Encapsulation of superparamagnetic Fe₃O₄@SiO₂ core/shell nanoparticles in MnO₂ microflowers with high surface areas

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ABSTRACT

Microflowers made of interconnected MnO₂ nanosheets have been successfully synthesized in a microwave reactor through a hydrothermal reduction of KMnO₄ with aqueous HCl at elevated temperatures in the presence of superparamagnetic Fe₃O₄@SiO₂ core-shell nanoparticles. Due to the chemical compatibility between SiO₂ and MnO₂, the heterogeneous reaction leads to the spontaneous encapsulation of the Fe₃O₄@SiO₂ core-shell nanoparticles in the MnO₂ microflowers. The resulting hybrid particles exhibit multiple properties including high surface area associated with the MnO₂ nanosheets and superparamagnetism originated from the Fe₃O₄@SiO₂ core-shell nanoparticles, which are beneficial for applications requiring both high surface area and magnetic separation.

1. Introduction

Nanostructured manganese dioxides (MnO₂) represent a class of most studied transition metal oxides due to their unique crystalline structures and wide applications in molecular adsorption [1–4], catalysis [5, 6], and electrochemical energy storage [7, 8]. For example, using nanostructured MnO₂ as active components of electrodes in energy storage devices has many advantages in terms of high specific energy capacity, low fabrication cost, and environmental benignity [9]. Similar to other transition metal oxides, MnO₂ nanostructures can also be used as absorbents to remove organic contaminations from waste water and the adsorbed organic species can be burned through a combustion at relatively low temperature catalyzed by the MnO₂ [1]. Previous studies have proven that performance of the MnO₂ nanostructures in these applications strongly depends on morphology and crystallinity of the MnO₂ nanostructures, which can be varied by controlling synthesis strategy and conditions [10]. In the past decade, a number of synthesis methods, such as co-precipitation [11], sol-gel technique [12], hydrothermal reaction [13], *etc.* were developed for preparing nanostructured MnO₂ with morphologies in a broad range including plates, urchin-like structures, spheres, flowers, cubes, wires, rods, belts, tubes, *etc.* Depending on how the repeated MnO₆ octahedron units in MnO₂ lattices share their faces and edges, the as-synthesized MnO₂ nanostructures can be crystallized in different phases (*e.g.*, α , β , δ , γ , and λ). Most recently we developed a microwave-assisted hydrothermal method that was capable of synthesizing MnO₂ nanostructures with well-controlled morphology and crystallinity in high uniformity and purity [14]. Using microwave energy to drive solution-phase reactions is superior to the conventional heating with respect to prompt start-up, uniform temperature distribution in solutions, efficient energy conversion and delivery, easy control over reaction conditions, and possible scaling up [15, 16]. We extend the microwave-assistant synthesis to integrate MnO₂ nanostructures with other nanostructures to generate hybrid nanomaterials. Synthesis of composite nanomaterials with multiple functionalities represents a most promising direction because novel properties can be achieved due to the coupling between two different types of components. For

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instance, hybridization of MnO_2 nanostructures with superparamagnetic Fe_3O_4 nanoparticles results in the composite nanostructures that can be mechanically manipulated on-demand with an external magnetic field. In the letter, we report the synthesis of MnO_2 microflowers composed of interconnected nanosheets that encapsulate superparamagnetic $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles through a microwave-assistant heterogeneous hydrothermal reaction.

