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# $\beta$ -Cyclodextrin-modified hybrid magnetic nanoparticles for catalysis and adsorption

Yan Kang,<sup>a</sup> Lilin Zhou,<sup>a</sup> Xia Li<sup>b</sup> and Jinying Yuan<sup>\*a</sup>

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β-Cyclodextrin-modified hybrid magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD) were synthesized *via* the combination of atom transfer radical polymerization on the surfaces of silica coated iron oxide particles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) and ring-opening reaction of epoxy groups. The feasibility of using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD as separable immobilized catalyst and adsorbent was demonstrated. It was found: (1) the prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD could be used as catalyst in substrate-selective oxidation of alcohols system and the catalytic efficiency was close to pure β-Cyclodextrin of equal quantity; (2) the resulting particles appeared remarkably dominant adsorption capacity compared with poly(glycidyl methacrylate) grafted magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA) in the removal of bisphenol A from aqueous solutions. The results suggest that the novel fabricated nanoparticles could serve as bifunctional materials in catalysis or adsorption and subsequently become potential multifunctional materials.

# Introduction

Magnetic nanoparticles (MNPs) have the advantage of good dispersibility in various solvents, high surface area, and strong magnetic responsivity.<sup>1,2</sup> MNPs have emerged as excellent materials in many fields, such as immobilized catalysts, labeling and sorting of biological species, targeted drug or gene delivery, magnetic resonance imaging, and hyperthermia treatment.<sup>3–15</sup> An important application among them is magnetic separation. Because of strong magnetism, MNPs can be the separable supports for catalyst and adsorbent, which make profound contributions to green chemistry.<sup>16–19</sup> The surfaces of these particles are often modified by capping agents such as polymers, inorganic metals or oxides, and surfactants to make them stable, biocompatible, and suitable for further functionalizations and applications.<sup>20–26</sup>

Cyclodextrins (CDs) are natural products resulting from the action of the enzyme cyclodextrinase on starch.<sup>27</sup> CDs, known as their interior cavities structure composing of cyclic oligosaccharides, are promising for applications in drug carrier systems, nanoreactors, bioactive supramolecular assemblies, molecular recognition, and catalysis.<sup>28–33</sup> The combination of CDs and inorganic nanoparticles has especially attracted increasing attention. These particles can be utilized for sensing, chirose-lective analysis, controlled hydrophobic drug delivery and so on.<sup>34,35</sup> However, there are few reports on multifunctional CDs-containing nanoparticles. In this work, we designed and fabricated the bifunctional  $\beta$ -Cyclodextrin ( $\beta$ -CD)-modified hybrid iron oxide MNPs which could be used in catalysis and adsorption efficiently and repeatedly.

The route for synthesizing the  $\beta$ -CD-modified MNPs is shown in Scheme 1. The iron oxide MNPs (Fe<sub>3</sub>O<sub>4</sub>) were prepared by thermal decomposition methods capping with a layer of oleylamine.36 Sol-gel process was adopted for coating iron oxides with silica to form core-shell structures (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>).<sup>37</sup> Silanes were employed to provide amino functional end groups  $(Fe_3O_4@SiO_2\text{-}NH_2)$  and then 2-bromopropionyl bromide was linked to the surfaces of MNPs to form atom transfer radical polymerization (ATRP) initiators (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Br).<sup>38</sup> Glycidyl methacrylate (GMA) containing an epoxy group was used as a monomer and the poly(glycidyl methacrylate) (PGMA) was synthesized by ATRP on the surfaces of MNPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA). The ethylenediamine modified CDs were appended to MNPs by ring-opening reaction of epoxy groups with amino groups. The resulting nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD, were obtained eventually. Further studies demonstrated the feasibility of using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD as catalyst and adsorbent. The substrate-selective oxidation of alcohols system was investigated utilizing the resulting nanoparticles as the catalyst. Benzyl alcohol and 1-octanol were used as the substrate molecules, which have different behaviors under mild condition using  $\beta$ -cyclodextrins ( $\beta$ -CDs) as catalyst.<sup>39</sup> In addition, the adsorption capacity of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD in the removal of bisphenol A was evaluated. The newly fabricated nanoparticles could serve as multifunctional materials, including the promising applications in catalysis and environmental pollution cleanup.

