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# Synthesis and characterization of magnetically nanoparticles of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> as a novel and reusable catalyst for convenient reduction of nitro compounds with glycerol

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**Abstract** The present paper describes the synthesis of magnetically nanoparticles of zirconocene-modified magnetic,  $Fe_3O_4@APTMS@ZrCp_2$ , as a new generation in heterogeneous and reusable type nanocatalysts. The prepared zirconocene nanocomposite was characterized using FT-IR, SEM, XRD, EDX, AGFM, ICP–OES, TGA and BET analyses. The core–shell nanocatalyst exhibited an excellent catalytic activity towards glycerol reduction of various nitro compounds to the corresponding amines. All reactions were carried out in H<sub>2</sub>O at room temperature (40–90 min) to afford amines in high to excellent yields. Reusability of the core–shell zirconocene was examined 5 times without significant loss of its catalytic activity.

**Keywords** Amines  $\cdot Cp_2ZrCl_2 \cdot Fe_3O_4 \cdot Glycerol \cdot Nitro compounds \cdot Reduction$ 

## Introduction

Reduction of nitro compounds is one of the most useful and straightforward methods for the preparation of amines. The amine synthesis is important from academic and industrial points of view. They are used frequently in the preparation of dyes, biologically active compounds, pharmaceuticals, rubber chemicals and photographic/agricultural chemicals [1–4]. During the last decades, numerous methods as well as reducing agents have been documented for reduction of nitro compounds to amines [5–8]. In this context and among

Behzad Zeynizadeh bzeynizadeh@gmail.com reducing agents such as  $NaBH_4$ ,  $H_2$ , hydrazine, formic acid (formats), alcohols and the others, reduction with hydrogen transferring agents is safer, highly selective and eco-friendly [9].

Recently, glycerol because of the significant physical and chemical properties such as polarity, low toxicity, high boiling point, biodegradability, non-flammability [10] and ability to dissolve inorganic salts, acids, bases and metal complexes as well as organic compounds is considered as an important biomass derived material [11, 12]. It is easily prepared as a by-product of biodiesel manufactures [13] and also is derived from sugars or sugar alcohols [14]. Nowadays, using glycerol as a green hydrogen transferring agent has attracted a great deal of attention in organic synthesis [15–18].

There is also an ever increasing interest in synthesis, characterization, surface modification and application of magnetically nanoparticles (MNPs). They have large surface area, and are easily prepared or functionalized. Simple separation and the frequent reusability as well as low toxicity are the prominent characteristics of magnetically nanoparticles [19–21]. In addition, MNPs because of many hydroxyl groups on their surfaces have emerged as efficient alternative supports for deposition of homogeneous catalysts [22].

In line with the outlined strategies and continuation of our research program directed to the preparation and application of deposited copper hydroxide on magnetite [23], herein, we wish to report the synthesis and characterization of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> as a novel, heterogeneous and reusable magnetically nanoparticles for the efficient reduction of aromatic and aliphatic nitro compounds to the corresponding amines with glycerol in H<sub>2</sub>O.

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## **Results and discussion**

# Synthesis and characterization of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ ZrCp<sub>2</sub> MNPs

Synthesis of zirconocene-modified magnetite was carried out in a three-steps procedure: (a) preparation of nanomagnetite  $Fe_3O_4$  by a chemical co-precipitation of  $FeCl_3 \cdot 6H_2O$ and  $FeCl_2 \cdot 4H_2O$  in aqueous ammonia, (b) coating of  $Fe_3O_4$ NPs with 3-aminopropyltrimethoxysilane (APTMS) and (c) deposition of  $Cp_2ZrCl_2$  on  $Fe_3O_4@APTMS$  to afford  $Fe_3O_4@APTMS@ZrCp_2$  nanoparticles (Scheme 1).

The prepared core-shell nanocomposite was then characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), alternating gradient force magnetometry (AGFM), inductively coupled plasma-optical emission spectrometry (ICP–OES), thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) analyses.

