Size and shape-dependent catalytic activity of Mnfe$_2$O$_4$ nanoparticles in the selective degradation of dye pollutants

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ABSTRACT

Shape and size controlled metal or metal oxide nanoparticles (NPs) have attracted wide attention due to the fact that the shape and size of nanoparticles play a crucial role for their physical and chemical properties. Herein, three different sizes and shapes of MnFe$_2$O$_4$ NPs prepared by a hydrothermal procedure was synthesized. The catalytic activity of different size and shape of MnFe$_2$O$_4$ NPs was evaluated by monitoring the reduction reaction of methylene blue (MB), rhodamine 6G (R6G), rhodamine B (RB) and methylene orange (MO). The results showed that the catalytic activities of the MnFe$_2$O$_4$ NPs towards degradation of same organic dyes were size- and shape-dependent and followed the order of 4 nm (spherical) > 18 nm (plate-like) > 27 nm (near-cubic). In addition, all these nanocatalysts exhibit selectivity to different dyes. This investigation is of great significance for realization of these goals and relies on the availability of size- and shape-controlled nanoparticles. In addition, MnFe$_2$O$_4$ NPs could also be readily harvested by a magnet and reused more than 10 times without appreciable loss of activity, rendering this catalyst safer for the environment.

Keywords: Metal oxide nanoparticles, MnFe$_2$O$_4$ NPs, organic dyes, industrial effluents.

INTRODUCTION

Water pollution by organic contaminants has become a serious environmental issue and received significant attention (Wang et al., 2008; Sui et al., 2012). Among many organic pollutants, it is of special importance to solve the pollution challenges with organic dyes due to their wide applications in industries such as printing, textile, paper, paints and plastics (Yu et al., 2012; Ali, 2012). A variety of technologies were exploited to remove these contaminants, such as adsorption, photocatalytic degradation, chemical oxidation, membrane filtration, flocculation and electro-oxidation (Ali, 2012; Shan et al., 2010). For example, various semi-conductor nanoparticles, such as TiO$_2$, ZnO, CeO$_2$ and SnO$_2$ were extensively investigated to photocatalytically decompose organic compounds under visible light irradiation (Shan et al., 2010; Zhang et al., 2010; Li et al., 2009; Yamada et al., 2007). Several adsorbents, such as activated carbon, layered double hydroxides and magnetic nanomaterials were widely studied to remove organic compounds by physical and/or chemical adsorption mechanisms (Purkait et al., 2007; Zhou et al., 2010; Dvininov et al., 2010; Liu et al., 2014).

Recently, ferromagnetic Ni/rGO and α-Fe$_2$O$_3$/rGO nanocomposites were synthesized with high performance for the removal of organic dye (rhodamine B) from water (Liu et al., 2012; Li et al., 2012). However, the exploration of novel materials and techniques for a highly efficient and economical removal of organic dyes from industrial effluents is still of great interest. Manganese ferrite (MnFe$_2$O$_4$) nanoparticles with spinel structure attracted much attention due to their outstanding properties, such as...
as large surface area, high saturation magnetization, and their size- and shape-dependent magnetic behavior (Wang et al., 2012; Guo et al., 2012; Comes et al., 2012; Prozorov et al., 2007; Liu et al., 2011; Wu et al., 2011; Yang et al., 2009). The potential applications of MnFe₂O₄ nanoparticles range from environmental remediation and catalysis to biomedical diagnosis and therapy and high density magnetic storage (Wang et al., 2008; Cannas et al., 2008; Bao et al., 2009; Goh et al., 2010; Yuan et al., 2010; Sheet et al., 2010). However, there have been few attempts to investigate the catalytic activities of MnFe₂O₄ with different size and shape towards degradation of organic dyes.

Here, we studied MnFe₂O₄ NPs with three kinds of sizes (4, 18, and 27 nm) and shapes for their ability to catalyze degradation of MB, R6G, RB and MO in aqueous media. These NPs can all catalyze the degradation of these organic dyes. The reaction catalyzed by these NPs followed a Michaelis–Menten behavior showing size- and shape-dependent catalysis properties in the order of 4 nm (spherical) > 18 nm (plate-like) > 27 nm (near-cubic). The different catalysis performances of the magnetic MnFe₂O₄ NPs on organic dyes provide promising potential for the highly efficient removal of organic pollutants from industrial effluents.