<sup>&</sup>lt;sup>a</sup>Key Lab of Organic Optoelectronic & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, China. E-mail: yuanjy@mail.tsinghua.edu.cn

<sup>&</sup>lt;sup>b</sup>College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, China



Scheme 1 Synthetic route for β-CD-modified MNPs.

# Experimental

# Materials

β-CD was procured from Kermel (China) and recrystallized from water. Tosyl chloride (TsCl), iron(III) acetylacetonate (Fe(acac)<sub>3</sub>), 1-octadecene, oleylamine, ethyl 2-bromobutyrate (EBB), and N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) were purchased from Acros (USA) and used as received. 3-Aminopropyl-trimethoxysilane (APTS) was obtained from Fluka (Germany). 2-Bromopropionyl bromide was got from Xinxiang Hongchen Technology Co. Ltd (China). GMA was obtained from Tokyo Chemical Industry Co. Ltd (Japan) and distilled in vacuum before use. Methanol, N,N-dimethylformamide (DMF), and toluene were received from Beijing Chemical Reagent Co. Ltd (China) and purified before use. All other reagents of analytical grade were commercially available and used without further purification. Distilled water was utilized throughout the studies.

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

0.71 g (2 mmol) of Fe(acac)<sub>3</sub> was dissolved in a mixture of 10 mL of 1-octadecene and 10 mL of oleylamine. The solution was dehydrated at 110 °C for 1 h. Then the solution was quickly heated to 300 °C and kept at this temperature for 1 h under argon atmosphere. 50 mL of ethanol was poured into the solution after it was cooled down to room temperature. The precipitation was collected by external magnetic field and washed with ethanol 3 times. The product was dried under vacuum overnight.

# Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles

200 mg of  $Fe_3O_4$  was added to a mixture of 80 mL of cyclohexane, 16 mL of 1-hexanol, 20 mL of triton X-100, and 3.4 mL of water. 2 mL of tetraethyl orthosilicate (TEOS) was added and then the solution was stirred for 6 h at room temperature. After 6 h, 2 mL of ammonia was added and the solution was stirred continuously for 24 h. The precipitation was washed with ethanol

3 times and collected by external magnetic field. The product was dried under vacuum overnight.

# Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanoparticles

0.5 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles, 2.5 mL of APTS, and 5 mL of toluene were placed in a dried 25 mL flask. After evacuating and filling with Ar for 3 times, the flask was immersed into an oil bath at 40 °C under Ar atmosphere with stirring for 24 h. The solution was cooled down to room temperature, and then exposed to air. The precipitation was washed with ethanol 3 times and collected using magnet. The product was dried under vacuum overnight.

# Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Br nanoparticles

0.4 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>, 20 mL of toluene, and 8 mL of triethyl amine (TEA) were placed in a dried 100 mL flask. The mixture of 8 mL of toluene and 4 mL of 2-bromopropionyl bromide was dripped slowly into the solution in an ice-water bath with stirring. After further stirring for 4 h, the precipitation was washed by toluene, water and ethanol and collected using a magnet. The product was dried under vacuum overnight.

# Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA nanoparticles

0.3 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Br as initiator, 30 mg (0.15 mmol) of EBB as co-initiator to estimate the molecular weight and polydispersity index (PDI), 24 mL of methanol, 24 mL (0.18 mol) of GMA, 240 mg of CuBr, and 348  $\mu$ L of PMDETA were placed in a dried flask. The flask was immersed into liquid-N<sub>2</sub> bath, followed by evacuating and filling with Ar. The freezing-evacuating-filling process was repeated 3 times. The flask was immersed into an oil bath at 50 °C with stirring for 4 h. Then the solution was cooled and exposed to air. The particles were washed with tetrahydrofuran (THF) and ethanol in turn, collected using a magnet, and dried under vacuum overnight. The THF solution was passed through a neutral alumina column