Figure 1 shows the recorded FT-IR spectra for (a)  $Fe_3O_4$ , (b)  $Fe_3O_4$ @APTMS and (c)  $Fe_3O_4$ @APTMS@ZrCp<sub>2</sub> MNPs. The spectrum for bare  $Fe_3O_4$  shows the bands of 440 and 590 cm<sup>-1</sup> for stretching vibration of FeO, and a broad band at 3370 cm<sup>-1</sup> for surface OH groups. In the case of  $Fe_3O_4$ @APTMS, the peaks at 1040, 3450 and 2900 cm<sup>-1</sup> are attributed to stretching vibration of SiO, NH and CH (aliphatic), respectively. In addition, the peak at 1616 cm<sup>-1</sup> (spectrum c) belongs to C=C stretching vibration of Cp groups. All these indicated that



Scheme 1 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs



Fig. 1 FT-IR spectrum of a Fe<sub>3</sub>O<sub>4</sub> b Fe<sub>3</sub>O<sub>4</sub>@APTMS and c Fe<sub>3</sub>O<sub>4</sub>@ APTMS@ZrCp<sub>2</sub> MNPs

silylpropylamine and  $Cp_2Zr$  fragments were successfully incorporated into the core of magnetite.

The morphology and size distribution of zirconocenemodified magnetite was determined using scanning electron microscopy (SEM). Figure 2 represents SEM images of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@APTMS and Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs. Image C shows that the zirconocene nanocomposite was made up uniform nanometer particles with diameter of 5–10 nm.

Elemental (Zr, Fe, N, Si, Cl, C and O) composition of  $Fe_3O_4@APTMS@ZrCp_2$  MNPs was also determined by energy dispersive X-ray spectroscopy (EDX). Figure 3 shows that all the titled elements are exited in the final nanocomposite. Through the inductively coupled plasmaoptical emission spectrometry (ICP–OES), the amounts of Fe and Zr in Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs were determined 52.75 and 3.72%, respectively.

X-ray diffraction patterns of  $Fe_3O_4$  and  $Fe_3O_4$ @ APTMS@ZrCp<sub>2</sub> MNPs are also shown in Fig. 4. In XRD pattern of  $Fe_3O_4$ , the peaks at 30.2°, 35.5°, 43.3°, 53.7°, 57.2° and 62.9° are attributed to (220), (311), (400), (422), (511) and (440) crystal planes of cubic spinal structure in pure  $Fe_3O_4$  (JCPDS: 65-3107) [24, 25]. In XRD of  $Fe_3O_4$ @APTMS@ZrCp<sub>2</sub>, though the peaks at 35.1°, 41.5°, 50.9°, 63.2°, 67.5° and 74.6° represent the characteristic pattern of XRD in pure  $Fe_3O_4$ , however, differences about 4.9°, 6°, 7.6°, 9.5°, 10.3° and 11.7° (2 $\theta$  angle) in respect to pure  $Fe_3O_4$  are observed. It was also reported that the pattern of XRD in pure Zr has two characteristic peaks at 35.1° and 36.5° (2 $\theta$  angle) [26]. These peaks in XRD of zirconocene-modified magnetite were overlapped with the peaks of  $Fe_3O_4$ . The core–shell concept for the prepared nanocomposite is also demonstrated by TGA analysis. Thermogravimetric analysis for (a)  $Fe_3O_4$ , (b)  $Fe_3O_4$ @APTMS and (c)  $Fe_3O_4$ @ APTMS@ZrCp<sub>2</sub> MNPs shows two weight-losing stages via heating of nanocomposites (Fig. 5). The first stage appears at 25–200 °C showing the elimination of crystallization water or residual solvent, and the second stage (200–800 °C) represents releasing of silylpropylamine and zirconocene groups.

Physical parameters of nitrogen absorption–desorption isotherms such as BET surface area ( $S_{BET}$ ) and total pore volumes ( $V_{total}$ ) for Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs are summarized in Table 1. A comparison shows that the specific surface area ( $S_{BET}$ ) of zirconocene nanocomposite in respect to Fe<sub>3</sub>O<sub>4</sub> was deceased 8.3%. These results show that the shell capacity of APTMS@ZrCp<sub>2</sub> for absorption of N<sub>2</sub> gas is lower than Fe<sub>3</sub>O<sub>4</sub>. The plots for N<sub>2</sub> absorption–desorption of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@APTMS@ ZrCp<sub>2</sub> MNPs are shown in Fig. 6.

