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Palladium nanoparticles supported on core-shell and yolk-shell Fe_3O_4 @nitrogen doped carbon cubes as a highly efficient, magnetically separable catalyst for the reduction of nitroarenes and the oxidation of alcohols



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ABSTRACT

The preparation of palladium nanoparticles (Pd NPs) supported on Fe₃O₄@nitrogen doped carbon (*N*-C) core-shell (C-S) and yolk–shell (Y-S) nanostructures is reported. The Fe₃O₄@*N*-C@Pd C-S nanostructures were synthesized by two different methods. The first method included two steps: (*i*) the annealing treatment of the Fe₂O₃@polydopamine (PDA) under a gas mixture of Ar/H₂ flow and (*ii*) the decorating Pd NPs on the surface of annealed structures by sodium borohydride as a reducing reagent. The second method, the *in-situ* reduction of Fe₂O₃ and Pd²⁺ in the structure of Fe₂O₃@PDA@Pd²⁺ by annealing treatment under H₂ flow as a reducing reagent led to Fe₃O₄@*N*-C@Pd C-S nanostructure. Additionally, the Y-S nanostructures were synthesized by using a HCl solution as an effective etching reagent to the partially etch the Fe₃O₄. Four types of Pd-based catalysts were tested in the selective reduction of *p*-nitrophenol (*p*-NP) to *p*-aminophenol (*p*-AP). Different catalytic activities were obtained through these catalysts. Furthermore, the reduction of nitroarenes and the oxidation of benzylic alcohols were also studies.

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1. Introduction

Tailoring the morphology of inorganic nanocrystal's have long been an attractive field of nanoscience and technology [1]. In particular, magnetic NPs with unique size- and shape-dependent magnetic properties inspired an intensive exploration of their potential applications in the past decade [2,3]. Numerous composites have been extensively investigated for their magnetic nanostructures including pure metals (Fe, Co, and Ni), metal oxides (Fe₃O₄ and γ -Fe₂O₃), MFe₂O₄ (M = Cu, Ni, Mn, and Mg), and metal alloys (FePt and CoPt) [4,5]. Among these magnetic NPs, ferrite (Fe_3O_4) nanoparticles have been widely used experimentally for numerous applications such as in the separation of biomolecules [6], drug and gene targeting [7], tissue engineering [8], magnetic resonance imaging [9], magnetic biosensors [10], biocatalysts [11], wastewater treatment [12], supports in heterogeneous catalysts [13], and as mediators of heat for cancer therapy [14]. The naked NPs tend to aggregate to form larger particles because of Van der Waals forces, resulting in a significant deterioration of their original activity [15]. When metal (0) NPs are supported on the bare surface of ferrite, the involvement of iron in the redox processes causes a significant decrease in catalytic activity [16]. Therefore, the Fe₃O₄ have been preferentially coated with catalytically inert materials such as polymer, carbon or silica to support the transition metal nanoparticles [17].

Dopamine (DA) is a biomolecule that contains catechol and amine functional groups, can self-polymerize at alkaline pH values under the oxygen atmosphere. The conformal and continuous polydopamine (PDA) shell can be spontaneously fixed onto various substrates and nanostructures such as hematite, ferrite, etc. due to the high binding affinity of catechol derivative anchor groups (phenolic hydroxyl) to iron oxide just through immersing the particles into the dopamine solution at room temperature [18]. It is also an excellent carbon source that can yield thin *N*-doped carbon coatings with similar structures and electrical conductivities compared to that of *N*-doped multilayered graphene. Metal salts could be readily adsorbed onto PDA surfaces or absorbed into PDA nanostructures, leading to metal-containing *N*-doped carbon nanostructures by carbonization [19].

Palladium catalysts have been developed, and widespread applications in organic transformations, including oxidation [20], alkylation [21], hydrogenation [22], hydroformylation [23], carbonylation [24], and cross-coupling reactions [25]. As a result of



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the toxicity and high price of Pd, in recent years, interest has grown in the organization and use of recoverable heterogeneous Pd catalysts. For this purpose, different solid materials such as modified silicas [26], zeolites [27] molecular sieves [28], polymers [29], mesoporous materials [30], ionic liquids [31], activated carbon [32], and natural supports [33] have been used as supports for the heterogenization of Pd catalysts.

Core-shell (C-S) and yolk–shell (Y-S) structured materials with tailored physical and chemical properties have shown great potential for a variety of applications including catalysis, drug delivery, energy storage and conversion [34–39]. Based on this introduction and also as part of our ongoing studies on the synthesis of carbon-based nanocomposite catalysts [40], herein, we report the successful synthesis of unique Fe₃O₄@N-C@Pd C-S and Y-S cubes. The proposed synthetic strategy for the preparation of Fe₃O₄@N-C@Pd C-S and Y-S is illustrated in scheme 1. The uniform Fe₂O₃ cubes were coated with PDA to obtained Fe₂O₃@PDA C-S cubes followed by transforming into Fe₃O₄@N-C C-S cubes after an annealing treatment under a gas mixture of Ar/H₂ flow. The Fe₃O₄@N-C Y-S was synthesized by the partial etching of the Fe₃O₄@N-C C-S and Fe₃O₄@N-C C-S structure by using HCl. The Fe₃O₄@N-C@Pd C-S and Fe₃O₄@N-C@Pd Y-S structures were prepared using two different methods.

