rhombic dodecahedral, cubic, and octahedral nanocrystals) could be synthesized with the assistance of halide ions, particularly Br^- and I^-, due to the selective interaction of halides with different crystal facets that alters their surface energies and growth rate [20-22]. Therefore, the influence of halide ions was investigated in this work by adding 2 mmol of NaX (X= Cl^-, Br^- and I^-) during the synthesis of Pd/Fe_3O_4 nanocomposites.

As observed in Fig. 6, the Pd/Fe_3O_4 nanocomposite synthesized with the addition of NaBr contained more uniform and well-dispersed Pd nanoparticles (ca. 5 nm) (b1-b3 in Fig. 6). In contrast, the Pd/Fe_3O_4 nanocomposites synthesized with the addition of NaCl and NaI contained Pd nanoparticles with broader size distributions (5-10 nm and 5-20 nm, respectively). Some Pd nanorods and bigger polyhedral nanoparticles were also observed in Fig. 6c. The non-uniform shape and size distribution were unbeneficial for the uniform dispersion of Pd particles on the surface of Pd/Fe_3O_4, which was clearly revealed in Fig.6.

In comparison with the Pd/Fe_3O_4 nanocomposite synthesized in the absence of NaX, the Pd/Fe_3O_4r nanocomposite synthesized with the addition of NaBr has lower Pd content (23.9 wt% vs. 33.8 wt%). This could be due to the interaction of Br^- with Pd nanoparticles, which prevents Pd from depositing on the surface of Fe_3O_4.

3.3. Catalytic performance of Pd/Fe_3O_4 nanocomposite

As shown in Table 1, the Pd/Fe_3O_4 nanocomposite exhibited excellent catalytic activity for Suzuki cross-coupling reactions of phenylboronic acid with various aryl bromides (entries 1-3) and aryl iodides (entries 4–5). The isolated yield of the corresponding coupling products reached up to 92-98 % after reaction for 0.5-3 h at 86 ^oC. In comparison, carbon-supported Pd nanoparticles of similar particle size (~5 nm, Fig. S3) showed inferior catalytic activity for all reactions studied, particular for deactivated p-bromophenol (isolated yield: 93% vs. 30%

in entry 3). This implied that there were some synergistic effects between supported Pd nanocatalysts and Fe_3O_4. Similar synergistic effects between Pd and iron oxide for CO oxidation have been recently reported due to strong metal–support interactions in the literature [23]. It would be reasonable to expect stronger metal–support interactions in our Pd/ Fe_3O_4 nanocatalysts since both components were formed in one pot with intimate contact with each other. The stronger metal–support interactions prevent Pd nanoparticles from aggregating into inactive Pd black during reaction, which is crucial to form stabile and recyclable magnetic nanocatalysts.

Sukuzi coupling reaction of 4-iodophenyl methyl ether with phenylboronic acid was used as a model reaction to test the recyclability of the Pd/Fe_3O_4 nanocatalyst under the same reaction conditions. The used Pd/Fe_3O_4 nanocatalyst was first separated and recovered from the reaction mixture with a magnet, then washed with deionized water (4 mL×3) and ethanol (4 mL×3), and finally dried in vacuum for 24 h before re-use. As depicted in Fig. 7, the isolated yield of product was still 88% after ten reaction cycles (i.e., the ninth re-use of Pd/Fe_3O_4 nanocatalyst). This demonstrated that the Pd/Fe_3O_4 nanocatalyst was magnetically recoverable and had excellent catalytic activity and stability.

4. Conclusions

A facile one-pot hydrothermal method has been developed to synthesize the Pd/Fe_3O_4 nanocomposite in HEPES buffer solution (200 mmol/L, pH 7.40) with the assistant of PVP. The addition of HEPES was crucial for the formation of Fe_3O_4 while PVP prevented the particles from aggregation. The obtained Pd/Fe_3O_4 nanocomposite consisted of uniform Pd nanoparticles (ca. 5 nm) deposited on Fe_3O_4 nanocrystals (ca. 15 nm). It exhibited excellent catalytic activity and stability for various Suzuki coupling reactions, and could be efficiently recovered with a magnet and recycled for at least 10 times without losing its catalytic activity.