to eliminate copper salt and then precipitated in the mixture of methanol and water. The polymer was dried at 50 °C in a vacuum oven. Resulting data of PGMA:  $M_{n,gpc} = 13180$ ,  $M_w/M_n = 1.11$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 4.29 (1H, COOCH<sub>2</sub>), 3.80 (1H, COOCH<sub>2</sub>), 3.21 (1H, CH<sub>2</sub>CHOCH<sub>2</sub>), 2.82 (1H, CH<sub>2</sub>CHOCH<sub>2</sub>), 2.62 (1H, CH<sub>2</sub>CHOCH<sub>2</sub>), 1.88 (2H, CH<sub>2</sub>CCH<sub>3</sub>), 1.22 (3H, CH<sub>2</sub>CCH<sub>3</sub>, isotactic), 1.07 (3H, CH<sub>2</sub>CCH<sub>3</sub>, heterotactic), 0.92 (3H, CH<sub>2</sub>-CCH<sub>3</sub>, syndiotactic).

#### Preparation of mono-6-deoxy-6-(p-tolysulfonyl)-β-CD

The mono-6-deoxy-6-(p-tolysulfonyl)-β-CD (mono-6-OTs-β-CD) was prepared according to reference 40. 20 g of  $\beta$ -CD (17.6 mmol) was suspended in 167 mL of water, and 2.19 g of NaOH (54.7 mmol) in 7 mL of water was added dropwise. The suspension turned to be homogeneous. The solution was immersed into an ice-water bath, and then 5.04 g of TsCl (26.4 mmol) in 10 mL of acetonitrile was dripped slowly, causing the formation of white precipitates. After further stirring for 2 h at 25 °C, the suspension was refrigerated overnight at 4 °C. The resulting precipitate was recovered by suction filtration and recrystallized from hot water 3 times. The product was dried under vacuum at 50 °C. Resulting data of mono-6-OTs-β-CD: <sup>1</sup>H NMR (DMSO, δ, ppm): 7.70 (2H, aromatic protons), 7.39 (2H, aromatic protons), 5.47-5.90 (14H, OH-2,3), 4.80 (4H, H-1), 4.71 (3H, H-1), 4.17-4.49 (6H, OH-6), 3.48-3.74 (28H, H-3, 5, 6), 3.18-3.43 (14H, H-2,4, overlaps with HOD), 2.35 (3H, -CH<sub>3</sub>).

#### Preparation of mono-6-deoxy-6-ethylenediamine-β-CDs

The mono-6-deoxy-6-ethylenediamine -β-CD (EDA-β-CD) was synthesized according to the previous report.<sup>41</sup> 5.0 g of mono-6-OTs-β-CD was reacted with an excess amount of ethylenediamine (EDA) at 80 °C for 4 h. After the reaction was completed, the solution was cooled down and most of the unreacted EDA was removed by rotary evaporation. EDA-β-CD was dissolved in water–methanol mixture and precipitated in acetone 3 times. The product was dried at 50 °C for 24 h in a vacuum oven. Resulting data of EDA-β-CD: <sup>1</sup>H NMR (D<sub>2</sub>O, δ, ppm), 4.92 (7H, H-1), 3.67–3.83(28H, H-3,5,6), 3.31–3.51 (14H, H-2,4), 2.89 (2H,  $-CH_2$ NH-β-CD), 2.70 (2H, NH<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>). MALDI-TOF MS *m*/*z*: 1199.27 [M + Na<sup>+</sup>].

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD nanoparticles

0.4 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA and 2.5 g of EDA- $\beta$ -CD were added to 15 mL of DMF. The flask was immersed into an oil bath at 60 °C with stirring for 24 h. The mixture was cooled down, washed in ultrasonic with DMF, water–methanol, and ethanol in turn, and collected using a magnet. The product was dried under vacuum overnight.

#### Oxidation of benzyl alcohol and 1-octanol

0.3 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD (or 0.3 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA, or 32 mg of  $\beta$ -CD) was suspended in 5 mL of water at 50 °C. Then 0.2 mmol of substrate (20 µL of benzyl alcohol or 17 µL of 1-octanol) and 1 mL of 10% NaOCl were added dropwise. After stirring for 24 h, the mixture was washed in ultrasonic with

10 mL of ethyl acetate 3 times and ethanol in turn. The nanoparticles were dried under vacuum overnight. The ethyl acetate solution was concentrated and the crude product was analyzed by GC-MS with ethyl acetate as the solvent.

