Supporting Information for *Polymer Chemistry* 

# **Electronic Supporting Information**

# Construction of thermo-responsive copolymer stabilized Fe<sub>3</sub>O<sub>4</sub>@CD@PdNP hybrid and its application in catalytic reduction

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## **Experimental section**

#### Synthesis of carbon dots (CDs)

Citric acid (4.0 g) was mixed with Tris-HMA (1.0 g) in a reaction flask, and then the reaction system was heated up to 225 °C for 20 min. The color of resultant molten substance was changed from colorless to orange, indicating the generation of CDs. The mixture was cooled down to 25 °C and added 10.0 mL deionized water to dissolve the solid product, and the obtained solution was neutralized with 1.0 M NaOH. After the final solution was purified by dialysis bag (molecular weight: 1000 Da) for 48 h, the CDs solid sample was obtained from its solution through lyophilization.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (NPs) was synthesized according to previous reported method.<sup>1</sup> Typically, FeCl<sub>3</sub> (1.3 g, 8.0 mmol) and trisodium citrate (0.40 g, 1.36 mmol) were mixed with ethylene glycol (40 mL). The mixture was stirred at 25 °C until the reaction solution became

transparent, and then 2.4 g of sodium acetate anhydrous was added and stirred vigorously for a period of time until it was dissolved completely. The obtained yellow solution was transferred into a Teflon-lined stainless-steel autoclave. After the reaction was performed at 200 °C for 10 h, the autoclave was cooled to 25 °C. The resulted Fe<sub>3</sub>O<sub>4</sub> NPs were washed with deionized water and absolute ethanol respectively, and then dried under vacuum.

## Synthesis of P(NIPAM-co-ETMA)

The copolymer was synthesized using typical RAFT polymerization. ETMA (0.043 g, 0.27 mmol), NIPAM (1.0 g), RAFT agent (44 mg) and AIBN (7.0 mg) were added in THF (5.0 mL) and the reaction system was maintained for 12 h at 70 °C under N<sub>2</sub> atmosphere. The resulted solution was precipitated by petroleum ether three times and the final sample was dried in vacuum for 12 h. <sup>1</sup>H NMR (500 MHz, MeOD, ppm): 7.26-7.91 (b, 1H, CO–NH–CH(CH<sub>3</sub>)<sub>2</sub>),<sup>2</sup> 6.48-6.72 (a, 3H,  $(HO)_2C_6H_3-)$ ,<sup>3</sup> 4.1 (c, 1H, CO–NH–CH(CH<sub>3</sub>)<sub>2</sub>),<sup>4</sup> 2.33-1.52 (e, 7H, CO–CH–CH<sub>2</sub>,  $(HO)_2C_6H_3-$  (CH<sub>2</sub>)<sub>2</sub>, 6.4-6.6 f, 6H, –(CH<sub>3</sub>)<sub>2</sub>), 1.20-0.91 (d, 6H, CO–NH–CH(CH<sub>3</sub>)<sub>2</sub>, g, 25H, –C<sub>12</sub>H<sub>25</sub>).

#### Synthesis of Pd doped Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Pd-Fe<sub>3</sub>O<sub>4</sub>)

Trisodium citrate (0.40 g, 1.36 mmol), FeCl<sub>3</sub> (1.3 g, 8.0 mmol) and PdCl<sub>2</sub> (10.0 mg, 0.06 mmol) were added into ethylene glycol (40 mL), and the mixture was stirred at 25 °C until the solution became transparent, and then anhydrous sodium acetate (2.4 g) was added and stirred vigorously for a period of time until it was dissolved completely. The above obtained solution was then transferred into a Teflon-lined stainless-steel autoclave and sealed to heat for 10 h at 200 °C. Finally, the autoclave was cooled to 25 °C. The obtained Pd doped Fe<sub>3</sub>O<sub>4</sub> NPs were washed with deionized water and absolute ethanol, and then dried under vacuum. The Pd metal content in Pd-Fe<sub>3</sub>O<sub>4</sub> was determined to be about 0.75 wt % via ICP-AES.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (Fe<sub>3</sub>O<sub>4</sub>@CD@PdNPs)

20.0 mg Fe<sub>3</sub>O<sub>4</sub> was dispersed in 20 mL distilled water under ultrasonic treatment, and then PdCl<sub>2</sub> (2.0 mL, 1.3 mg mL<sup>-1</sup>) was added into the Fe<sub>3</sub>O<sub>4</sub> solution. After magnetic stirring for 1 h, 2.0 mL CDs (0.011 g mL<sup>-1</sup>) were added, and the stirring was maintained for 24 h. The above mixture was centrifuged and washed with water and ethanol three times, separately. The final precipitated product was re-dispersed in water for further use in catalytic studies (0.1 mg mL<sup>-1</sup>). The Pd content in PdNPs@Fe<sub>3</sub>O<sub>4</sub> was determined to be about 4.48 wt % via ICP-AES.