Acknowledgements

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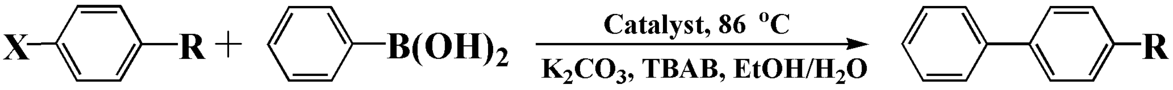
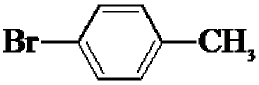
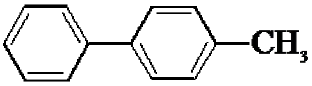
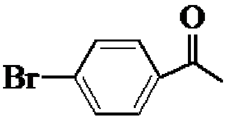
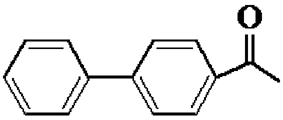
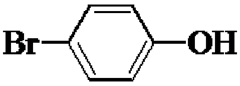
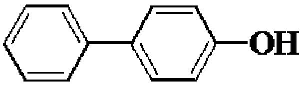
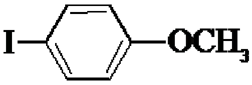
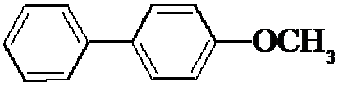
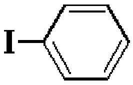
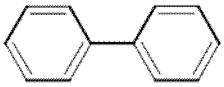
Table 1 Suzuki coupling reactions of phenylboronic acid with various aryl halides over different Pd nanocatalysts.



Entry	Substrates	Products	Time (h)	Isolated yield (%)	
				Pd/Fe$_3$O$_4$	Pd NPs
1			1.5	92	85
2			1.5	94	40
3			3	93	30
4			0.5	98	94
5			0.5	95	92

Figures captions:

Fig. 1. XRD pattern of Pd/Fe_3O_4 nanocomposite.

Fig. 2. TEM images of Pd/Fe_3O_4 nanocomposite. Inset in Fig. 2a is the SAED pattern.

Fig. 3. Magnetization curve of Pd/Fe_3O_4 nanocomposite at 298 K.

Fig. 4. XRD pattern of Pd/Fe_3O_4 composite prepared in the absence of PVP. Asterisk-marked peaks were assigned to minor γ-Fe_2O_3 impurity (PDF No. 4-755) in the product.

Fig. 5. TEM images of the Pd/Fe_3O_4 composite prepared in the absence of PVP.

Fig. 6. TEM images and corresponding particle size distributions of Pd/Fe_3O_4 nanocomposites synthesized with the addition of different NaX salts. **(**a1-a3) NaCl, (b1-b3) NaBr and (c1-c3) NaI.

Fig. 7. Recyclability of the Pd/Fe_3O_4 nanocomposite as catalyst for Suzuki coupling reaction of phenylboronic acid with 4-iodophenyl methyl ether.

Fig. 1.

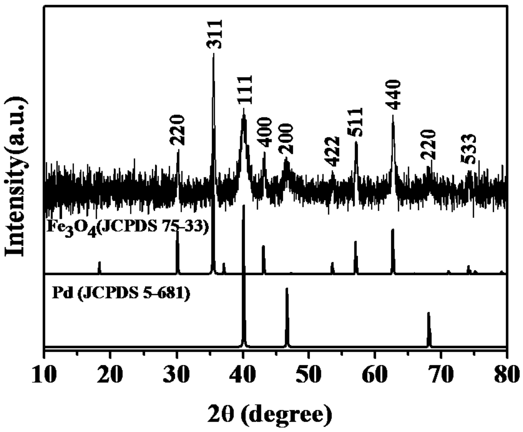
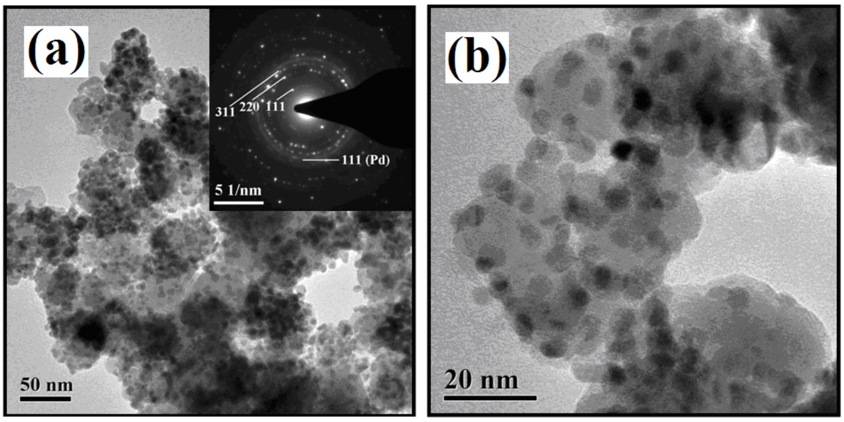