MATERIALS AND METHODS

Experimental chemicals

Iron (III) acetylacetonate, Manganese (II) acetylacetonate, oleic acid, oleylamine, 1,2-hexadecanediol, phenyl ether, polyethylene glycol (MW = 4000) and 3,4-dihydroxybenzaldehyde were purchased from Sigma Aldrich. MB, R6G, RB and MO were obtained from Beijing Chemicals Inc (Beijing, China). All chemicals were used without further purification, except CHCl₃ and triethyamine used anhydrously. Aqueous solutions were prepared with double-distilled water (ddH₂O) from a Millipore system (> 18 MΩ·cm). The 1,ω-Diaminopolyoxyethylene (MW = 4000) and DIB-PEG-NH₂ were synthesized according to the published method (Liu et al., 2013; Pal et al., 2014). All the dialysis bags (MWCO 8000 to 14000) were obtained from Shanghai Medical Technology.

Instrumentation

A TEM measurements was conducted with Philips EM 420 (120 kV) under ambient conditions with the deposition of the hexane or H₂O dispersions of the particles on amorphous carbon-coated copper grids. The hysteresis loop was obtained at 300 K with a LakeShore 7400 VSM system. The UV-vis absorbance measurement experiments were carried out on a UV-1750 spectrophotometer (Shimadzu, Japan). The Fourier Transform Infrared (FT-IR) spectrum was recorded on a Therom Mattson FT-IR spectrometer using the KBr pellet technique. Powder X-ray Diffraction (XRD) analyses were performed on a Bruker AXS D8-Advanced diffractometer with Cu Ka radiation (λ = 1.5418 Å) and the scanning angle ranged from 20 to 80 of 2θ. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was executed with a FWS-1000.

Synthesis of 4 nm MnFe₂O₄ nanoparticles

Iron (III) acetylacetonate (2 mmol, 1.413 g), Manganese (II) acetylacetonate (1 mmol, 0.327 g) and 1,2-hexadecanediol (10 mmol, 2.548 g) were dissolved in oleic acid (6 mmol, 2.11 ml), oleylamine (6 mmol, 2.81 ml) and phenyl ether (20 ml) in a 100 ml four-necked round-bottomed flask. The mixture was stirred under a gentle flow of nitrogen at 200°C for 30 min. Then under a blanket of nitrogen, the solution was heated to reflux (265°C) and kept at that temperature for 30 min. When it cooled down to room temperature, the particles were separated by adding 40 ml isopropyl alcohol and centrifuged. The final products were washed thrice using petroleum ether/ethanol and finally dispersed into hexane for storage (Wang et al., 2014; Peng et al., 2015).

Synthesis of 18 and 27 nm MnFe₂O₄ NPs

The 18 and 27 nm MnFe₂O₄ NPs were synthesized in oleic acid (15 ml) system, respectively. The difference is the molar quantities, 18 nm MnFe₂O₄ NPs equals to 2 mmol of Fe(acac)₃ and 1 mmol of Mn(acac)₂ and 27 nm MnFe₂O₄ NPs corresponds to 8 mmol of Fe(acac)₃ and 4 mmol of Mn(acac)₂. Under N₂ atmosphere, the reaction mixture was heated at 120°C for 1 h and then under a blanket of nitrogen, the solution was heated to reflux (330°C) and kept at that temperature for 4 h. Each MnFe₂O₄ NPs were precipitated upon the addition of 50 ml of isopropyl alcohol and centrifuged. In order to remove the excess oleic acid on the surface of NPs, the NPs were washed with petroleum ether and ethanol mixed solution thrice. The product was finally dispersed in hexane (Wang et al., 2014; Peng et al., 2015).

Synthesis of 4 nm MnFe₂O₄-DIB-PEG-NH₂ (1a), 18 nm MnFe₂O₄-DIB-PEG-NH₂ (1b) and 27 nm MnFe₂O₄-DIB-PEG-NH₂ (1c) NPs

In a 50 ml round-bottomed flask, DIB-PEG-NH₂ (0.025 mmol, 0.1 g) was dissolved in CHCl₃ (15 to 20 ml) at room temperature with continuous stirring. After a while, the solution of different sizes of MnFe₂O₄ NPs (0.01409 mmol,
2 ml) was dropped into the aforementioned solution and stirred 24 h at room temperature. The products were washed thrice using petroleum ether and ethanol. The products were put into dialysis bags which were suspended in water for a few days. After that, the products were dissolved in ddH₂O (Wang et al., 2014; Peng et al., 2015).

Catalytic activity measurement

The catalytic activity of the samples was determined by the degradation of MB, R6G, RB and MO with the help of NaBH₄. Experiments were conducted at ambient temperature unless otherwise stated: one of the different sizes of MnFe₂O₄-DIB-PEG-NH₂ NPs (Mn²⁺ 0.01409 mol/L) were added into ddH₂O (2 ml) containing the MB, (10⁻⁷ mM) aqueous solution or equal-molar R6G, RB and MO aqueous solution. Then, NaBH₄ (1 mol/L) was added to the above reaction mixture. At a given time interval (2 min) of irradiation, the concentrations of the remnant dye were recorded by measuring the absorbance of solution at 664, 526, 552 and 464 nm, respectively, during the degradation process on a UV-1750 spectrophotometer.