### Adsorption of bisphenol A

The solution of bisphenol A (0.2 mM) was prepared by dissolving the drug in the mixture of methanol and water (methanol : water, v/v = 1 : 19). Determined amounts of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA or Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD were added into 5 mL of bisphenol A solution respectively. The solutions were stirred for 20 h and then the MNPs were removed by magnet. The residual aqueous solutions were characterized by UV-vis spectra.

#### Characterization

Fourier transform infrared (FT-IR) spectra were recorded on an AVATAR 360 ESP FT-IR spectrometer. The molecular weight and molecular weight distribution of polymer were measured on a gel permeation chromatograph-Wyatt DAWN HELEOS II 18-angle light scattering detector equipped with two columns (MZ-Gel SDplus 10E4 Å, MZ-Gel SDplus 500 Å). THF was utilized as eluent at a flow rate of 1.0 mL min<sup>-1</sup> at 35 °C. <sup>1</sup>H NMR spectra were obtained from a JEOL JNM-ECA300 NMR spectrometer with DMSO- $d_6$ , D<sub>2</sub>O, and CDCl<sub>3</sub> as the solvent. The chemical shifts of protons were relative to tetramethylsilane at  $\delta = 0$  ppm. Thermogravimetric analysis (TGA) was carried out on a TGA 2050 thermogravimetric analyzer with a heating rate of 10 °C min<sup>-1</sup> from 30 °C to 900 °C under a nitrogen atmosphere. Transmission electron microscope (TEM) observations were performed on a JEOL JEM-2010 electron microscopy operated at an acceleration voltage of 120 kV. Vibrating sample magnetometry (VSM) was implemented on a LakeShore 7307 vibrating sample magnetometer. The BET surface area of  $Fe_3O_4$  (aSiO<sub>2</sub> was measured by nitrogen adsorption on a Micromeritics ASAP 2010C instrument. XPS spectra were measured with a PHI-5300 ESCA X-ray photoelectron spectroscopy (XPS) with a monochromatic Al X-ray source, the power is 250 W. Matrix-assisted laser desorption ionization Time-of-flight (MALDI-TOF) mass spectrum was recorded on Bruker Autoflex MALDI-TOF mass spectrometry, using a nitrogen laser (337 nm) and  $\alpha$ -cyano-4-hydroxycinnamic acid (CCA) as matrix. Gas chromatography-mass spectrometry (GC-MS) measurements were carried out on a Shimadzu GCMS-QP2010. UV-vis spectra were recorded by using a Hitachi U-3010 spectrophotometer.

#### **Results and discussion**

#### **Characterization of MNPs**

The monodisperse MNPs  $Fe_3O_4$  were synthesized by thermal decomposition methods with a lay of oleylamine as both reducing agent and stabilizer.<sup>42</sup> TEM image of  $Fe_3O_4$  is shown in Fig. 1a. The diameter of  $Fe_3O_4$  is about 9 nm and the particles are soluble in hexane and other nonpolar organic solvents. Fig. 1b shows the  $Fe_3O_4$ @SiO<sub>2</sub> nanoparticles with a diameter of 60 nm, which were prepared by sol–gel process according to the



Fig. 1 TEM images of (a)  $Fe_3O_4$ , (b)  $Fe_3O_4@SiO_2$ , (c) and (d)  $Fe_3O_4@SiO_2$ -PGMACD.

published procedure.<sup>37</sup> The process relied on the well-known Stöber method,43 in which silica was formed though the hydrolysis and subsequent condensation of TEOS in basic alcohol/ water mixture. The dark point is  $Fe_3O_4$  and the light shell is  $SiO_2$ . Silica can prevent core from unfavorable interactions and aggregation, lead to simple surface functionalization, and make the MNPs more biocompatible and hydrophilic compared to Fe<sub>3</sub>O<sub>4</sub> capping with oleylamine. Silanes were anchored to the surfaces of SiO<sub>2</sub>, which could provide functional end group for further modification. ATRP macroinitiator was synthesized by the reaction of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> with 2-bromopropionyl bromide.<sup>38</sup> ATRP, a kind of controlled/"living" polymerization, is often used to prepare well-defined polymers. Hybrid nanoparticles Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA were prepared by surface-initiated ATRP of monomer GMA. The co-initiator of EBB was utilized to synthesize the PGMA homopolymers to estimate the molecular weight and PDI of the polymers on the surface of the MNPs, which were characterized by GPC and NMR. The molecular weight was 13180, which indicated the degree of polymerization was 93. The PDI was 1.11 and the narrow distribution was the character of controlled polymerization. EDA-B-CD was appended to GMA by ring-opening reaction of epoxy group. Fig. 1c shows the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD nanoparticles, while Fig. 1d is the high resolution TEM image of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD. The undertone outer shell is the PGMACD part with a thickness of 10 nm, which hints of successful modification by organics.