Magnetically nanoparticles are more desirable for magnetic separation. Magnetic property of  $Fe_3O_4$  and  $Fe_3O_4$ @ APTMS@ZrCp<sub>2</sub> NPs was investigated at room temperature by alternating gradient force magnetometer (AGFM). Ms value (saturation magnetization) for  $Fe_3O_4$  and  $Fe_3O_4$ @ APTMS@ZrCp<sub>2</sub> was 0.13 and 0.095 a.u., respectively. Figure 7 shows that though Ms value for  $Fe_3O_4$ @APTMS@ ZrCp<sub>2</sub> in respect to  $Fe_3O_4$  was decreased 27%, however, it was still large enough for magnetic separation.

# Reduction of nitro compounds with glycerol/Fe<sub>3</sub>O<sub>4</sub>@ APTMS@ZrCp<sub>2</sub> system

After synthesis and characterization of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ ZrCp<sub>2</sub> MNPs, the catalytic activity of the prepared nanocomposite on reducing capability of glycerol towards reduction of nitroarenes was investigated. In order to optimize reaction conditions, reduction of nitrobenzene with glycerol as a model reaction was examined under different reaction conditions. The illustrated results in Table 2 show that reduction of nitrobenzene with glycerol in the absence of  $Fe_3O_4@$ APTMS@ZrCp<sub>2</sub> MNPs was not efficient (entry 1). However, the addition of little amounts of zirconocene-modified magnetite dramatically accelerated the rate of reduction (entries 2–11). Performing of the titled reaction in various protic and aprotic solvents exhibited that H<sub>2</sub>O was the best solvent of choice and using the molar equivalents of 1:2 for PhNO<sub>2</sub>:glycerol in the presence of 7 mg Fe<sub>3</sub>O<sub>4</sub>@APTMS@ ZrCp<sub>2</sub> MNPs is the requirements to complete reduction of nitrobenzene. Subsequently, aniline was obtained as a sole product within 40 min at room temperature (Scheme 2) (entry 3). To discover the potentiality of  $Fe_3O_4$ @APTMS@ ZrCp<sub>2</sub> MNPs versus ZrCp<sub>2</sub>Cl<sub>2</sub>, we also examined the promoter activity of ZrCp<sub>2</sub>Cl<sub>2</sub> in glycerol reduction of nitrobenzene in H<sub>2</sub>O (entry 12). Comparison of the results showed Fig. 2 SEM image of a Fe<sub>3</sub>O<sub>4</sub> b Fe<sub>3</sub>O<sub>4</sub>@APTMS and c Fe<sub>3</sub>O<sub>4</sub>@  $\blacktriangleright$  APTMS@ZrCp<sub>2</sub> MNPs

that ziroconocene-modified magnetite exhibited a prominent and reliable activity versus zirconocene dichloride.

The scope and generality of this synthetic protocol was more studied with the reduction of various aromatic nitro compounds at the optimized reaction conditions. The summarized results in Table 3 show that reduction of nitroarenes possessing electron-releasing or withdrawing groups was successfully carried out with 2 molar equivalents of glycerol and 7 mg Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs within 40-90 min at room temperature. It is noteworthy that in the case of nitroarenes having formyl and keto groups, both of nitro and carbonyl moieties were reduced with the same reactivity. Subsequently, higher molar equivalents of glycerol and the nanocomposite were required to complete the reductions. Capability of glycerol/Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> system towards reduction of aliphatic nitro compounds was also examined by reduction of 1-nitrohexane and 2-nitroheptane with 2 molar equivalents of glycerol and 7 mg Fe<sub>3</sub>O<sub>4</sub>@ APTMS@ZrCp<sub>2</sub> MNPs in H<sub>2</sub>O at room temperature. The results showed that as aromatic nitro compounds, this protocol was also efficient and the corresponding aliphatic amines were obtained successfully in 90-92% yields within 45–50 min (Table 2, entries 17 and 18).

The reducing capability of glycerol/Fe<sub>3</sub>O<sub>4</sub>@APTMS@ ZrCp<sub>2</sub> system for reduction of nitro compounds was highlighted by a comparison of the obtained results for current protocol with those of reported for other systems (Table 4). Observation of the results shows that in view points of green reaction conditions, efficiency, availability, the kind and amounts of reducing agent or nanaocatalyst as well as reusability of the catalyst, the present protocol is more efficient or has a comparable potentiality.