Fig. 2.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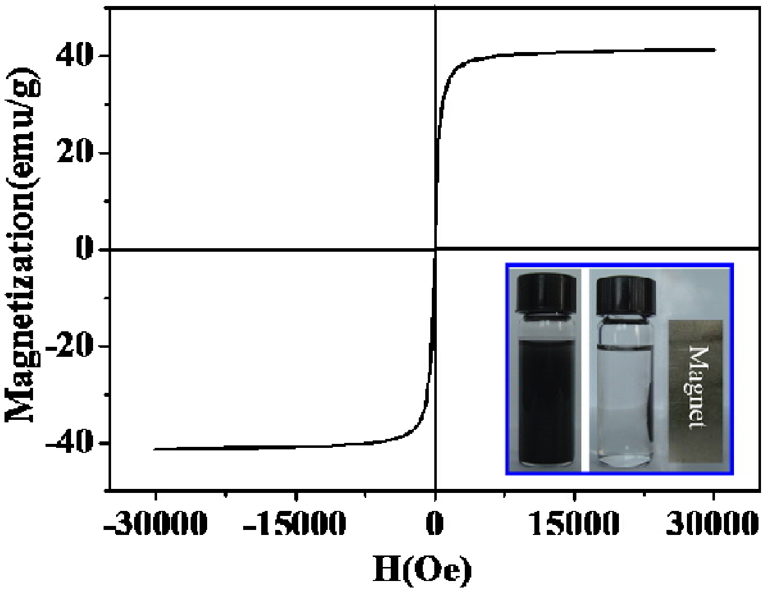
311
220
111
111 (Pd)
5 1/nm
50 nm
(b)
20 nm

Fig. 3.


Magnetization(emu/g)
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0
-20
-40
-30000
-15000
0
15000
30000
H(Oe)
Magnet

Fig. 4.