2. Experimental

Superparamagnetic $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles were first synthesized through the following multiple steps. Synthesis of Fe_3O_4 nanoparticles was realized through a combination of controlled hydrolysis and reduction of Fe(III) at elevated temperatures [17]. In detail, FeCl_3 salt (Aldrich) was hydrolyzed and partially reduced in basic diethylene glycol (DEG, Fisher Scientific) at 220 °C. The basicity was adjusted with addition of appropriate amount of NaOH (Fisher Scientific). Poly(acrylic acid) (PAA, MW = 1800, Aldrich) was added to the reaction solution to serve as surface capping molecules that stabilize the as-grown Fe_3O_4 nanoparticles. The Fe_3O_4 nanoparticles were then coated with silica shells through a modified Stöber process. In a typical reaction, to 3 mL of aqueous solution containing ~23 mg Fe_3O_4 nanoparticles was added 20 mL of ethanol (Fisher Scientific). 1 mL of ammonium hydroxide aqueous solution (28%, Fisher Scientific) was added to the nanoparticle solution to adjust the pH value of the solution for controlled hydrolysis of tetraethyl orthosilicate (TEOS, Aldrich). Injection of 0.1 mL of TEOS to the nanoparticle solution initiated the deposition of silica shells on the surfaces of the Fe_3O_4 nanoparticles. Thickness of the resulting silica shells was tuned by terminating the hydrolysis reaction at different reaction times. Mechanical stirring and room temperature were maintained throughout the reaction. The as-prepared $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles were then washed with ethanol for two times. The nanoparticles were re-dispersed in 20 mL of deionized (DI) water and stored for characterization and other purposes.

Growth of MnO_2 microflowers with encapsulation of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles was carried out through the procedure similar to that for growing pure MnO_2 microflowers [14]. In detail, 2 mL of the stock solution of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles was mixed with 21 mg of KMnO_4 (Aldrich), 0.4 mL of 1.2 mol/L HCl aqueous solution (Aldrich), and 3.6 mL of DI water in a 10-mL microwave reaction tube that was then placed in a CEM Discover® microwave reactor. The solution was then heated to 150 °C at the maximum ramping rate under the sealed vessel mode with microwave irradiation. The pressure above the reaction solution reached to 95 psi at temperature of 150 °C. By controlling the reaction time, the size of the MnO_2 nanosheets in the microflowers was able to tune. Reaction temperature and acidity of the reaction solutions were also changed to serve as control experiments. After reaction, the solid products were collected via either centrifugation or magnetic separation followed by washing with DI water.

The as-synthesized samples were characterization with a JEOL JSM-7500F field emission scanning electron microscope for collecting scanning electron microscopy (SEM) images as well as with a JEOL JEM-2100F microscope operated at a voltage of 200 kV for recording transmission electron microscopy (TEM) images and electron diffraction patterns. Energy dispersive x-ray spectroscopy (EDS) was studied with a Thermo Scientific microanalysis system equipped on the JEOL JSM-7500F field emission scanning electron microscope. A VARIAN CARY-50 spectrophotometer was used to measure the UV-vis-NIR spectra of the reaction solution as well as the concentration of methyl orange.

3. Results and discussion

Superparamagnetic $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles were synthesized according to the strategy well used in our group [18-21]. Fig. 1A presents a SEM image of randomly assembled core-shell particles on a Si substrate, showing their uniform size. Fig. 1B shows a typical TEM image of the particles, highlighting their core-shell configuration with dark cores and gray shells corresponding to the different mass densities of Fe_3O_4 and SiO_2 . Each Fe_3O_4 core (inset, Fig. 1B) is an assembly of many crystalline domains with sizes less than 10 nm. Such bimodal length scale in the Fe_3O_4 nanoparticles is critical for them to preserve superparamagnetism associated with small crystallites at room temperature [17]. As a result, the $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell nanoparticles can be easily manipulated with an external magnetic field. The SiO_2 shells can not only protect the Fe_3O_4 cores from being degraded in harsh environment (such as dissolution of Fe_3O_4 in acidic solutions), but also provide surfaces compatible with many reactions and compositions due to the easy modification of SiO_2 surface chemistry. The EDS spectrum (Fig. 1C) collected from the area shown in Fig. 1A exhibits strong signal of Si that is attributed to the SiO_2 shells and the Si substrate, signal of Fe corresponding to the Fe_3O_4 cores, and signal of O originated from both Fe_3O_4 cores and SiO_2 shells. The weak signal of C is probably due to the organic contaminations in the course of sample preparation.