# Recycling of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs

For practical purposes, the ability for easy recycling of the catalyst is highly desirable. This issue was investigated by examining the reusability of  $Fe_3O_4@APTMS@ZrCp_2$  MNPs in glycerol reduction of nitrobenzene. After completion of the reaction, nanoparticles of zirconocene-modified magnetite were separated from the reaction mixture by an external magnet and were then washed with EtOAc to remove residual contaminants. The vessel of reaction was again charged with fresh nitrobenzene, glycerol and  $H_2O$  to run the reduction reaction for a second time. The examinations resulted that the core–shell MNPs can be reused 5 times without significant loss of its catalytic activity (Fig. 8).









Fig. 3 EDX spectrum of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs



Fig. 4 XRD spectra of a  $Fe_3O_4$  and b  $Fe_3O_4@APTMS@ZrCp_2$  MNPs

# Conclusions

In this paper, the synthesis of zirconocene-modified magnetite,  $Fe_3O_4@APTMS@ZrCp_2$ , was introduced. The prepared nanocomposite was characterized by FT-IR, SEM,



Fig. 5 TGA spectrum for a Fe<sub>3</sub>O<sub>4</sub>, b Fe<sub>3</sub>O<sub>4</sub>@APTMS and c Fe<sub>3</sub>O<sub>4</sub>@ APTMS@ZrCp<sub>2</sub> MNPs

Table 1 Physical parameters for  $N_2$  absorption–desorption isotherms of  $Fe_3O_4$  and  $Fe_3O_4@APTMS@ZrCp_2\,MNPs$ 

Sample	$S_{\rm BET} ({\rm m^2/g})$	$V_{\text{total}} (\text{cm}^3/\text{g})$
Fe <sub>3</sub> O <sub>4</sub>	88.65	0.3
Fe <sub>3</sub> O <sub>4</sub> @APTMS@ZrCp <sub>2</sub>	81.32	0.26



Fig. 6  $N_2$  absorption–desorption isotherms for  $Fe_3O_4$  and  $Fe_3O_4@APTMS@ZrCp_2\,MNPs$ 

XRD, EDX, AGFM, ICP–OES, TGA and BET analyses. The core–shell zirconocene exhibited an excellent catalytic activity towards glycerol reduction of various aromatic and aliphatic nitro compounds. All reactions were carried out in H<sub>2</sub>O at room temperature within 40–90 min to afford amines



Fig. 7 Magnetization curve for a  $Fe_3O_4$  and b  $Fe_3O_4@APTMS@\ ZrCp_2\ MNPs$ 

in high to excellent yields. The nanocomposite can be reused for 5 times without significant loss of its catalytic activity. Easy separation of the catalyst, remarkable reusability, high yields and mild reaction conditions as well as the benefits of using water as a green solvent are the advantages which make this protocol a prominent choice for reduction of nitro compounds. further purification. <sup>1</sup>H, <sup>13</sup>C NMR and FT-IR spectra were recorded on Bruker Avance 300 MHz and Bruker VRTEX 70 model FT-IR spectrophotometer. The products are known and they were characterized by their <sup>1</sup>H, <sup>13</sup>C NMR and FT-IR spectra followed by a comparison with authentic data. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60  $F_{254}$  aluminum sheet. XRD spectra were obtained by PANalytical X'PertPro diffractometer (Holland) in 40 kV and 30 mA with a CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å). Diffraction patterns were also recorded in  $2\theta$  range ( $10^{\circ}-80^{\circ}$ ). Morphology of particles was determined by measuring SEM images using FESEM-TESCAN MIRA3 instrument. Magnetic properties of the samples were measured on alternating gradient force magnetometer (AGFM, Meghnatis Daghigh Caviar Co., Iran) at room temperature. Thermogravimetric curves were recorded using Shimadzu DTG-60 instrument. The contents of Fe and Zr were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). N2 absorption-desorption was examined on Belsorp-Max instrument (Japan). The specific surface area was determined using Brunauer-Emmett-Teller (BET) method. The pore volume and pore size distribution were determined from desorption profile of isotherms using Barrett-Joyner-Halanda method. Melting points were measured on Electrothermal 9100 apparatus.

