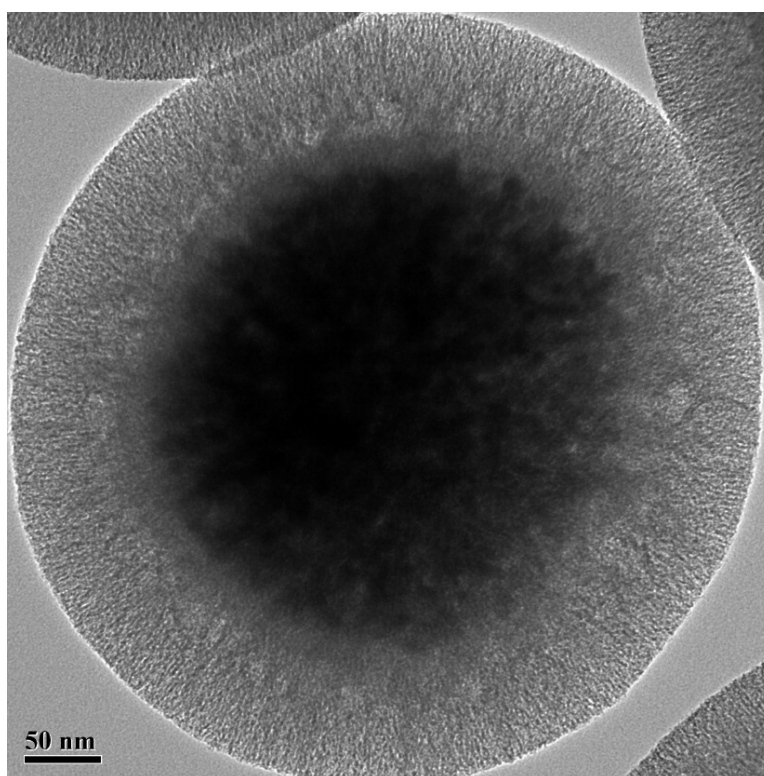## Communication

Superparamagnetic High-Magnetization Microspheres with an FeO@SiO Core and Perpendicularly Aligned Mesoporous SiO Shell for Removal of Microcystins

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Superparamagnetic High-Magnetization Microspheres with an Fe₃O₄@SiO₂ Core and Perpendicularly Aligned Mesoporous SiO₂ Shell for Removal of Microcystins

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Core−shell structured microspheres have recently been subject to extensive research for the combined functionalities of cores and shells which endow them with great application potentials in various fields.[1−6] Magnetic microspheres consisting of an iron oxide core and silica shell have attracted particular attention[7] for their unique magnetic responsivity, low cytotoxicity, and chemically modifiable surface. The core−shell magnetic silica microspheres have shown great potential in bioseparation,[8] enzyme immobilization,[9] diagnostic analysis,[10] and so on.

Since the first discovery in 1992,[11] ordered mesoporous materials have gained much attention for the applications in catalysis, adsorption, and separation. The integration of mesoporous silica with magnetic particles to form core−shell composite microspheres is undoubtedly of great interest for practical applications. Up to now, several papers have reported the synthesis of magnetic mesoporous silica nanocomposites.[12] However, these materials either show poor magnetic response due to the difficulty in increasing Fe₃O₄ mass fraction[12a−c] or possess irregular core−shell structures,[12b] and they could not be readily dispersed in water due to the sintering caused by the calcination for the removal of organic templates.[12d] Furthermore, these composites possess randomly aligned mesochannels or disordered mesopores[12d] that are difficult to access. As a result, these magnetic mesoporous silicas are limited in the applications, particularly, in biosystems and biomedicine. Therefore, core−shell magnetic mesoporous silica microspheres with strong magnetic responsivity, orientated and accessible mesopores and high dispersibility are highly valuable.

Herein, we report a novel synthesis of sandwich structured mesoporous silica microspheres (∼500 nm) with a silica-coated magnetite core and ordered mesoporous silica shell with perpendicularly oriented channels using a surfactant-templating approach. The obtained microspheres possess superparamagnetism, high magnetization (53.3 emu/g), uniform accessible mesochannels (2.3 nm), high surface area (365 m²/g), and large pore volume (0.29 cm³/g). Furthermore, they can be used as efficient adsorbents to fast remove large microcystins (1000 Da) in the solution.