FT-IR could confirm the synthesis of modified MNPs. From Fig. 2a, for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, the peak at 3416 cm<sup>-1</sup> is due to the O–H stretching vibrations of hydroxyl group on the surface of silica; the band at 1092 cm<sup>-1</sup> is related to Si–O–Si stretching vibration; peak at 956 cm<sup>-1</sup> is associated to Si–OH vibration. Fig. 2b shows the FI-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>. The peak at 956 cm<sup>-1</sup> becomes weak which shows most of the hydroxyl groups on the surface of silica were substituted; C–H stretching vibrations of alkyl at 2942 cm<sup>-1</sup> occur; the bands at 1632 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> are the bendings of N–H, characteristic of the presence of NH<sub>2</sub> group. From Fig. 2c, for the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and Br can clarify the successful synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and



Fig. 2 FT-IR spectra of (a)  $Fe_3O_4@SiO_2$ , (b)  $Fe_3O_4@SiO_2-NH_2$ , (c)  $Fe_3O_4@SiO_2-Br$ , (d)  $Fe_3O_4@SiO_2-PGMA$ , (e)  $Fe_3O_4@SiO_2-PGMA$ -CD.

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Br. Fig. 2d is the spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA, in which the prominent peak at 1724 cm<sup>-1</sup> is related to C=O stretching vibration of ester. The results show PGMA is grafted. The FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD shows in Fig. 2e. The characteristic peaks of CDs at 945 cm<sup>-1</sup> and 1157 cm<sup>-1</sup> are visible, but the one at 1028 cm<sup>-1</sup> is overlapped by the Si–O–Si stretching vibrations. The peak at 945 cm<sup>-1</sup> is due to the R-1,4- bond skeleton vibration of CDs, while the peaks at 1028 cm<sup>-1</sup> and 1157 cm<sup>-1</sup> and 1157 cm<sup>-1</sup> are attributable to the antisymmetric glycosidic C–O–C vibration and the coupled C–C/C–O stretching vibration.<sup>35</sup>

The synthesis of MNPs is also substantiated by TGA. The results of TGA are shown in Fig. 3, in which the weight loss is due to the decomposition of organics. The grafting percentage, grafting ratio and grafting density could be calculated by the margin of weight loss percentage. The grafting percentage is defined as the weight percentage of newly grafted component. The grafting density of component a ( $\rho_a$ , chains/nm<sup>2</sup>) is calculated according to eqn (1):

$$\rho_a = \frac{m_a}{M_a} \times \frac{N_A}{S_o} \tag{1}$$

where  $m_a$  is the mass of component a for 1 g of inorganic component which is calculated by TGA data;  $M_a$  is the molar mass of a;  $S_o$  is the specific surface area of magnetite nanoparticles, for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>,  $S_o$  is 45.39 m<sup>2</sup> g<sup>-1</sup> measured by BET. The grafting ratio is defined as  $\rho_{\text{product}}/\rho_{\text{reaction}}$ , where the  $\rho_{\text{product}}$ 

Table 1 XPS results of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Br

Element	Molar ratio <sup><i>a</i></sup>	Molar ratio <sup>b</sup>	
Si	2.4	14	
N	1.0	4.2	
Br	0	1.0	

 $^a$  The element molar ratio of Fe\_3O\_4@SiO\_2-NH\_2.  $^b$  The element molar ratio of Fe\_3O\_4@SiO\_2-Br.