In the first method, the Fe₃O₄@N-C@Pd C-S (A) and Fe₃O₄@N-C@Pd Y-S (A) structures were obtained from reducing H₂PdCl₄ with NaBH₄ over Fe₃O₄@N-C C-S and Fe₃O₄@N-C Y-S structures, respectively. For the second method, the Fe₃O₄@N-C@Pd C-S (B) was obtained from the *in-situ* reduction of the Fe₂O₃ and Pd²⁺ in the structure of Fe₂O₃@PDA@Pd²⁺ by using H₂ as a reducing reagent. Furthermore, the Fe₃O₄@N-C@Pd Y-S (B) was synthesized *via* the partial etching of the Fe₃O₄ core of Fe₃O₄@N-C@Pd C-S (B) nanostructure using HCl.

2. Experimental

2.1. Instrumentation

Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation (λ = 1.5406 Å). Field emission scanning electron microscopy (FESEM) images were characterized using an electron microscope ZEISS SIGMA VP-500. Transmission electron microscopy (TEM) images were characterized using a transmission microscope Philips CM-30 electron microscope with an accelerating voltage of 150 kV.



Scheme 1. Schematic illustration of the formation procedure of Fe₃O₄@N-C@Pd C-S (A), Fe₃O₄@N-C@Pd Y-S (A), Fe₃O₄@N-C@Pd C-S (B), and Fe₃O₄@N-C@Pd Y-S (B) nanostructures.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific, ESCALAB 250Xi with Mg X-ray resource. The concentrations of iron and palladium were estimated using inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. The nitrogen adsorption-desorption isotherms were collected using a Micromeritics MicroActive for TriStar II Plus 2.03 surface area analyzer with N₂ at 77 K. ¹H NMR spectra were recorded on a Bruker DRX-300 AVANCE spectrometer at 300.13 MHz. UV/Vis spectra were recorded employing an Analytik Jena Specord S600 Diode Array spectrometer. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx[®]-1 capillary column. The magnetic properties of the prepared nanocomposites were measured using a homemade LBKFB model vibrating sample magnetometer (Meghnatis Daghigh Kavir Company, Iran) at r.t.

2.2. Material synthesis

2.2.1. Material

Commercially available iron(iii) chloride hexahydrate (99%), sodium hydroxide (99%), tris(hydroxymethyl)aminomethane hydrochloride (99%), hydrochloric acid (37%), palladium(ii) chloride (99%), potassium carbonate (99%) and sodium borohydride (98%) were purchased from Merck Millipore. 1-Phenylethanol (98%), 4-chlorobenzyl alcohol (99%), 4-methylbenzyl alcohol (98%), 4-nitrobenzyl alcohol (99%), benzyl alcohol (99%), diphenylmethanol (99%), 1-indanol (98%), dopamine hydrochloride (99%), 3-nitrophenol (98%), 4-nitrophenol (99%), 2-nitrophenol (98%), 4-nitroanisole 97%, 4-nitrotoluene (99%) and 1-chloro-4nitrobenzene (99%) were purchased from Sigma-Aldrich. 4-(Dimethylamino)benzyl alcohol (97%) and nitrobenzene (99%) were purchased from TCI. All the chemical reagents were used as received without further purification. Deionized water was used throughout the experiment.

2.2.2. Synthesis of Fe_2O_3 cubes

The Fe₂O₃ cubes were synthesized by a precipitation method. In a typical synthesis, 50 mL of 5.4 M NaOH solution was added to 50 mL of 2.0 M FeCl₃ solution within 5 min under continuous stirring at 75 °C. The resultant Fe(OH)₃ gel was continuously stirred at the same temperature for 5 min and was then aged in a preheated oven at 100 °C for 4 days (in a sealed 250 mL round-bottom flask). The red product was collected and washed three times with deionized water (300 mL) and ethanol (300 mL) and dried at 70 °C overnight [41].

2.2.3. Synthesis of Fe₂O₃@PDA C-S

80 mg of Fe_2O_3 cubes was dispersed into 100 mL of Tris-buffer solution (10 mM) under sonication for 30 min. Afterward, 40 mg of dopamine was slowly added to the mixture solution under sonication for 50 min which was then vigorously stirred for 4 h with magnetic stirring. The resultant product was collected *via* centrifugation and washed with deionized water (200 mL) and ethanol (200 mL) for three times and dried at 70 °C overnight.

2.2.4. Synthesis of Fe₃O₄@N-C C-S

Fe₂O₃@PDA C-S was heated in a furnace at 360 °C for 5 h under a continuous flow of Ar–H₂ (9:1) with a heating rate of 3 °C min⁻¹ to transform into the Fe₃O₄@N-C C-S.

2.2.5. Synthesis of Fe₃O₄@N-C Y-S

The annealed Fe₃O₄@N-C C-S was stirred in 100 mL HCl (2 M) solution for 2 h. The Fe₃O₄@N-C Y-S was collected by external magnetic field and washed with water (200 mL) and ethanol (200 mL) and dried at 70 °C overnight.