The synthesis procedure is shown in Scheme 1. First, uniform magnetite microspheres were coated with a thin silica layer through a sol−gel approach to obtain nonporous silica−Fe₃O₄ composites (designated Fe₃O₄@nSiO₂). Second, through a surfactant-templating approach with cetyltrimethylammonium bromide (CTAB) as a template, a mesostructured CTAB/silica composite was deposited on the Fe₃O₄@nSiO₂ microspheres. Third, CTAB templates were removed in a mild way by acetone extraction to form a mesoporous SiO₂ shell, resulting in well-dispersed Fe₃O₄@nSiO₂@mSiO₂ microspheres.

The Fe₃O₄ particles were prepared via a solvothermal method as described previously.[8] These particles have a mean diameter of about 300 nm and consist of nanoparticles with the diameter of

Scheme 1. The Formation of Fe₃O₄@nSiO₂@mSiO₂ Microspheres
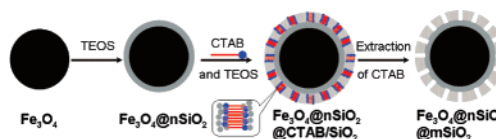
∼15 nm (Figure 1a and inset). Selected-area electron diffraction reveals that the particles have a polycrystalline feature (Figure S1). After coated with a nonporous silica layer, core−shell Fe₃O₄@nSiO₂ microspheres with a thin silica layer of ∼20 nm in thickness were obtained (Figure 1b). The second surfactant-templating process results in a CTAB/SiO₂ mesophase coated on the Fe₃O₄@nSiO₂ microsphere surface. The subsequent treatment with refluxing acetone could remove CTAB templates and lead to a uniform mesoporous silica shell (ca. 70 nm in thickness) (Figure 1c). FT-IR analysis (Figure S2) shows that CTAB templates can be successfully removed by the 3× mild acetone extraction. A typical sandwich structure with a magnetite core, a nonporous silica layer in the middle layer, and an ordered mesoporous silica phase with cylindrical channels in the outer layer can be clearly observed (Figure 1d). Interestingly, the mesopore channels are found to be perpendicular to the microsphere surface (Figure 1e). The SEM image shows that the microspheres are very uniform in both size and shape (Figure 1f). In our synthesis system, the silica oligomers interact with the CTAB template via Coulomb forces, and both of them cooperatively assembly on the Fe₃O₄@silica microspheres' surface, and the ordered mesostructure is formed. The mesopore orientation may result from the preferable alignment fashion of the rod-shaped silicate/CTAB complexes on the carved surface of the Fe₃O₄@nSiO₂ microspheres, which could effectively decrease the surface energy in the synthesis system (Scheme 1). The unique microstructure of the obtained microspheres would be very useful for many applications. First, the middle nonporous silica layer could protect the magnetite from etching in harsh application occasions. Second, the mesoporous silica shell not only offers high surface area for the derivation of numerous functional groups but also provides large accessible pore volume for the adsorption and encapsulation of biomacromolecules and even functional nanoparticles (e.g., quantum dots). Notably, due to their unique perpendicular orientation, the mesopore channels of the microspheres are readily accessible, favoring the adsorption and release of large guest objects triggered by external stimulus.

The low-angle XRD pattern reveals that the Fe₃O₄@nSiO₂@mSiO₂ microspheres have hexagonal mesopore symmetry (Figure S3). Because the mesopore channels are perpendicular to the surface, ethanol can lower the hydrolysis and condensation rate of TEOS and favor the coating and curving. The microspheres possess short-range mesoscopic ordering character. N₂ sorption−desorption
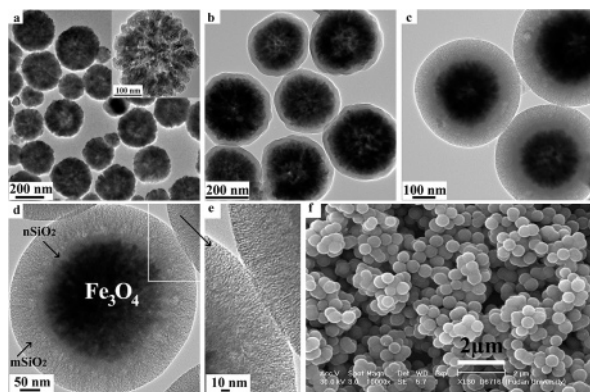
Figure 1. TEM images of (a) Fe_3O_4 particles, (b) $Fe_3O_4@nSiO_2$, (c−e) $Fe_3O_4@nSiO_2@mSiO_2$ microspheres, and (f) SEM image of $Fe_3O_4@n$-$SiO_2@mSiO_2$ microspheres.
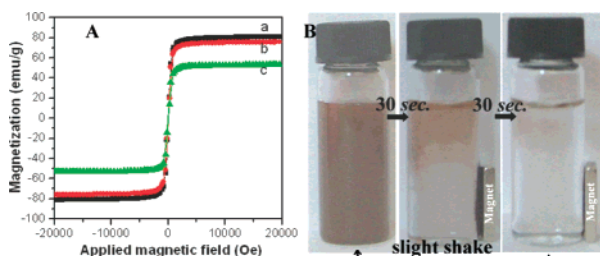
Figure 2. (A) The magnetic hysteresis loops of (a) Fe_3O_4 particles, (b) $Fe_3O_4@nSiO_2$, and (c) $Fe_3O_4@nSiO_2@mSiO_2$ microspheres, and (B) the separation−redispersion process of $Fe_3O_4@nSiO_2@mSiO_2$ microspheres.