Fig. 3 TGA curves of (a)  $Fe_3O_4@SiO_2$ , (b)  $Fe_3O_4@SiO_2-NH_{2,(c)}$  $Fe_3O_4@SiO_2-Br$ , (d)  $Fe_3O_4@SiO_2-PGMA$ , (e)  $Fe_3O_4@SiO_2-PGMACD$ .

is the grafting density of product and  $\rho_{reactant}$  is the grafting density of reactant. The results are listed in Table 2. From the TGA results, the amount of CD grafted on the MNPs could be calculated as 108.2 mg g<sup>-1</sup>. Based on these data from FT-IR, and TGA, it can be concluded that the resulting product Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-PGMA-CD was prepared affirmatively.

The magnetic property of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD was proved in Fig. 4. The MNPs can be separated quickly and facilely under a magnetic field in 2 min, and redisperse immediately once the outer magnetic field disappeared. VSM curves in Fig. 4 reveal that the samples have low coercivity and no obvious hysteresis, which indicate the MNPs have superparamagnetism. Superparamagnetism means that when the outer magnetic field withdrew, there is no residual magnetism for nanoparticles. If the nanoparticles have residual magnetism, it is very possible for these nanoparticles to aggregate irreversibly. The saturation magnetization of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD is 5.50 emu/g.

#### Catalysis in substrate-selective oxidation of alcohols

The CDs could be utilized as the catalyst in the substrate-selective oxidation of alcohols system, in which NaOCl was the oxidant and water was the only solvent.<sup>39</sup> It was found that the

Table 2 The grafting results calculated by TGA

Samples	TGA/ % <sup>a</sup>	Grafting percentage/ % <sup>b</sup>	Grafting density/ chain · nm <sup>-2</sup> <sup>c</sup>	Grafting ratio/% <sup>d</sup>
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	82.16	_	_	_
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub>	76.10	7.38	18.21	
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Br	69.23	9.03	9.75	53.57
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -PGMA	48.06	30.58	0.44	4.51
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -PGMACD	42.86	10.82	1.37	3.35 <sup>e</sup>

<sup>*a*</sup> The remaining weight percent after TGA. <sup>*b*</sup> The grafting percentage is defined as the weight percentage of newly grafted component. <sup>*c*</sup> Calculated by eqn (1). <sup>*d*</sup> The grafting ratio is defined as  $\rho_{\text{Product}}/\rho_{\text{reaction}}$ . <sup>*e*</sup> The grafting ratio of CD is defined as  $\rho_{\text{CD}}/\rho_{\text{GMA}}$  and  $\rho_{\text{GMA}}$  represents the grafting density of GMA units.



**Fig. 4** Magnetic curves of (a)  $Fe_3O_4@SiO_2$ , (b)  $Fe_3O_4@SiO_2-NH_2$ , (c)  $Fe_3O_4@SiO_2-Br$ , (d)  $Fe_3O_4@SiO_2-PGMACD$ . Inset: the separation and redispersion of  $Fe_3O_4@SiO_2-PGMACD$  in distilled water in the absence (left) and presence (right) of an external magnetic field.

alcohol which had proper size, shape, and hydrophobicity, such as benzylic primary alcohols and pyridinemethanol, would be oxidized in the presence of  $\beta$ -CD and no product was formed without the addition of β-CD. Meanwhile, some alcohols, including benzylic secondary alcohols, 2-adamantanol, and 1-octanol, would not be conversed to aldehyde even if  $\beta$ -CDs were added and the time was enough. The reason was that 2-adamantanol and β-CD could form inclusion complex with a high complex constant which led to a more rigid structure and made the hydroxyl group of 2-adamantanol lack activity, while the long chain aliphatic alcohol and β-CD had very weak interactions and hardly formed an inclusion complex. In addition, the existence of hydrogen bonds between CDs' secondary hydroxyl group and substrates' hydroxyl group impacted the oxidation dramatically. In our work, benzyl alcohol and 1-octanol were considered and the results list in Table 3. Oxidation of benzyl alcohol was compared under different conditions. Only a few benzaldehyde were obtained in the absence of  $\beta$ -CD. The conversion of oxidation using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD (containing 32 mg  $\beta$ -CD) as the catalyst is close to the one using pure  $\beta$ -CD (32 mg). Interestingly, using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA as the catalyst, low reactivity towards oxidation was found, which was due to the load of benzyl alcohol by polymer chains and the hydrogen bond between polymer and substrate's hydroxyl group. As we all know, the catalyst immobilizing on MNPs