RESULTS AND DISCUSSION

Structural characteristics of MnFe₂O₄ NPs

Hydrophobic MnFe₂O₄ NPs were prepared through a facile thermal decomposition method in an oleic acid system. Thereafter, the hydrophilic MnFe₂O₄-DIB-PEG-NH₂ was synthesized by the ligand-exchange chemistry between oleic acid and DIB-PEG-NH₂, changing the as-synthesized hydrophobic MnFe₂O₄ NPs into hydrophilic counterparts. It is commonly known that FT-IR spectroscopy is an essential technique to identify the stretching and bending vibrations of different materials. Figure 7a to c shows the FT-IR spectra of DIB-PEG-NH₂, 4 nm MnFe₂O₄ NPs and 1a, respectively. In Figure 7a, the absorption peaks at 1107 cm⁻¹ was assigned to phenolic hydroxyl group of DIB-PEG-NH₂. Compared with Figure 7b and c, the peak of the phenolic ν(C-O) at 1108 cm⁻¹ was not observed in Figure 7b, while it appeared in Figure 7c. However, a new absorption peak of C-O-Mn and C-O-Fe appeared at 1415 and 1454 cm⁻¹, respectively indicating that the phenolic hydroxyl group of DIB-PEG-NH₂ are bound to the surface of MnFe₂O₄ NPs. Meanwhile, the peak of ν(N-H) was shifted from 1345 to 1385 cm⁻¹, respectively after forming 1a. After modification, the Fe-O and Mn-O bonds were assigned to 612 and 440 cm⁻¹ (Pal et al., 2014).

The high reaction temperature under the inertia atmosphere and the thermal decomposition reaction led to the magnetic nanoparticles with narrow size distributions and relatively good crystal. Figure 1 shows the representative TEM images of MnFe₂O₄ NPs and MnFe₂O₄-DIB-PEG-NH₂ in different sizes displayed. As can be seen from the images, MnFe₂O₄ NPs coated with oleic acid were monodispersed nanocrystals of nearly spherical, sphericoidicity, near-cubic morphology with narrow size distributions in the range of ~4, ~18 and ~27 nm, respectively. After covalently modified ~18 nm MnFe₂O₄ NPs with DIB-PEG-NH₂, the resulting 1b (Figure 8A and B) could be well-dispersed into water without obvious aggregation. In addition, the morphology and diameter of the MnFe₂O₄ NPs was also unchanged after chemical modification. The high-resolution TEM (HRTEM) imaging (inset of Figure 1A, C and E) revealed that MnFe₂O₄ NPs had a relatively good crystal. The resolved lattice fringes of 0.295, 0.476 and 1.253 nm agreed with the (311) (400) (440) facet of 4 nm MnFe₂O₄ NPs, 18 nm MnFe₂O₄ NPs and 27 nm MnFe₂O₄ NPs, respectively. The selected area electron diffraction (SAED) pattern (inset of Figure 1A, C and E) also confirmed the presence of MnFe₂O₄ NPs. Moreover, the energy dispersive X-ray spectroscopy (EDX) analysis (Figure 1B, D and F) of pure MnFe₂O₄ NPs confirmed that the MnFe₂O₄ NPs are composed of Mn, Fe and O (Wang et al., 2014; Peng et al., 2015; Bateer et al., 2014).

To thoroughly understand the crystal structures of MnFe₂O₄ NPs, an X-ray diffraction (XRD) analysis was conducted at the 2θ mode. Figure 2A shows XRD patterns of pure MnFe₂O₄ NPs in different sizes and the diffraction peaks of MnFe₂O₄ NPs ascribed to (311), (400), (422), (511), (440), (622) and (444). The positions and relative intensities of all diffraction peaks matched well with the data of standard MnFe₂O₄ NPs (JCPDS Cards: 73-1964). No impurity peaks were observed, revealing that the pure phase of the MnFe₂O₄ sample was synthesized (Zeng et al., 2015; Zhang et al., 2014).