2.2.6. Synthesis of Fe₃O₄@N-C@Pd C-S (A) and Fe₃O₄@N-C@Pd Y-S (A)

The 100 mg of Fe₃O₄@N-C C-S or Fe₃O₄@N-C Y-S was dispersed in 100 mL of deionized water by sonication. The H₂PdCl₄ solution (prepared by dissolving 8.3 mg of PdCl₂ in 6.8 μ L of HCl and bring volume to 5 mL) was added dropwise over 10 min. After stirring for 1 h, the NaBH₄ solution (17.70 mg dissolved in 5 mL of deionized water) was added dropwise over 10 min, and stirred for another 2.5 h. The Fe₃O₄@N-C@Pd was collected by external magnetic field. The structure was washed with water (200 mL) and ethanol (200 mL) and dried at 70 °C overnight.

2.2.7. Synthesis of Fe₃O₄@N-C@Pd C-S (B)

The 100 mg of Fe₂O₃@PDA C-S was dispersed in 100 mL of deionized water by sonication. The H₂PdCl₄ solution (prepared by dissolving 8.3 mg of PdCl₂ in 6.8 μ L of HCl and bring volume to 5 mL) was added dropwise over 10 min followed by vigorously stirring for 3 h at r.t. The resulting material was washed three times with deionized water (200 mL) and ethanol (200 mL) and dried at 70 °C overnight. The prepared Fe₂O₃@PDA@Pd²⁺ was heated in a furnace at 360 °C for 5 h under a continuous flow Ar-H₂ (9:1 as v/v%) with a heating rate of 3 °C min⁻¹ to transform into Fe₃O₄@N-C@Pd C-S (B).

2.2.8. Synthesis of $Fe_3O_4@N-C@Pd Y-S (B)$

The annealed Fe₃O₄@*N*-C@Pd C-S (B) was stirred in 100 mL HCl (2 M) solution for 1 h. The Fe₃O₄@*N*-C Y-S was collected by external magnetic field and washed with water and ethanol and dried at 70 °C overnight.

2.2.9. General procedure for the reduction of p-nitrophenol (p-NP)

The 30 mL of p-NP (0.12 mM) was mixed with 30 mL of a freshly prepared aqueous NaBH₄ solution (0.17 M) to form a yellow solution. The catalyst (1 mol% of Pd) was added to the resulting solution under open air conditions, and the reaction conversion was monitored by UV–Vis spectroscopy.

2.2.10. General procedure for the reduction of nitroarenes

30 mL of 0.12 mM nitroarene (H₂O:EtOH (1:1)) and 30 mL of 0.17 M NaBH₄ (H₂O:EtOH (1:1)) were mixed in a 100 mL roundbottom flask. Then, 2 mg of Fe₃O₄@*N*-C@Pd Y-S (B) (1 mol% of Pd) was added to the resulting solution. The mixture was stirred vigorously at r.t under open air conditions. The progress of the reaction was monitored by thin-layer chromatography (TLC). After the completion of the reaction, the catalyst was separated from the reaction mixture by external magnetic field and washed with ethanol and ethyl acetate. The reaction mixture was concentrated, and the residue was purified by thin-layer chromatography on SiO₂ (*n*-Hexane:Ethyl acetate 8:2 as v:v%). The solvent was removed under vacuum to yield pure product.

2.2.11. General procedure for the oxidation of benzyl alcohols

A mixture of K_2CO_3 (1 mmol) and 2 mg of $Fe_3O_4@N-C@Pd$ Y-S (B) (1 mol% of Pd) in PhCH₃ (5 mL) was prepared in a twonecked rounded bottom flask. A solution of the benzyl alcohol (1 mmol) in PhCH₃ (5 mL) was injected into the solution, and the resulting mixture was stirred at 90 °C under air. The progress of the reaction was monitored by thin-layer chromatography (TLC). After the completion of the reaction, the catalyst was separated from the reaction mixture by external magnetic field and washed with ethanol and ethyl acetate. Then the reaction mixture was concentrated, and then the residue was purified by using thin layer chromatography over SiO₂ (*n*-Hexane:Ethyl acetate 9:1 as v:v%). The solvent was removed under vacuum to yield pure product.

3. Result and discussion

3.1. Characterization

The morphologies of the samples were characterized by transmission electron microscope (TEM) (Fig. 1). Fe₃O₄@*N*-C C-S particles presented a C-S structure with the *N*-C shell thickness of about 30 nm (Fig. 1a and b). After the etching the structure with HCl for 2 h, hollow voids were created in Fe₃O₄@*N*-C Y-S structure (Fig. 1c and d). The surface of Fe₃O₄@*N*-C@Pd C-S (A) and Fe₃O₄@*N*-C@Pd Y-S (A) were decorated with Pd NPs with the size of about 10–15 nm (Fig. 1e–f and g–h). However, aggregated Pd NPs were observed in these samples. The size of the Pd NPs was increased to about 25–30 nm without aggregation in the Fe₃O₄@*N*-C@Pd C-S (B) and Fe₃O₄@*N*-C@Pd Y-S (B) structures (Fig. 1i–1). These results indicated that the particle size of Pd NPs supported by the NaBH₄ reduction method smaller than those supported by the H₂ reduction method. These results are in agreement with a previous report in reduction metal NPs [42].