Table 3 Oxidation of alcohols under different conditions

Entry	Condition	Substrate	Product	Conv. (%)
1	No CD	Benzyl alcohol	Benzaldehyde	5
2	CD	Benzyl alcohol	Benzaldehyde	89
3	Fe3O4@SiO2-PGMA	Benzyl alcohol	Benzaldehyde	34
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -PGMACD	Benzyl alcohol	Benzaldehyde	84
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -PGMACD	1-Octanol	1-Octanal	Trace



Fig. 5 Recycling and reuse of the nanocatalyst  $Fe_3O_4@SiO_2$ -PGMACD for oxidation.

always have less activity than the free catalyst, but Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD is similar with unmodified CD, which is related to the cooperation of both CDs and polymers. In the meantime, 1-octanol could not be conversed under the condition of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD. The results proved that the resulting nanoparticles could be utilized in the substrate-selective oxidation of alcohols system with obvious catalytic capability.

Recycling of the MNPs was conducted for oxidation of benzyl alcohol. After each cycle,  $Fe_3O_4$ @SiO<sub>2</sub>-PGMACD was washed in ultrasonic with ethyl acetate and ethanol in turn, magnetically separated, dried under vacuum, and reused in the system of oxidation of benzyl alcohol. The separation was easy and high yielding. Fig. 5 illustrates the conversion from benzyl alcohol to benzaldehyde in each cycle. After 5 cycles, the catalyst is still active and efficient. The schematic representation was shown in Scheme 2.

#### Adsorption of bisphenol A

CDs have hydrophilic outer surface and hydrophobic interior cavity, where poorly water-soluble molecules can shelter their



Scheme 2 The schematic representation of the substrate-selective catalysis and recycling of the immobilized catalyst  $Fe_3O_4@SiO_2$ -PGMACD.



Scheme 3 The schematic representation of the selective adsorption and separation of bisphenol A by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD.

hydrophobic parts. The molecules with proper size, shape, and polarity could fit the cavity to form inclusion complex through host-guest interactions, which contribute to the application of CDs in environmental pollution cleanup (see Scheme 3). CDs can remove typical organic pollutants, such as bisphenol A and aromatic molecules, from large volumes of water.44,45 In our work, bisphenol A, a key monomer in production of epoxy resins and in the most common production process of polycarbonate plastic, was selected as the research model. Bisphenol A was adsorbed by different amounts of MNPs. Fig. 6 is the UV-vis spectra of bisphenol A in the existence and presence of MNPs. It was found that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD had higher adsorption capability than Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA. Taking 5 mg Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-PGMACD as consideration, it contained  $4.6 \times 10^{-4}$  mmol of  $\beta$ -CD. The absorbance of bisphenol A (5 mL, 10 × 10<sup>-4</sup> mmol) decreased apparently and near 67% of bisphenol A was adsorbed. Compared with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD, only 24% was adsorbed by 5 mg of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA. In addition, there is a linear relation between the amount of MNPs and the decrease



Fig. 6 UV-vis spectra of bisphenol A ( $2 \times 10^{-4}$  M) upon addition of (a) 0 mg MNPs; (b) 2 mg Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA; (c) 5 mg Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMA; (d) 2 mg Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD; (e) 5 mg Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD.

of absorbance. The results indicate Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD is a potential material in the enrichment and removal of bisphenol A from the aqueous solution.

## Conclusion

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD was successfully fabricated by a sequence of methods including thermal decomposition, sol-gel process, ATRP and ring-opening reaction of epoxy group. The resulting nanoparticles inherit the catalysis and inclusion properties of CD, the reactivity and assistance properties of PGMA, and the magnetic separation property of MNPs. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-PGMACD can be used in catalysis and adsorption with high efficiency. The average conversion of oxidation of benzyl alcohol is up to 84%, close to free CD, while the adsorption capability has a linear relation with the quantity of MNPs. Furthermore, due to the high activity of CDs in the resulting product, they have promising applications in much more extensive fields.

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