## Experimental

## General

All reagents and substrates were purchased from commercial sources in high purity and they were used without



Scheme 2 Reduction of nitrobenzene with glycerol/Fe $_{3}O_{4}@$  APTMS@ZrCp $_{2}$  system

**Table 2** Optimizationexperiments for reduction ofnitrobenzene with glycerol/ $Fe_3O_4@APTMS@ZrCp_2$ system

Entry	Glycerol (mmol)	Fe <sub>3</sub> O <sub>4</sub> @ APTMS@ZrCp <sub>2</sub> (mg)	Solvent (2 mL)	Tempera- ture (°C)	Time (min)	Conversion (%)
1	2	_	H <sub>2</sub> O	rt	360	15
2	2	4	H <sub>2</sub> O	rt	120	80
3	2	7	H <sub>2</sub> O	rt	40	100
4	2	10	H <sub>2</sub> O	rt	40	100
5	2	7	H <sub>2</sub> O	60	35	100
6	1	7	H <sub>2</sub> O	rt	360	65
7	2	7	EtOH	rt	120	70
8	2	7	MeOH	rt	120	70
9	2	7	PEG-400	rt	60	93
10	2	7	THF	rt	120	55
11	2	7	CH <sub>3</sub> CN	rt	120	50
12	2	$7 (ZrCp_2Cl_2)$	H <sub>2</sub> O	rt	360	45

All reactions were carried out with 1 mmol of nitrobenzene

 $\begin{array}{l} \textbf{Table 3} \quad \mbox{Reduction of nitro} \\ \mbox{compounds with glycerol}/ \\ \mbox{Fe}_3O_4@APTMS@ZrCp_2 \\ \mbox{system} \end{array}$ 

Entry	Substrate	Product Time (min)		Yield (%) <sup>a</sup>	Mp/Bp (°C) [27]
1	NO <sub>2</sub>	NH <sub>2</sub>	40	96	184–185/760 mmHg
2	H <sub>2</sub> N NO <sub>2</sub>	H <sub>2</sub> N NH <sub>2</sub>	50	95	138–142
3	NO2 NH2	NH <sub>2</sub> NH <sub>2</sub>	85	85	100–102
4	NH <sub>2</sub>	NH <sub>2</sub>	60	90	64–66
5	H <sub>3</sub> C NO <sub>2</sub>	H <sub>3</sub> C	45	93	43–44
6	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> NH <sub>2</sub>	45	87	203–204/ 760mmHg
7	CH <sub>3</sub> CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> CH <sub>3</sub> NH <sub>2</sub>	90	95	221–222/ 760mmHg
8	Br NO <sub>2</sub>	Br NH <sub>2</sub>	60	98	60–62
9		Cl NH2	55	96	67–70
10	OHC NO2	HOH <sub>2</sub> C	60	88	60–63
11	CHO NO2	CH <sub>2</sub> OH	75	90	81–83
12	CHO NO <sub>2</sub>	CH <sub>2</sub> OH	60	90	92–93
13	OHC NO <sub>2</sub>	HOH <sub>2</sub> C NH <sub>2</sub>	65	78	97–98
14	NO <sub>2</sub>	OH NH2	40	87	70–73
15	NO <sub>2</sub>	OH NH <sub>2</sub>	40	92	66–69
16	NO <sub>2</sub>	NH2 N	65	88	55-58
17	1-Nitrohexane	1-Hexylamine	45	90	131–132/ 760mmHg
18	2-Nitroheptane 2-Aminoheptane		50	92	142–144/ 760mmHg

#### Table 3 (continued)

All reactions were carried out in H<sub>2</sub>O (2 mL) at room temperature <sup>a</sup>Yields refer to isolated pure products