isotherms exhibit IV-type curves for the microspheres (Figure S4). The mesopore size distribution (Figure S4, inset) exhibits a sharp peak centered at the mean value of 2.3 nm, indicating a uniform mesopore. The BET surface area and total pore volume are calculated to be 365 m^2/g and 0.29 cm^3/g, respectively. Wide-angle XRD patterns (Figure S5) show that the microspheres have diffraction peaks similar to that of the parent Fe_3O_4 particles, suggesting that the Fe_3O_4 particles were well retained in the silica matrix. Magnetic characterization using a magnetometer at 300 K indicates that the Fe_3O_4, $Fe_3O_4@nSiO_2$, and $Fe_3O_4@nSiO_2@mSiO_2$ microspheres have magnetization saturation values of 80.7, 78.0, and 53.3 emu/g (Figure 2A), respectively. Additionally, no remanence was detected for all of the samples. The magnified hysteresis loops further confirmed the superparamagnetism of the particles (Figure S6). The Fe_3O_4 content of $Fe_3O_4@nSiO_2@mSiO_2$ microspheres is calculated to be 65 wt %, indicating a high magnetization. As a result, the microspheres in their homogeneous dispersion show fast moment to the applied magnetic field (1000 Oe) and redisperse quickly with a slight shake once the magnetic field is removed (Figure 2B). It suggests that the microspheres possess excellent magnetic responsivity and redispersibility, which is an advantage to their applications.

Microcystins, such as MC-RR, MC-YR, and MC-LR, are disocyclic heptapeptides (Figure S7) with molecular weights of about 1000 Da. Numerous research results have indicated that MCs are extremely toxic and are produced in cyanobacterial blooms widely occurring in many eutrophic waters. Conventional approaches such as coagulation and sand filtration are effective for the removal of particulate cyanobacterial cells but not for the dissolved toxins. Activated carbon can be used to remove MCs, but it requires large carbon doses due to deficiency of accessible mesopores for adsorption of large MCs.[13] Chlorination and ozonation could be used for removing MCs, but the required high dosage may result in the formation of carcinogenic substances.[14] Biological methods require a long reaction time and are thus not

viable.[15] Here, we attempt to explore the applicability for the removal of MCs by using our magnetic mesoporous silica spheres. A low dose (0.05 mg/μg MCs) of the microspheres can be used to remove MC-RR, MC-LR, and MC-RY from their aqueous solution with a magnet. The removal efficiencies were analyzed by using the high-pressure liquid chromatography (HPLC) (see Supporting Information for experimental details). The results indicate that 95.4% MC-RR, 97.2% MC-YR, and 97.5% MC-LR can fast be removed in one isolation process within 60 s (Figure S8). Such high removal efficiency is mainly attributed to the high surface area from the numerous accessible mesopores. Additionally, after extraction of the trapped MCs with acetonitrile/water mixture, the microspheres can be reused with MC removal efficiency higher than 90% even after used for eight times (Figure S9; see Supporting Information for experimental details).

In conclusion, we have demonstrated the synthesis of superparamagnetic microspheres with an $Fe_3O_4@SiO_2$ core and perpendicularly aligned mesoporous SiO_2 shell. The microspheres possess very high magnetization, high surface area, large pore volume, and uniform accessible mesopores. It was found that the high-magnetic mesoporous silica microsphere can be used as a reusable absorbent for fast, convenient, and highly efficient removal of MCs. Additionally, because of the useful magnetic properties and unique microstructure, the microspheres may provide great promise for many applications such as magnetically controlled drug delivery and so on.

Supporting Information Available: Experimental procedures, N_2 sorption isotherms, pore size distribution, XRD patterns, chemical structure of microcystins, and HPLC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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