Additionally, the morphologies of the samples were characterized by the field emission scanning electron microscope (FESEM) (Fig. 2). The cubic structure was maintained after the annealing treatment in all of the samples. Moreover, the aggregated Pd NPs were detected in the prepared samples by NaBH₄ as the reducing reagent (Fig. 2c and d), in accordance with TEM observation.

 N_2 sorption isotherms were used to investigate the surface areas and pore structures of the as-prepared structures. The

Brunauer–Emmett–Teller (BET) surface area, average pore volumes, and average pore sizes are summarized in Table 1. After decorating Pd NPs on the surface of $Fe_3O_4@N$ -C structures, the surface area increases, which the Pd NPs played as the spacer to between structures and thereby preventing their agglomeration [43,44]. The Y-S structures showed a higher BET surface area than the C-S structures, which indicates the formation of hollow void in Y-S structures. As shown in Fig. 3, the N₂ isotherms of all structures displayed a type-IV curve manifesting both micro/mesoporosity, which possibly originates from the gasification of various raw materials during the pyrolysis [45,46].

The XRD patterns of Fe₂O₃, Fe₃O₄@*N*-C C-S, Fe₃O₄@*N*-C Y-S, Fe₃O₄@*N*-C@Pd C-S (A), Fe₃O₄@*N*-C@Pd Y-S (A), Fe₃O₄@*N*-C@Pd C-S (B), and Fe₃O₄@*N*-C@Pd Y-S (B) structures were shown in Fig. S1. The XRD pattern of Fe₂O₃ showed diffraction peaks positions at $2\theta = 24.14^{\circ}$, 33.15° , 35.61° , 49.48° , 54.10° , 62.45° , and 63.99° can be attributed to the (0 1 2), (1 0 4), (1 1 0), (0 2 4), (1 1 6), (2 1 4), and (3 0 0) planes of Fe₂O₃, respectively. The absence of the Fe₂O₃ peaks in the XRD patterns after thermal annealing treatment demonstrated the transformation from Fe₂O₃ to Fe₃O₄ without visible Fe₂O₃ residue. The diffraction peaks for the Pd nanoparticles are not detected. Additionally, the peaks at $2\theta = 44^{\circ}$ and 64° correspond to the stainless-steel sample holder of the powder diffractometer.

The chemical composition of the yolk-shell structures was characterized by X-ray photoelectron spectroscopy (XPS). As shown in



Fig. 1. TEM images of the (a and b) Fe₃O₄@N-C C-S, (c and d) Fe₃O₄@N-C Y-S, (e and f) Fe₃O₄@N-C@Pd C-S (A), (g and h) Fe₃O₄@N-C@Pd Y-S (A), (i and j) Fe₃O₄@N-C@Pd C-S (B), (k and l) Fe₃O₄@N-C Y-S (etching time: 1 h) (B) structures.



Fig. 2. FESEM images of the (a) Fe₃O₄@N-C C-S, (b) Fe₃O₄@N-C Y-S, (c) Fe₃O₄@N-C@Pd C-S (A), (d) Fe₃O₄@N-C@Pd Y-S (A), (e) Fe₃O₄@N-C@Pd C-S (B), and (f) Fe₃O₄@N-C@Pd Y-S (B) structures.

Table 1

N2 adsorption-desorption analysis results.

Structure	Fe ₃ O ₄ @N-C C-S	Fe ₃ O ₄ @N-C Y-S	Fe ₃ O ₄ @N-C@Pd C-S (A)	Fe ₃ O ₄ @N-C@Pd Y-S (A)	Fe ₃ O ₄ @N-C@Pd C-S (B)	Fe ₃ O ₄ @N-C@Pd Y-S (B)
Surface area (m²/g)	7.96	28.57	16.82	27.41	12.75	36.66
Average pore volume (cm³/g)	0.01	0.09	0.05	0.09	0.03	0.13
Average pore size (nm)	6.3	12.8	11.2	12.5	9.5	14.4



Fig. 3. N_2 adsorption-desorption isotherms.

Fig. S2a and e, the peaks corresponding to C 1s, Fe 2p, N 1s, O 1s, Pd 3d were observed in the XPS full spectra. The high-resolution XPS spectra of the N 1s core level, it can be deconvoluted into three component peaks at the binding energy of about 398.3, 399.7,

and 400.5 eV, corresponding to pyridinic N, pyrrolic N, and quaternary N, respectively [47] (Fig. S2b and f). These results indicated that PDA transformed into nitrogen-doped carbon by carbonization process. Moreover, the N atomic content percent on the N-C



Fig. 4. The VSM curve of structures.



Fig. 5. Plot of $ln(C_t/C_0)$ *vs.* reaction time for the reduction of *p*-NP.

Table 2The constant rate k the reduction of *p*-NP.