To gain a better understanding of the magnetic properties of MnFe₂O₄ NPs (Wang et al., 2014; Peng et al., 2015; Chen et al., 2013; Kong et al., 2013), the magnetic properties of the obtained samples were studied using a VSM at room temperature. The magnetization curves in Figure 2B depicted that 4, 18 and 27 nm MnFe₂O₄ NPs were super-paramagnetic at room temperature with the saturation magnetization (Ms) value 65.02, 54.67 and 42.83 emu/g, respectively. These magnetic properties make the nanocrystals easily separable from the mixture detection solution and recovery utilization with high efficiency. Figure 2B demonstrates that MnFe₂O₄-DIB-PEG-NH₂ in aqueous solution can be harvested and separated by a NdFeB magnet, which was extremely important for the magnetic separation and reusability of MnFe₂O₄-DIB-PEG-NH₂ from the reaction mixture.

Catalytic properties of the 1a, b and c in the degradation of MB

In order to accurately monitor the catalytic efficiency, the
catalytic degradation of MB by 1a, b or c as typical reactions and UV-vis spectrum detection was used to reflect the degradation effect. The process was operated as follows: 1a, b or c (Mn²⁺ 0.01409 mol/L) was added or not.
added into ddH₂O (2 ml) containing the MB (10⁻⁵ mol/L) aqueous solution, followed by adding NaBH₄ (0.1 mmol/L) aqueous solution to the aforementioned reaction mixture. From the systematic experiments, the optimal result to degrade MB within 6 min was obtained.

The results showed that without the catalytic properties no visible absorption changes in UV-vis spectrum of MB will occur (Figure 10) (Li et al., 2015). However, after the addition of 1a, b or c in the MB solution, the colour changes and the absorption peak was flattened. Figure 3 shows the inserted photographs with three degradation processes: the beginning, intermediate and the final state. It can be seen from Figure 3A to C that all of these different sizes and shapes catalysis have the abilities to degrade MB in the same concentration within 6 min. The degradation efficiency was 99.79, 92.89 and 85.77% corresponding to 4, 18 and 27 nm, respectively (Figure 3D and E). Thus, in the same time the degradation efficiency follows the order of 4 nm (spherical) > 18 nm (plate-like) > 27 nm (near-cubic). This implies that the size plays a significant role in the degradation process.

To better understand the reaction kinetics of MB degradation, the experimental data were fitted by a first-order model as expressed. The initially obtained data
Figure 5: The catalytic degradation efficiency of 1a, b and c towards R6G, RB and MO.

were designated as the start for the reaction time (t_\text{initial}). Subsequently, the absorbance of the MB was recorded every 2 min to track the reaction. When the intensity of the absorbance bands at 664 nm disappeared, the
Figure 6: The reusability of 1c for the degradation of MB.

Figure 7: Fourier transformed infrared (FT-IR) spectra of (a) DIB-PEG-NH$_2$; (b) 4 nm MnFe$_2$O$_4$ NPs; (c) 1a.
Figure 8: TEM images of the as synthesis 18 nm (A) MnFe$_2$O$_4$ NPs (B) MnFe$_2$O$_4$-DIB-PEG-NH$_2$.

Figure 9: (A) Extinction spectra of various pre-defined MB concentrations, (B) Extinction spectra of various pre-defined MO concentrations, (C) Extinction spectra of various pre-defined R6G concentrations, (D) Extinction spectra of various pre-defined RB concentrations, (E) their corresponding calibration curve relating absorbance, at characteristic 664 nm, with the concentrations of MB, (F) their corresponding calibration curve relating absorbance, at characteristic 464 nm, with the concentrations of MO, (G) their corresponding calibration curve relating absorbance, at characteristic 526 nm, with the concentrations of R6G, (H) their corresponding calibration curve relating absorbance, at characteristic 552 nm, with the concentrations of RB.

corresponding time was designated as the final reaction time ($t_{\text{final}}$). Meanwhile, the ratios $C_t/C_0$ of the MB concentrations $C_t$ ($t = t_{\text{final}}$) to its initial value $C_0$ ($t = 0$) were directly given by the relative intensity of the respective
Figure 10: UV spectra of alone MB and MB in the presence of NaBH₄.

Figure 11: UV-Vis spectra of the optimal experimental result: (A) R6G, (B) RB, (C) MO, (D) The C_t/C₀ of 1a to R6G, RB and MO.
Figure 12: UV-Vis spectra of the optimal experimental result: (A) R6G, (B) RB, (C) MO, (D) The $C_t/C_0$ of 1b to R6G, RB and MO.

Figure 13: UV-Vis spectra of the optimal experimental result: (A) R6G, (B) RB, (C) MO, (D) The $C_t/C_0$ of 1c to R6G, RB and MO.
Table 1: The k, k', and $R^2$ of MnFe$_2$O$_4$-DIB-PEG-NH$_2$ in different sizes.