The strong hydrophilicity and high-density negative charges of SiO_2 surfaces makes the SiO_2 nanoshells ideal as nucleation sites for growing transition metal oxides, for example, MnO_2 nanostructures. We have developed a microwave-assistant hydrothermal approach for the synthesis of MnO_2 nanostructures with controlled morphology and crystallinity

[14, 22]. Similar MnO₂ nanostructures can also be synthesized in the presence of Fe₃O₄@SiO₂ core-shell nanoparticles, which provide active nucleation sites for condensation of MnO₂. MnO₂ nanostructures are formed from the hydrothermal reaction between KMnO₄ and HCl at elevated temperatures in a microwave reactor. When the precursor chemicals are mixed at room temperature, there is no apparent reaction observed. Once the reaction vessel is sealed, quickly heating the solution to 150 °C within 1 min with the microwave reactor triggers a redox reaction:

because the half reaction $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$ exhibits a higher standard electrode potential (1.70 V *versus* SHE, standard hydrogen electrode) than that of the half reaction $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$ (1.36 V *versus* SHE). The reaction indicates that both Cl⁻ ions and H⁺ ions play important roles to drive the formation of MnO₂, *i.e.*, Cl⁻ ions are reducing species to reduce MnO₄⁻ ions to form MnO₂ solids and H⁺ ions provide an acidic environment to promote the redox reaction. The reaction leads to the formation of precipitated black powders of MnO₂ while the concentration of the precursor KMnO₄ gradually decreases (Fig. S1 in Supporting information). The reaction is very fast, for example, reaction for 5 min at 150 °C consumes ~94% KMnO₄ precursor and no KMnO₄ can be detected in the reaction solution after 10 minutes of reaction. The black powders dispersed in aqueous solutions are responsible to external magnetic fields, indicating that the superparamagnetic Fe₃O₄@SiO₂ core-shell nanoparticles are wrapped in the MnO₂ powders.

Figs. 2A and 2B are SEM images of the black powders formed at 5 min, clearly showing flower-like morphology of the MnO₂ particles consisting of interconnected nanosheets with thickness of several nanometers. The enlarged image reveals that the spherical Fe₃O₄@SiO₂ core-shell nanoparticles are trapped in the pockets formed among the interconnected nanosheets. The TEM image of an individual MnO₂ microflower with many Fe₃O₄@SiO₂ core-shell nanoparticles is presented in Fig. 2C, revealing that most Fe₃O₄@SiO₂ core-shell nanoparticles stay in the center region of the flower. The result indicates that a number of Fe₃O₄@SiO₂ core-shell nanoparticles are slightly aggregated into nanoparticle clusters at the beginning followed by growth of MnO₂ nanosheets from the SiO₂ surfaces to form microflowers surrounding the Fe₃O₄@SiO₂ core-shell nanoparticles. Because of their thin thickness, the extremely flexible MnO₂ nanosheets form conformal contact with the amorphous surfaces of Fe₃O₄@SiO₂ core-shell nanoparticles (Fig. 2D). Selected area electron diffraction (SAED) pattern recorded from a section of a single MnO₂ nanosheet highlighted by the circle in Figure 2D is presented in Figure 2E, showing two diffraction rings consistent with the (111) and (020) reflections of δ -phase MnO₂. Analysis of the SAED pattern indicates that the basal surfaces of the MnO₂ nanosheets orientate along the [001] direction and the nanosheets are polycrystalline. The high-resolution TEM image of the portion highlighted by the square in Fig. 2D clearly shows the interface between the crystalline MnO₂ nanosheet and the amorphous SiO₂ nanoshell (Fig. 2F). The crystalline domains in the MnO₂ nanosheet are very small with size of only several nanometers, consistent with their polycrystalline property.