Structure	Fe ₃ O ₄ @N-C@Pd C-S (A)	Fe ₃ O ₄ @N-C@Pd Y-S (A)	Fe ₃ O ₄ @N-C@Pd C-S (B)	Fe ₃ O ₄ @N-C@Pd Y-S (B)
Rate constant k (min^{-1})	0.0328	0.1618	0.2667	0.9626

Table 3

Optimization of the reaction conditions.^a

	Fe ₃ O ₄ @N-C@Pd Y-S (B) (1 mol% Pd)	
1a	NaBH.	2 a

Entry	Solvent	Catalyst (mol of Pd%)	Time (min)	Yield ^b (%)	TOF (h^{-1})
1	H ₂ O	1	45	72	96
2	EtOH	1	270	79	17.6
3	EtOH:H ₂ O (1:1)	0.5	45	47	125.3
4	EtOH:H ₂ O (1:1)	1	45	81	108
5	EtOH:H ₂ O (1:1)	2	45	84	56
6 ^c	EtOH:H ₂ O (1:1)	-	1440	Trace	-

^a 30 mL of 0.12 mM nitrobenzene (solvent) and 30 mL of 0.17 M NaBH₄ (solvent), r.t, under air.

^b Isolated yields.

^c Without catalyst.

Table 4

The scope of Fe₃O₄@N-C@Pd Y-S (B) catalyzed reduction of nitroarenes.^a

	Ar-N	Fe ₃ O ₄ @N-C@Pd Y-S (B)) (1 mol% Pd)	-NH ₂	
	1 a-	EtOH:H ₂ O (1:1), M g	NaBH ₄ 2	2 a-g	
Entry	Nitroarene	Aniline	Time (min)	Yield ^b (%)	TOF (h^{-1})
1			45	81	108
2			7	98	840.5
3			3	98	1960
4			110	80	43.7
5	$ NO_2$		120	84	42
6			45	85	113.3

^a 30 mL of 0.12 mM nitroarene (H₂O:EtOH (1:1)), 30 mL of 0.17 M NaBH₄ (H₂O:EtOH (1:1)), Fe₃O₄@N-C@Pd Y-S (B) (1 mol% of Pd), r.t., under air.

^b Isolated yields.

shell of Fe₃O₄@N-C@Pd Y-S (A) and Fe₃O₄@N-C@Pd Y-S (B) structures was calculated to be 5.06 and 5.88 at%, respectively, according to XPS. The core level region of Pd 3d for the Fe₃O₄@N-C@Pd Y-S (A) and Fe₃O₄@N-C@Pd Y-S (B) structures included two components. The first one is constituted by two doublets, situated at 335.3 and 340.6 eV, attributable to Pd⁰ that arises due to the reduction of Pd²⁺ by reducing reagents (NaBH₄ (Fig. S2c) and H₂ (Fig. S2g)) and proved that Pd mainly exists as Pd⁰. N-C layer increases the binding energy of Pd atom (in contrast with 3d_{5/2} of metallic Pd 335.0 eV [48]). This result shows a charge transfer between Pd and the carbon support, and agreement with a previous report on the presence of an additional Pd^{δ^+} contribution in the Pd/C catalyst [49]. The second component, located at 337.3 and 342.4 eV, is attributable to the Pd²⁺, which may be ascribed to the oxidation of surface atoms exposed to air. The synergistic action of the Pd and PdO species may play an important role in highly active catalytic species in the oxidation of alcohols [50] and reduction of nitroarenes [51]. The core level regions of Fe 2p showed in Fig. S2c and g, the two peaks at 725.2 and 711.5 eV, are assignable to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ for Fe₃O₄, respectively, that indicated the transformation from Fe₂O₃ to Fe₃O₄ [52].

The magnetic properties of the Fe₃O₄@*N*-C C-S, Fe₃O₄@*N*-C Y-S, Fe₃O₄@*N*-C@Pd C-S (A), Fe₃O₄@*N*-C@Pd C-S (A), Fe₃O₄@*N*-C@Pd C-S (B), and Fe₃O₄@*N*-C@Pd Y-S (B) structures were investigated using a vibrating sample magnetometer (VSM) at room temperature (Fig. 4). The magnetic saturation (Ms) values of the Fe₃O₄@*N*-C C-S, Fe₃O₄@*N*-C Y-S, Fe₃O₄@*N*-C@Pd C-S (A), Fe₃O₄@*N*-C@Pd Y-S (A), Fe₃O₄@*N*-C@Pd C-S (A), Fe₃O₄@*N*-C@Pd C-S (A), Fe₃O₄@*N*-C@Pd C-S (B), and Fe₃O₄@*N*-C@Pd Y-S (B) structures was 67.8, 62.8, 59.2, 44.7, 69.9, and 55.9 emu g⁻¹, respectively. After depositing Pd NPs on the surface of Fe₃O₄@*N*-C C-S and Fe₃O₄@*N*-C Y-S structures, the saturation magnetization decreased. This can be explained by considering the probable reduction in the dipolar–dipolar interactions between the magnetic nanoparticles [53]. Additionally, the lower Ms values of Y-S structures were due to the partial etching Fe₃O₄ core with HCl and the low loading of the iron in these structures. Also, the Fe₃O₄@*N*-C@Pd C-S (B)



Fig. 6. (a) Reusability of the Fe₃O₄@N-C@Pd Y-S (B) nanostructure as the catalyst in ten consecutive cycles for the reduction of *p*-NP (b) TEM image of Fe₃O₄@N-C@Pd Y-S (B) nanostructure after ten cycles.