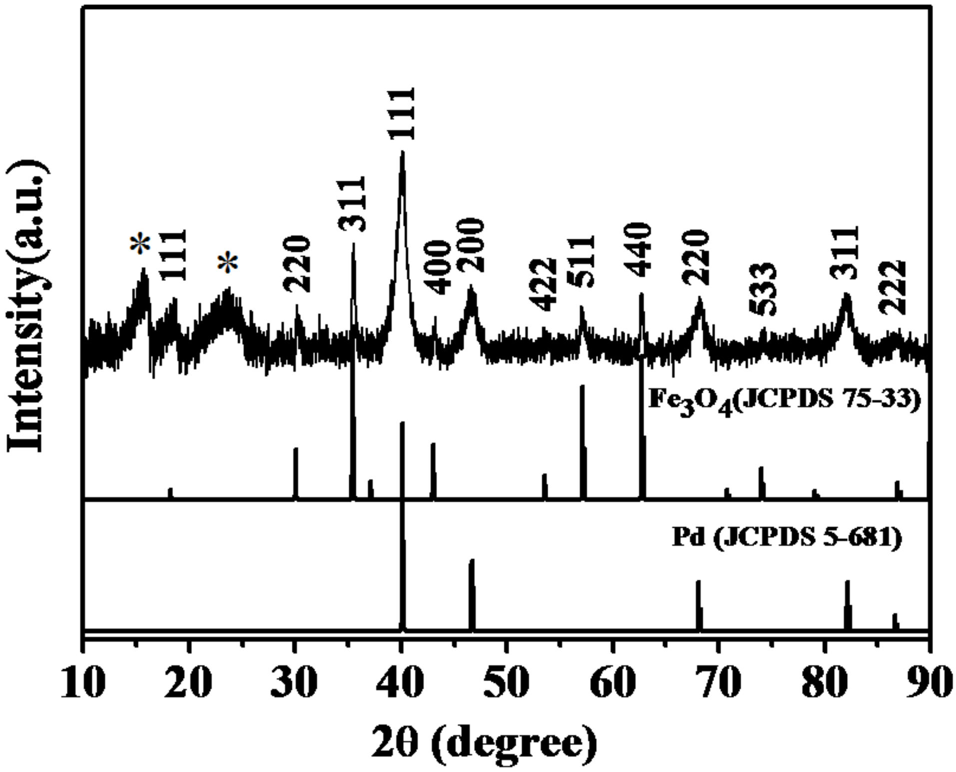

*
111
*
220
311
111
400
200
422
511
440
220
533
311
222
Fe_3O_4(JCPDS 75-33)
Pd (JCPDS 5-681)
Intensity(a.u.)
10
20
30
40
50
60
70
80
90
2θ (degree)

Fig. 5.

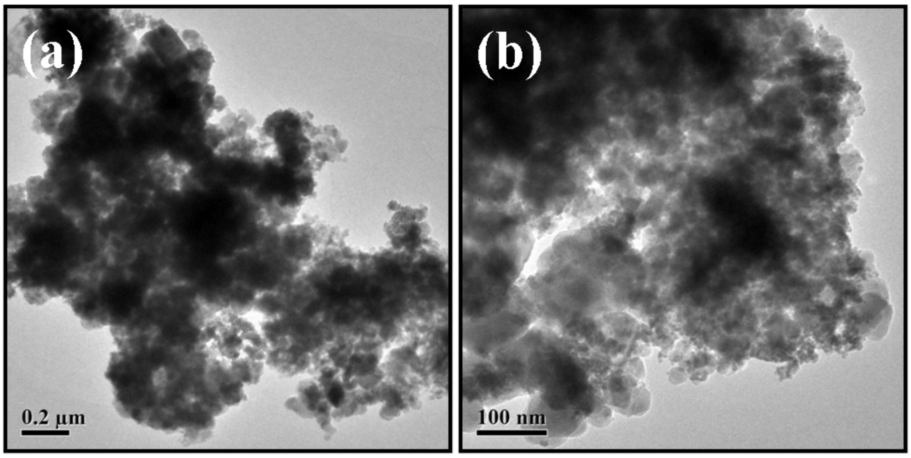


Fig. 6.