When the reaction time is elongated, continuous growth of the MnO₂ nanosheets can enlarge the size of the flowers. For example, the products formed at 10 min still maintain the flower-like morphology with larger nanosheets (Fig. 3A). The enlarged MnO₂ nanosheets form deeper pockets to hide the Fe₃O₄@SiO₂ core-shell nanoparticles, leading them to be barely observed in the SEM images. The EDS spectrum (Fig. 3B) of the hybrid flowers exhibit extra peaks corresponding to Mn and a much stronger peak of O compared to the EDS spectrum shown in Fig. 1C, confirming the hybridization of MnO₂ nanosheets and Fe₃O₄@SiO₂ core-shell nanoparticles in the flowers shown in Figure 3A. Previous studies indicate that overcooking the δ -phase MnO₂ nanosheets always transforms them into α -phase MnO₂ nanostructures with either wire/tube morphology (in solution) [14] or sheet morphology (at dry condition) [23] because the δ -MnO₂ nanosheets composed of small crystalline domains represent a metastable phase. We notice that the MnO₂ nanosheets start to fold at their edges and merge into thicker stripes as highlighted by arrows in Fig. 3C. The crystalline structure of these stripes is eventually reconstructed into more stable α -phase MnO₂ lattices and the stripes continuously grow into α -MnO₂ nanowires by consumption of other metastable δ -MnO₂ nanosheets. In the product formed at 10 min we can observe the existence of very few nanowires with α -phase lattice (inset, Fig. 3D) as well as fragments of nanosheets. Such fragmentation of nanosheets and phase transformation releases the Fe₃O₄@SiO₂ core-shell nanoparticles from the composite microflowers due to the failure in maintaining the flower-like morphology. Such morphological failure results in the significant decrease in surface areas of MnO₂ nanosheets and the loss of ability for magnetic manipulation of MnO₂ nanostructures. As a result, reaction for even longer time is not beneficial for maintaining the hybrid microflowers of MnO₂ nanosheets with embedded Fe₃O₄@SiO₂ core-shell nanoparticles.

The reduction of KMnO₄ strongly depends on the reaction temperature. The reaction becomes dramatically slowly at lower temperature, leading to a difficulty to form MnO₂ flowers. Fig. S2 in Supporting information presents the SEM and TEM images of the products formed from reaction at 100 °C for 30 min, showing that the Fe₃O₄@SiO₂ core-shell nanoparticles are surrounded/interconnected with amorphous species and nanosheets are barely observed. Variation of

acidity of reaction solutions can also lead to morphological change of the MnO_2 structures. When HCl is replaced with NaCl, the reaction produces agglomerated MnO_2 nanoparticles that serve as a matrix to embed the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles (Fig. S3 in Supporting information). The resulting black powders are magnetically responsible, but they cannot be dispersed well in solvents for applications such as catalysis and adsorption that require high surface area. Both temperature and acidity of reaction solutions represent the determining parameters that can influence the reaction kinetics. According to the classic nucleation and growth theory, the difference in reaction kinetics always leads to the formation of nanostructures with different morphologies.