Table 5

Optimization of the reaction conditions.^a



Entry	Solvent	Temp. (°C)	Base	Yield ^b (%)	Conversion ^b (%)	Carbonyl selectivity ^b (%)	Carboxyl selectivity ^b (%)	TOF (h^{-1})
1	PhCH ₃	90	K ₂ CO ₃	92	96	99	-	9.2
2	DMF	90	K ₂ CO ₃	51	55	99	-	5.1
3	CH ₃ CN	Reflux	K ₂ CO ₃	38	41	99	-	3.8
4	H_2O	90	K ₂ CO ₃	26	38	72	27	2.6
5	PhCH ₃	90	DBU	40	44	99	-	4.0
6	PhCH ₃	90	K ₃ PO ₄	88	94	96	3	8.8
7 ^c	PhCH ₃	90	K ₂ CO ₃	45	51	99	-	9
8 ^d	PhCH ₃	90	K ₂ CO ₃	94	99	99	-	6.3
9	PhCH ₃	80	K ₂ CO ₃	79	82	99	-	7.9
10	PhCH ₃	100	K ₂ CO ₃	92	96	99	-	9.2
11 ^e	PhCH ₃	90	K ₂ CO ₃	25	27	99	-	2.5
12 ^f	PhCH ₃	90	K ₂ CO ₃	32	35	99	-	3.2
13 ^g	PhCH ₃	90	K ₂ CO ₃	59	63	99	-	5.9
14 ^h	PhCH ₃	90	K ₂ CO ₃	-	-	-	-	-

^a Benzyl alcohol (2 mmol), base (1 eq.), solvent (5 mL), *n*-dodecane as an internal standard (0.1 mL) and Fe₃O₄@*N*-C@Pd Y-S (B) (1 mol% of Pd), 10h, air.

^b Determined by GC analysis.

^c Fe₃O₄@N-C@Pd Y-S (B) (0.5 mol% of Pd).

^d Fe₃O₄@N-C@Pd Y-S (B) (1.5 mol% of Pd).

^e Fe₃O₄@*N*-C@Pd C-S (A) (1 mol% of Pd).

^f $Fe_3O_4@N-C@Pd Y-S (A) (1 mol\% of Pd).$

 $^{g}\,$ Fe₃O₄@N-C@Pd C-S (B) (1 mol% of Pd).

^h Without catalyst.

showed higher Ms values than the $Fe_3O_4@N-C@Pd$ C-S (A) that could be related to the low carbon content in $Fe_3O_4@N-C@Pd$ C-S (B) structures [54].

3.2. The catalytic activity of $Fe_3O_4@N-C@Pd$ C-S and $Fe_3O_4@N-C@Pd$ Y-S structures on the reduction of nitroarenes

The reduction of p-NP by NaBH₄ to investigate the catalytic performance. As shown in Fig. S6a, the p-NP solution exhibited a strong UV absorption band at 317 nm which shifts to 400 nm after the addition of freshly prepared NaBH₄ solution, due to the formation of p-nitrophenolate anion under alkaline conditions. On the addition of the catalyst, the intensity of the characteristic absorption peak of *p*-nitrophenolate ion decreased, and the feature absorption of *p*-AP at around 300 nm also appears (Fig. S6b–e). As shown in Fig. 5, a linear relationship between $\ln(C_t/C_0)$ vs. reaction time was obtained in the reduction catalyzed, which indicates that the reduction follows pseudo-first order reaction kinetics. The constant rates k for the reduction of *p*-NP catalyzed by using 1.0 mol% Pd loading of Fe₃O₄@N-C@Pd C-S (A), Fe₃O₄@N-C@Pd Y-S (A), Fe₃O₄@N-C@Pd C-S (B), and Fe₃O₄@N-C@Pd Y-S (B) nanostructures are 0.0328, 0.1618, 0.2667, and 0.9626 min⁻¹, respectively (Table 2). The higher rate constants in Y-S structures than the C-S structures could be due to the nanorattle structure

Fe₃O₄@N-C@Pd Y-S (B) (1 mol% Pd)

0

Table 6

Aerobic oxidation of alcohols catalyzed by Fe₃O₄@N-C@Pd Y-S (B) nanostructure.^a

OH

		Ar´`R 3a-h	PhCH ₃ , K ₂ CO ₃ , 90)°C Ar∽	`R 4a-h	
Entry	Alcohol	Aldehyde	Yield ^b (%)	Conversion ^c (%)	Carbonyl selectivity ^c (%)	TOF (h^{-1})
1	OH 3a	4a	92	96	99	9.2
2	OH 3b		87	93	99	8.7
3	O N 3c OH		74	79	>97	7.4
4	O ₂ N OH 3d		90	94	>99	9.0
5	Me OH		61	66	>99	6.1
6 ^d	Me ₂ N OH	Me₂N ∽ O	89	95	>99	4.5
7 ^d	3f OH		94	98	97	4.7
8 ^d	OH	O O	92	96	>99	4.6
	l 3h	4h				

^a Reaction conditions: alcohol (2 mmol), K₂CO₃ (2 mmol), PhCH₃ (5mL), 10 h, 90 °C, air.