## Synthesis of Fe<sub>3</sub>O<sub>4</sub>@PdNPs (Fe<sub>3</sub>O<sub>4</sub>@PdNPs)

40 mg of the as-prepared  $Fe_3O_4$  were dispersed in 40 mL water by ultrasonication, and the formed black suspension was mixed with  $PdCl_2$  (4.0 mL, 2.6 mg mL<sup>-1</sup>). After 1 h under ultrasonic vibration, 6.0 mL fresh prepared NaBH<sub>4</sub> (0.022 g mL<sup>-1</sup>) was added before the mixture was stirred for 24 h to get a homogeneous solution. The sample was collected with a magnet, and washed several times with deionized water and ethanol to remove any unloaded palladium nanoparticles and PdCl<sub>2</sub>, and then dried under vacuum for 12 h. The Pd content in PdNPs@Fe<sub>3</sub>O<sub>4</sub> was determined to be about 3.90 wt % via ICP-AES.



Fig. S1 (a) XPS spectra of a wide scan survey of different samples, (b) high-resolution Fe 2p spectrum of  $PFe_3O_4@PdNPs$ , and (c, d) high-resolution S 2p and Pd 3d spectra of Pd-Fe<sub>3</sub>O<sub>4</sub>.



**Fig. S2** TEM images of (a) CDs (inset: HRTEM image and diameter distribution of individual CD) and (b) Fe<sub>3</sub>O<sub>4</sub> nanoparticles.



**Fig. S3** (a, b) TEM and HRTEM images of Fe<sub>3</sub>O<sub>4</sub>@CD@PdNPs, (c) TEM and (d) HRTEM images of Fe<sub>3</sub>O<sub>4</sub>@PdNPs.



**Fig. S4** (a) SEM image of PFe<sub>3</sub>O<sub>4</sub>@PdNPs, (b) EDX spectrum and (c–h) EDX mappings of C–K; N–K; O–K; S–K; Pd–K and Fe–K.



**Fig. S5** Successive reduction of MB using (a) Pd/C (20  $\mu$ L), (b) CDs (20  $\mu$ L), (c) Fe<sub>3</sub>O<sub>4</sub> (20  $\mu$ L) and (d) ln ( $C_t/C_0$ ) vs. reaction time (*t*) plots for PFe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (20  $\mu$ L), Pd/C (20  $\mu$ L), CDs (20  $\mu$ L) and Fe<sub>3</sub>O<sub>4</sub> (20  $\mu$ L) catalysts (0.1 mg mL<sup>-1</sup> catalyst, 2.0 mL of 0.013 mM MB and 1.0 mL of 0.5 M NaBH<sub>4</sub> were used for the reduction of MB).



**Fig. S6** Successive reduction of MB using (a) Fe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (20  $\mu$ L), (b) Fe<sub>3</sub>O<sub>4</sub>@PdNPs (20  $\mu$ L) and (c) ln ( $C_t/C_0$ ) vs. reaction time (*t*) plots for PFe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (20  $\mu$ L), Fe<sub>3</sub>O<sub>4</sub>@CD@ PdNPs (20  $\mu$ L) and Fe<sub>3</sub>O<sub>4</sub>@PdNPs (20  $\mu$ L) catalysts (0.1mg mL<sup>-1</sup> catalyst, 2.0 mL of 0.013 mM MB and 1.0 mL of 0.5 M NaBH<sub>4</sub> were used for the reduction of MB).



**Fig. S7** Time-dependent UV-vis spectra of the reaction mixtures containing (a) CR, (b) RhB, (c) MO, (d) RZ and (e) R6G aqueous solutions in the presence of NaBH<sub>4</sub> as a reducing agent and  $PFe_3O_4@CD@PdNPs$  as a catalyst. Reaction conditions:  $PFe_3O_4@CD@PdNPs$  (20 µL, 1 mg mL<sup>-1</sup>), 2.0 mL of 0.013 mM CR, RhB, MO, RZ, R6G and 1.0 mL of 0.5 M NaBH<sub>4</sub>.



**Fig. S8** Time-dependent UV-vis spectra of the reaction mixtures containing (a) CR, (b) RhB, (c) MO, (d) RZ, and (e) R6G aqueous solutions in the presence of NaBH<sub>4</sub> as a reducing agent and  $PFe_3O_4@PdNPs$  as a catalyst. Reaction conditions:  $PFe_3O_4@PdNPs$  (20 µL, 0.1mg mL<sup>-1</sup>), 2.0 mL of 0.013 mM CR, RhB, MO, RZ, R6G and 1.0 mL of 0.5 M NaBH<sub>4</sub>.



Fig. S9 UV-vis absorption spectra of *p*-NP solution before and after adding NaBH<sub>4</sub>.