The MnO_2 -nanosheet flowers shown in Fig. 3A exhibit strong magnetic response due to the inclusion of the superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles. The as-synthesized microflowers in the reaction solution can be easily collected when a magnet is placed near the reactor (Fig. S4 in Supporting information). The black powders can be easily re-dispersed with water after the removal of the magnet. Such magnetic response is beneficial for recovering the MnO_2 -nanosheet flowers that are used for applications such as removal of contamination molecules from water. The thin thickness of the MnO_2 nanosheets enables the particles shown in Fig. 3A to exhibit very high surface area. Mixing the particles (~15 mg) with 10 mL of 50 mg/L aqueous solution of methyl orange quickly decreases the concentration of methyl orange in the solution, indicating that methyl orange molecules are adsorbed on the MnO_2 nanosheets (Fig. 4). The dependences of the absorption spectra (Fig. 4A) and the normalized concentration of methyl orange on the time (Fig. 4B) clearly show that the methyl orange molecules are quickly adsorbed on the MnO_2 nanosheets within 5 min. When time is longer than 5 min, the decrease of intensity at the characteristic peak (at 465 nm) of methyl orange becomes much slower while the intensity at the valley increases and eventually a new peak at 340 nm is developed. The change of spectral characteristics indicates that the methyl orange molecules at longer soaking time may be oxidized through a reaction catalyzed by the MnO_2 nanosheets [4]. The hybrid $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MnO}_2$ microflowers can be easily recovered from the solution with the assistance of a magnet (inset photograph in Fig. 4B). If we can find a way to efficiently remove the adsorbed methyl orange molecules from the MnO_2 nanosheets, the recovered hybrid microflowers can be reused.

4. Conclusion

In summary, superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles can be directly encapsulated in MnO_2 microflowers made of interconnected MnO_2 nanosheets through a microwave-assistant hydrothermal reduction of KMnO_4 in acidic aqueous solution in the presence of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles that serve as seeds to prompt nucleation and growth of the MnO_2 nanosheets. Successful hybridization of the MnO_2 nanosheets and the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles enables the synthesized microflowers to exhibit both superparamagnetism corresponding to the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles and high surface area associated with the thin MnO_2 nanosheets, leading them to be promising in applications such as catalysis, molecule adsorption, *etc.*

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Figure 1. Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles with (A) SEM, (B) TEM, and (C) EDS.

Figure 2. Characterization of the MnO_2 microflowers with encapsulation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles formed at the reaction time of 5 min. (A) Low-magnification SEM image of a number of microflowers randomly assembled on a Si substrate. (B) High-magnification SEM image of microflowers showing that the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles sit in the pockets formed between the interconnected MnO_2 nanosheets. (C, D) TEM images of an individual microflower with different magnifications. (E) SAED pattern recorded from the area highlighted by the circle in (D). (F) High-resolution TEM image of the small region highlighted by the square in (D). The lattice fringes correspond to the crystalline lattices of δ -phase MnO_2 .

Figure 3. Characterization of the MnO_2 microflowers with encapsulation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles formed at the reaction time of 10 min. (A) SEM image of several microflowers showing that the pockets between the interconnected MnO_2 nanosheets are deeper than those

shown in Figure 2A. Most of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles are barely observed due to the deeper pockets. The red arrows highlight some $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell nanoparticles observed only when the corresponding pockets face the detector. (B) EDS spectrum of the samples shown in (A). (C) TEM image taken at the edge of an individual microflower showing the MnO_2 nanosheets are folded (highlighted by the arrows). (D) TEM image of a region with species that are rarely observed in this sample. The inset is the high-resolution TEM image of the area highlighted by the white rectangular box on the nanowire.

Figure 4. (A) UV-visible absorption spectra of methyl orange after methyl orange was mixed with the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MnO}_2$ microflowers shown in Figure 3A for different times (labeled with the legend). (B) The normalized concentration of methyl orange against the original concentration as a function of the soaking time. The insets are photographs of (left) the aqueous solution of methyl orange, (middle) the aqueous solution of methyl orange with hybrid microflowers, and (right) the rest solution after adsorption and removal of the microflowers. The hybrid microflowers are dragged to the right side wall of the vial due to the existence of the magnet that can provide a magnet field.

Supporting Information

Encapsulation of superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$
core/shell nanoparticles in MnO_2 microflowers with
high surface areas

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Graphical Abstract

Encapsulation of superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core/shell nanoparticles in MnO_2 microflowers with high surface areas
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Superparamagnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core/shell nanoparticles are caught by the microflowers made of MnO_2 nanosheets with high surface areas. The hybrid particles exhibit multifunctionalities including superparamagnetism and strong adsorption associated with high surface areas.