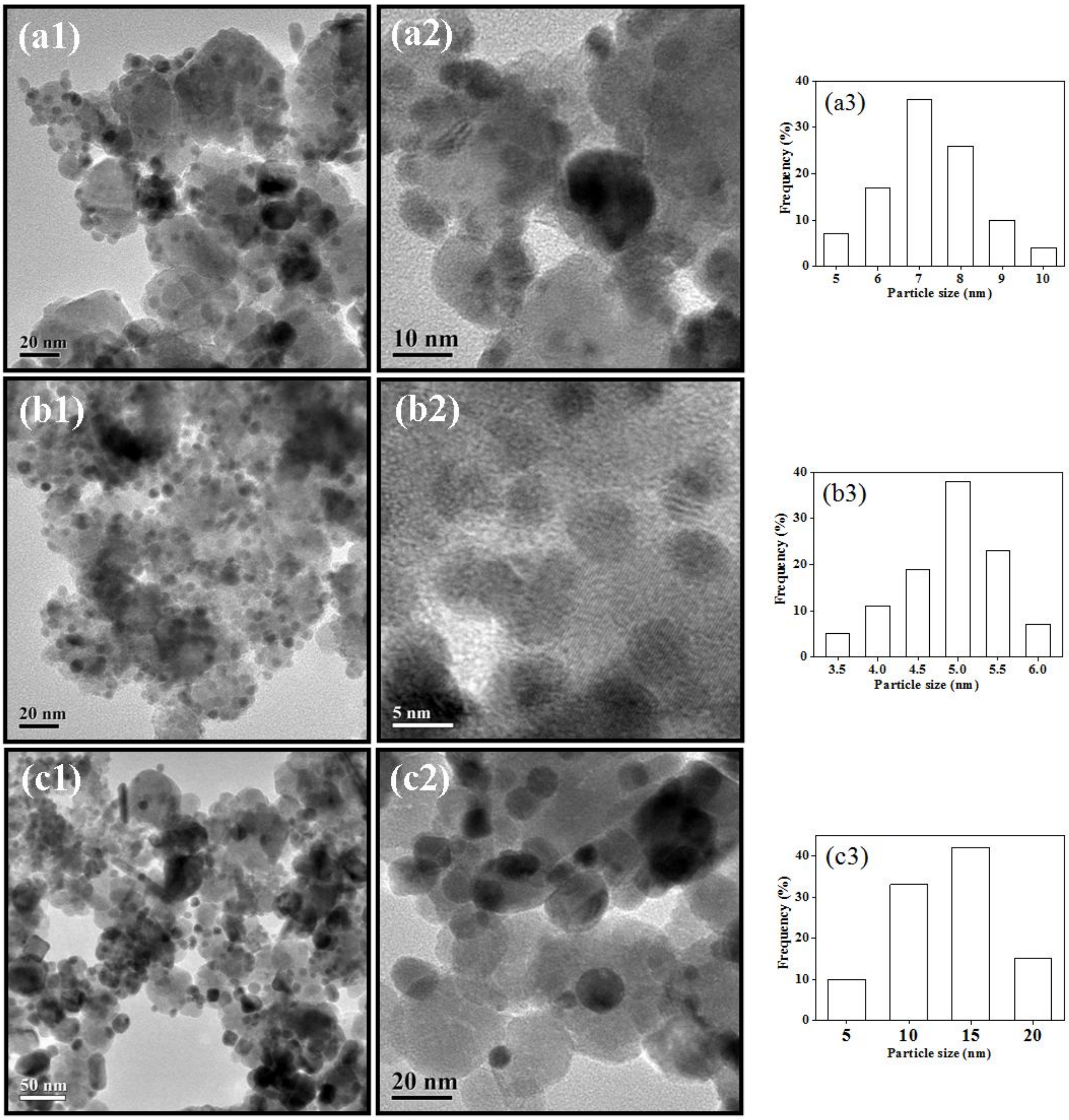
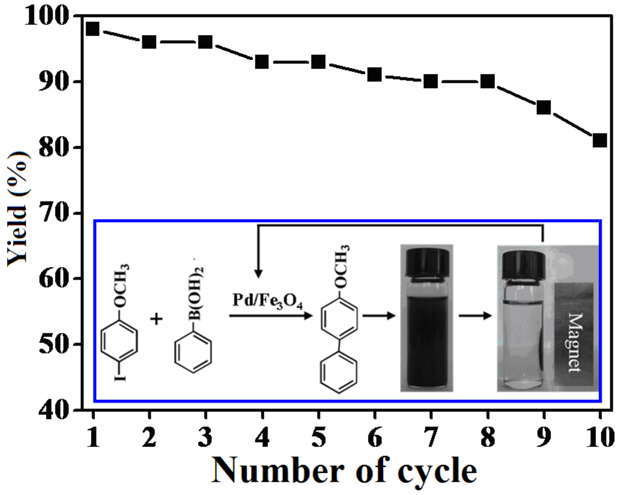

(a1)
20 nm
(a2)
10 nm
(a3)
Frequency (%)
0
10
20
30
40
5
6
7
8
9
10
Particle size (nm)
(b1)
20 nm
(b2)
5 nm
(b3)
Frequency (%)
0
10
20
30
40
3.5
4.0
4.5
5.0
5.5
6.0
Particle size (nm)
(c1)
50 nm
(c2)
20 nm
(c3)
Frequency (%)
0
10
20
30
40
5
10
15
20
Particle size (nm)

Fig. 7.


100
90
80
70
60
50
40
Yield (%)
1
2
3
4
5
6
7
8
9
10
Number of cycle
OCH3
I
+
B(OH)2
Pd/Fe3O4
OCH3
Magnet