Entry	Substrate	Catalytic system	Reaction conditions	Yield (%)	References
1	Nitrobenzene	Fe <sub>3</sub> O <sub>4</sub> @APTMS@ZrCp <sub>2</sub>	Glycerol, H <sub>2</sub> O, rt, 40 min	96	а
2	Nitrobenzene	Nano Ni	N <sub>2</sub> H <sub>4</sub> , 75 min, rt	99	[28]
3	Nitrobenzene	Nano Co	N <sub>2</sub> H <sub>4</sub> , 300 min, rt	50	[28]
4	p-Nitroaniline	CuBr <sub>2</sub>	NaBH <sub>4</sub> , EtOH, 14 h	84	[29]
5	Nitrobenzene	Co <sub>3</sub> O <sub>4</sub> –NGr/C	HCO <sub>2</sub> H, 15 h, 100 °C	96	[30]
6	p-Nitroaniline	Ni–Boride–Silica	NaBH <sub>4</sub> , MeOH, 10 min	95	[31]
7	<i>m</i> -Nitroaniline	Au/MgO NPs	NaBH <sub>4</sub> , H <sub>2</sub> O, 20 min	98	[32]
8	p-Nitrophenol	rGO@Pd	NaBH <sub>4</sub> , H <sub>2</sub> O-EtOH, rt, 120 min	92	[33]

Table 4 Comparison of reduction of nitroarenes with different reducing systems

<sup>a</sup>Current protocol



Fig. 8 Reusability of  $Fe_3O_4@APTMS@ZrCp_2$  MNPs in glycerol reduction of nitrobenzene

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> NPs

#### Preparation of $Fe_3O_4$ NPs

Magnetically nanoparticles of  $Fe_3O_4$  were prepared by a chemical co-precipitation protocol [23]. In a two-neck round-bottom flask, a solution of  $FeCl_3 \cdot 6H_2O$  (5.838 g, 0.022 mol) and  $FeCl_2 \cdot 4H_2O$  (2.147 g, 0.011 mol) in distilled water (100 mL) was prepared. The solution was stirred vigorously by a mechanical stirrer for 5 min (85 °C) under N<sub>2</sub> atmosphere. To the prepared solution, aqueous NH<sub>3</sub> (25%, 10 mL) was quickly added. Upon the addition, the black nanoparticles of  $Fe_3O_4$  were precipitated. The resulting mixture was continued to stirring for 30 min at 85 °C followed by cooling to the room temperature. The nanoparticles were collected by an external magnet, washed with distilled water and then with a solution of NaCl (0.02 M). Drying under air atmosphere affords the pure nanoparticles of  $Fe_3O_4$  (size: 4–8 nm).

#### Synthesis of $Fe_3O_4$ @APTMS MNPs

Functionalization of magnetite nanoparticles was carried out by refluxing  $Fe_3O_4$  (1.5 g) with 3-aminopropyltrimethoxysilane (APTMS) (2 g) in *n*-hexane (100 mL) under N<sub>2</sub> atmosphere for 24 h. At the end of reaction, the resulting  $Fe_3O_4@APTMS$  MNPs was washed with ethanol and then dried under vacuum at room temperature.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs

The prepared Fe<sub>3</sub>O<sub>4</sub>@APTMS MNPs (1 g) were dispersed in ethanol by ultrasonic bath for 15 min. Subsequently,  $Cp_2ZrCl_2$  (1 g) was then added and the resulting mixture was stirred mechanically at reflux for 10 h. After completion of the reaction, the mixture was cooled to the room temperature. Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> MNPs were collected by an external magnet and washed with acetone and then deionized water. The obtained MNPs were then dried under vacuum for 6 h (size: 5–10 nm).

## A typical procedure for reduction of nitrobenzene with glycerol/Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> system

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a mixture of nitrobenzene (1 mmol, 0.123 g) and  $H_2O$  (2 mL) was prepared. Fe<sub>3</sub>O<sub>4</sub>@APTMS@ZrCp<sub>2</sub> (7 mg) was then added and the resulting mixture was stirred for 3 min. Next, glycerol (2 mmol) was added and the reaction mixture was stirred for 40 min at room temperature. TLC monitored the progress of the reaction (eluent, *n*-hexane/EtOAc: 5/2). After completion of the reaction, the catalyst

was separated by an external magnet and the reaction mixture was extracted with EtOAc ( $2 \times 5$  mL). Drying organic layer over anhydrous Na<sub>2</sub>SO<sub>4</sub> followed by evaporation of the solvent affords pure liquid aniline in 96% yield (0.089 g, Table 3, entry 1).

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