<table>
<thead>
<tr>
<th>Variable</th>
<th>4 nm</th>
<th>18 nm</th>
<th>27 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (min$^{-1}$)</td>
<td>1.034</td>
<td>0.440</td>
<td>0.329</td>
</tr>
<tr>
<td>K'(min$^{-1}$mol$^{-1}$)</td>
<td>587083</td>
<td>249822</td>
<td>186799</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.975</td>
<td>0.977</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Figure 14: The VSM of MnFe$_2$O$_4$ and 1c at 300K.

In order to confirm that the concentrations of NPs and NaBH$_4$ have different influences on the degradation MB, we take 1c as an example and conducted a series of experiments. It can be seen from Figure 4 when 1c concentration increased from 0.07 to 0.70 mM that the degradation efficiency was from 8.5 to 76.2%. However, on increasing 1c concentration from 0.88 to 1.23 mM, the efficiency was almost unchanged and can be 99.1%. Meanwhile, when the amount of NaBH$_4$ was increased from 0.0050 to 0.0500 mM, the degradation efficiency also increased correspondingly from 8.7 to 94.2% due to an increase in BH$_4^-$ anions with increased concentration of NaBH$_4$. When dosage increased from 0.0625 to 0.0875 mM, the efficiency was 97.5%. Hence, the optimal 1c nanocatalyst and NaBH$_4$ concentrations were 0.88 and 0.0625 mM, respectively. Thus, subsequent experiments...
were performed under these conditions.

**Catalytic properties of the 1a, b and c in the degradation of other organic dyes**

The catalytic performance of 1a, b and c was measured using different dyes, such as R6G, RB and MO. The UV-vis absorption and the colour change of equal-molar R6G, RB and MO aqueous solution could also be tested in the same condition with MB (Figure 9A to H). As shown in Figures 5 and 11 to 13, 1a, b and c exhibit degradation ability to three organic dyes, but the different size NPs showed different degradation efficiency to same dyes and in the same time the degradation efficiency also follows the order of 4 nm (spherical) > 18 nm (plate-like) > 27 nm (near-cubic), which further indicated that the small size NPs have high catalytic activity. At the same time, all the NPs exhibited selective degradation to different dyes, indicating all these nanocatalysts exhibit selectivity.

**Reusability**

After modification, MnFe$_2$O$_4$-DIB-PEG-NH$_2$ (take 1c as an example) still had the super-paramagnetic capacity and expressed the Ms value at 18.33 emu/g, which endowed these nanoparticles with magnetic recycling property (Figure 14). As is known, the recycle times and reaction times are very important for industrial application (Guo et al., 2012; Fu et al., 2012). For further study the reusability of 1c and MB was taken as an example. In brief, MnFe$_2$O$_4$-DIB-PEG-NH$_2$ (Mn$^{2+}$ 0.01409 mol/L) was added into ddH$_2$O (2 ml) containing the MB (10$^{-5}$ mol/L) aqueous solution, followed by adding NaBH$_4$ (0.1 mol/L) to the aforementioned reaction mixture. When the catalytic process ended, the supernatant was poured out with the help of the external magnet, and the absorption peaks of supernatant tested through the UV-VIS. The MnFe$_2$O$_4$-DIB-PEG-NH$_2$ was washed by ddH$_2$O several times. The aforementioned process was repeated until the absorption and colour of the MB no longer changed in 30 s. Figure 6 shows that MnFe$_2$O$_4$-DIB-PEG-NH$_2$ could be reused 10 times with the conversion higher than 90%. The stability of the catalyst was also investigated by measuring the Mn loss after ten successive cycles with ICP-MS. The test showed that there was about 1.3 wt% of Mn in reaction solution after 10 cycles, indicating slight leaching of the Mn. Moreover, the XRD spectrum of 1c after 10 cycles matches well with the as-synthesized product (Figure 15).

**Conclusion**

In summary, three MnFe$_2$O$_4$ NPs with different sizes and
shapes exhibit different levels of catalytic activity towards degradation of four organic dyes in the order of 4 nm (spherical) > 18 nm (plate-like) > 27 nm (near-cubic) > 16 nm (spherical) was demonstrated; this order was closely related to their surface-to-volume ratio and atom arrangements. In addition, all these nanocatalysts exhibit selectivity to different organic dyes, which is very important to selectively remove the harmful pollutants from other less-harmful pollutants.

Moreover, MnFe2O4 nanoparticles possessed good sustainability even after 10 cycles of MB degradation and furthermore, the conversion of the catalysts was nearly unaffected. All these features suggest that selective fabrication of stable nanocatalysts with different size and shape is very important to harness their catalytic activities for environment remediation applications.

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