^b Isolated yield.

^c Based on GC analysis.

^d 20 h.

characteristics that indicated the large free reaction voids inside the Y-S structures [40]. Also, the results indicated that the catalytic activity of catalysts prepared by the method B higher than those prepared by the method A. On the other hand, the activity of the Pd catalysts generally increased with an increase in the Pd particle size. A similar particle size effect has been reported for the hydrogenation of 1-nitrohexane over Pd/mesoporous silica catalysts [55] as well as for the hydrogenation of 2,4-dinitrotoluene (2,4-DNT) over Pd/C catalysts [56]. It could be suggested that a different adsorption geometry of the substrate on particles of different size could influence the rate and the distribution products [56]. Another explanation for this size effect, it may be related to the increase of the hydrogen adsorption with the Pd particle sizes [55].

To optimize the reaction conditions, a series of experiments with different parameters were performed for the reduction of nitrobenzene. The effect of the solvent was investigated, and results showed in Table 3. It can be seen that, using H_2O as the solvent, the yield is just 72% in 45 min (Table 3, entry 1), partially due to the insolubility of the nitrobenzene in H_2O . When using EtOH as the reaction solvent, the NaBH₄ cannot be completely dissolved

and the yield is 79% in 270 min (Table 3, entry 2). It can be seen that the mixed solvent $EtOH:H_2O$ (v:v = 1:1) was chosen as the best solvent in the reduction of nitrobenzene (Table 3, entry 4). The reason is that the mixed solvent of $EtOH:H_2O$ (v:v = 1:1) can make both the nitrobenzene and the NaBH₄ completely dissolved. The effect of the amount of catalyst was also investigated under the optimum reaction conditions (Table 3, entries 3–5). When the amount of catalyst was increased from 0.5 to 1 and 2 mol%, the yield increased from 47% to 81% and 84%, respectively. The concentration of the catalyst of 1 mol% was sufficient for the reaction to occur (Table 3, entry 4). Probably, the agglomeration of catalyst particles occurred for high catalyst amount, which led to decreased the number active catalyst sites (Table 3, entry 5). NaBH₄ was not able to reduce nitrobenzene even after one day without catalyst (Table 3, entry 6).

Next, the scope of the well-defined catalyst $Fe_3O_4@N-C@Pd$ Y-S (B) was examined in the reduction of various nitroarenes possessing both electron-withdrawing and donating substituents. 2- and 3-nitrophenols gave good yields of anilines in a very short amount of time (Table 4, entries 2–3). Nitroarenes possessing

Table 7		
The reusability of the Fe ₃ O ₄ @N-C@Pd Y-S (B)) nanostructure in aerobic oxidation	n of benzyl alcohol. ^a

Reaction cycle	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Yield ^b (%)	92	92	90	89	86	84	83	80	80	76

^a Benzyl alcohol (7 mmol), K₂CO₃ (7 mmol), PhCH₃ (20 mL), n-dodecane (0.2 mL) and Fe₃O₄@N-C@Pd Y-S (B) nanostructure (1 mol% of Pd), 10 h, 90 °C, air.

^b Yield determined by GC analysis.

electron-donating groups such as *p*-OMe and *p*-Me and electronwithdrawing group such as *p*-Cl also afforded good yields of the corresponding aniline products (Table 4, entries 4–6).

Reusability is an important characteristic of the heterogeneous catalysis which should be examined in catalytic reactions. The recovery and reuse of the Fe₃O₄@N-C@Pd Y-S (B) nanostructure were examined. Therefore, we performed a reusability test for the Fe₃O₄@N-C@Pd Y-S (B) catalyst in the reduction of p-NP. After the first run of the reduction, the catalyst could be efficiently and easily recovered by external magnetic field and then washed with H₂O and EtOH, and dried in air to reuse for the next run. The Fe₃O₄@N-C@Pd Y-S (B) nanostructure was recycled up to ten times (Fig. 6a). The catalyst shows high catalytic activity with the k of 0.9554 min⁻¹ after 10th cycle, indicating the excellent reusability of the catalyst. TEM image of the recovered catalyst in the 10th cycle shows the retained Y-S structure and the absence the aggregation of Pd NPs. (Fig. 6b). The heterogeneous nature of the catalyst was tested by ICP analysis. The result indicated that the leaching of 1.3% of palladium after the ten cycles. Additionally, to ensure that the reaction was truly heterogeneous, a filtration test (~50% conversion of *p*-NP) was performed. The filtrates were transferred to another flask. Upon further heating of the catalyst-free solution for 100 min, no considerable progress (UV analysis) was observed. These results confirmed the heterogeneous character of the catalytically active species in this reaction.

A comparison was made of the present method with other reported heterogeneous catalytic systems for the reduction of *p*-NP and the results are presented in Table S2. The present method represents a simple, highly effective, and high TOF ($980 h^{-1}$) method for the reduction of *p*-NP.