**Fig. S10** Successive UV-vis absorption spectra for the NaBH<sub>4</sub> reduction of (a) *o*-NP, (b) *m*-NP and (c) *p*-NP catalyzed by PFe<sub>3</sub>O<sub>4</sub>@PdNPs. (d) Absorbance ratios versus reaction time (ln ( $C_t/C_0$ ) vs *t*) for the reduction of three isomeric nitrophenols catalyzed by the PFe<sub>3</sub>O<sub>4</sub>@PdNPs catalyst.



**Fig. S11** Successive reduction of *p*-NP using (a) Pd/C (40  $\mu$ L), (b) CDs (40  $\mu$ L), (c) Fe<sub>3</sub>O<sub>4</sub> (40  $\mu$ L), and (d) ln ( $C_t/C_0$ ) vs. reaction time (*t*) plots for PFe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (40  $\mu$ L), Pd/C (40  $\mu$ L) and Fe<sub>3</sub>O<sub>4</sub> (40  $\mu$ L) catalysts (0.1mg mL<sup>-1</sup> catalyst, 2.0 mL of 0.325 mM *p*-NP and 1.0 mL of 0.2 M NaBH<sub>4</sub> were used for the reduction of *p*-NP).



**Fig. S12** Successive reduction of *p*-NP using (a) Fe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (40  $\mu$ L), (b) Fe<sub>3</sub>O<sub>4</sub>@PdNPs (40  $\mu$ L), and (c) ln ( $C_t/C_0$ ) vs. reaction time (*t*) plots for PFe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (40  $\mu$ L), Fe<sub>3</sub>O<sub>4</sub>@CD@PdNPs (40  $\mu$ L), PFe<sub>3</sub>O<sub>4</sub>@PdNPs(40  $\mu$ L) and Fe<sub>3</sub>O<sub>4</sub>@PdNPs (40  $\mu$ L) catalysts (0.1mg mL<sup>-1</sup> catalyst, 2.0 mL of 0.325 mM *p*-NP and 1.0 mL of 0.2 M NaBH<sub>4</sub> were used for the reduction of *p*-NP).

Samples	Time (s) <sup>[a]</sup>	k (min <sup>-1</sup> ) <sup>[b]</sup>	TOF (h <sup>-1</sup> ) <sup>[c]</sup>	References
CN-supported PdNP nanohybrids	43200	1.8	114.6	5
Au/Pdop/SiO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	1200	-	-	6
Ag/MFC	600	0.34	-	7
MgAlCe-LDH@Au	90	1.8	2200	8
Pd NPs (pc-7)	420	1.006	6840	9
PS/Au@PPy/Fe <sub>3</sub> O <sub>4</sub>	1200	0.266	-	10
CDs/Ag@Mg-Al-Ce-LDH	120	1.38	140000	11
MpSi-Pd	4	0.655	106.8	12
PFe <sub>3</sub> O <sub>4</sub> @PdNPs	250	1.04	41640	This work
PFe <sub>3</sub> O <sub>4</sub> @CD@PdNPs	20	9.20	148800	This work

Table S1. Comparison of the ability of various catalysts for catalyzing the reduction of MB.

[a] The reduction time of MB in the presence of catalyst. [b] Apparent rate constant. [c] Turnover frequency.

Samples	Concentration (mM)	<i>k</i> (min <sup>-1</sup> )	<b>TOF</b> ( <b>h</b> <sup>-1</sup> )	References
Ag/MFC	0.2	1.03	-	8
MpSi-Pd	1	0.159	84	12
Au@DHBC NP	0.75	0.333	798	13
Fe <sub>2</sub> O <sub>3</sub> @Au@SiO <sub>2</sub>	5	0.38	138	14
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Ag	0.12	0.665	-	15
Fe <sub>3</sub> O <sub>4</sub> @C@Ag-Au	5	0.22	-	16
Pd/CNs	0.12	0.342	882	17
CMF@PDA/Pd	0.05	-	1.8	18
Ag/HNTs/Fe <sub>3</sub> O <sub>4</sub>	5	0.58	-	19
PFe <sub>3</sub> O <sub>4</sub> @PdNPs	50	0.16	2300	This work
PFe <sub>3</sub> O <sub>4</sub> @CD@PdNPs	50	0.88	18706	This work

Table S2. Comparison of the ability of various catalysts for catalyzing the reduction of *p*-NP.

The turnover frequency (TOF) values of the catalytic reactions were calculated according to

following equation: <sup>20</sup>

$$TOF = \frac{[MB] \times conversion}{[Pd] \times t}$$

were the molar concentration of methylene blue [MB] was fixed to be  $1.04 \times 10^{-5}$  M, and [Pd] was determined by ICP-AES. The conversion at time *t* can be obtained from ln ( $C_t/C_0$ ) vs. reaction time (*t*). The TOF values for all the runs was calculated with the conversion of MB, CR, RhB, MO, RZ, R6G at 30%. The calculation for TOF values of the catalytic reduction of nitrophenols with the conversion of NPs at 100 %.

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