3.3. The catalytic activity of $Fe_3O_4@N-C@Pd Y-S (B)$ structure on the oxidation of benzylic alcohols

Aerobic oxidation of benzyl alcohol was selected as a model reaction, and the effects of solvent, base, temperature, and amount of catalyst were studied. The various solvents, such as PhCH₃, DMF, CH₃CN, and H₂O were tested (Table 5, entries 1–4). The best result was obtained by using PhCH₃ as a solvent in the model reaction (Table 5, entry 1). Among the various solvents studied, aprotic polar solvents such as CH₃CN and DMF were found to be least effective and provided poor conversion of benzyl alcohol to benzaldehyde (Table 5, entries 2 and 3). This is probably due to the coordination of the solvent molecules to the palladium metal, resulting in poisoning and deactivation of the catalyst. The different bases such as DBU, K₂CO₃, and K₃PO₄, were also screened (Table 5, entries 1 and 5-6). A superior yield obtained when K₂CO₃ was used as the base. To study the effect of the amount of the catalyst, the reactions were carried out at different amounts of Fe₃O₄@N-C@Pd Y-S (B) nanostructure ranging from 0.5 to 1.5 mol% of Pd and 1 mol% loading of Pd was found to be optimal (Table 5, entries 1 and 7–8). Additionally, as for the reaction temperature, 90 °C was optimal (Table 5, entries 1 and 6–7). The other synthesized catalysts (Fe₃O₄@N-C@Pd C-S (A), Fe₃O₄@N-C@Pd Y-S (A) and Fe₃O₄@N-C@Pd C-S (B)) were used (Table 5, entries 11-13). These results indicated that the order of the rate of the catalytic activity was Fe₃O₄@N-C@Pd Y-S (B) > Fe₃O₄@N-C@Pd C-S (B) > Fe₃O₄@N-C@Pd Y-S (A) > Fe₃O₄@N-C@Pd C-S (A). The activity of the Pd catalysts generally increased with an increase in the Pd particle size. A similar particle size effect has been reported for the oxidation of cinnamyl alcohol over Pd/C catalyst [57]. As shown in Table 5, the reaction can't proceed in the absence of catalyst (Table 5, entry 14).

As evident from Table 6, under optimum reaction conditions, various primary benzylic alcohols possessing both electronwithdrawing (Table 6, entries 2 and 3) and donating substituents (Table 6, entries 4 and 5) are converted to the corresponding aldehydes in good to high yields. Additionally, the secondary benzylic alcohols are converted to the corresponding ketones in good yields (Table 6, entries 6 and 8).

The reusability of Fe₃O₄@*N*-C@Pd Y-S (B) nanostructure was examined in aerobic oxidation of benzyl alcohol. It was found that the recovery can be successfully achieved in ten successive reaction runs (Table 7). We also examined the heterogeneous nature of the catalyst was tested by ICP analysis and a hot filtration test. ICP result of the used Fe₃O₄@*N*-C@Pd Y-S (B) nanostructure indicated the leaching of 3.5% of palladium after the ten cycles. Furthermore, to ensure that the reaction was truly heterogeneous, a hot filtration test (~50% conversion of benzyl alcohol) was performed. The hot filtrates were then transferred to another flask containing PhCH₃ (3 mL) at 90 °C. Upon further heating of the catalyst-free solution for 12 h, no significant conversion (~1% by GC analysis) was observed. These results confirmed the heterogeneous characteristic of the catalytically active species in this reaction.

4. Conclusions

In this study we demonstrated for the first time the preparation of Pd NPs supported on Fe₃O₄@N-C C-S and Y-S nanostructures. The Fe₃O₄@N-C@Pd C-S nanostructures were synthesized by two different methods. The first method includes two steps: (i) the annealing treatment of the Fe₂O₃@PDA under a gas mixture of Ar/H₂ flow and (*ii*) the decorating Pd NPs on the surface of annealed structures by sodium borohydride as a reducing reagent that led to the formation of the aggregate and small size of Pd NPs on the surface of the Fe₃O₄@N-C structure. The second method, the *in-situ* reduction of Fe₂O₃ and Pd²⁺ in the Fe₂O₃@PDA@Pd²⁺ structure by annealing treatment under H₂ flow as a reducing reagent led to Fe₃O₄@N-C C-S nanostructure, which results to the no aggregate and medium size of Pd NPs on the surface of C-S nanostructure. Additionally, the HCl solution is used as an effective etching reagent to the partially etch the Fe₃O₄ core to obtain Y-S nanostructures. The C-S and Y-S nanostructures were used as the magnetic heterogeneous catalyst in the reduction of nitroarenes and the oxidation of benzylic alcohols. The catalysts having large Pd particles exhibited high activities. It could be suggested that a different adsorption geometry of the substrate on particles of different size could influence the rate and the distribution products. Another explanation for this size effect, it may be related to the increase of the hydrogen adsorption with the Pd particle sizes. Additionally, the yolk-shell structures showed high catalytic activity than the core-shell structures. This might be to the nanorattle structure characteristics that indicated the large free reaction voids inside the Y-S structures. The heterogeneous nature of the catalyst was proved using ICP analysis and a hot filtration test.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.05.003.

S.K. Movahed et al./Journal of Catalysis 364 (2018) 69-79

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