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Fluorescent Functionalized Mesoporous Silica for Radioactive Material Extraction

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Mesoporous silica with covalently bound salicylic acid molecules incorporated in the structure was synthesized with a one-pot, co-condensation reaction at room temperature. The as-synthesized material has a large surface area, uniform particle size, and an ordered pore structure as determined by characterization with transmission electron microscopy, thermal gravimetric analysis, and infrared spectra, etc. Using the strong fluorescence and metal coordination capability of salicylic acid, functionalized mesoporous silica (FMS) was developed to track and extract radionuclide contaminants, such as uranyl [U(VI)] ions encountered in subsurface environments. Adsorption measurements showed a strong affinity of the FMS toward U(VI) with a Kd value of 10^5 mL/g, which is four orders of magnitude higher than the adsorption of U(VI) onto most of the sediments in natural environments. The new materials have a potential for synergistic environmental monitoring and remediation of the radionuclide U(VI) from contaminated subsurface environments.

Keywords fluorescent functionalization; mesoporous silica; radioactive material

INTRODUCTION

Mesoporous silica materials with a large surface area, ordered pore structure, and controlled particle size have been shown to be ideal host or carrier materials for functional molecules or nanoparticles such as inorganic dyes (1–7), organic semiconducting quantum dots, (8–12) and bio-molecules (8–14). Therefore, mesoporous silica materials have been applied in a wide variety of different areas such as catalysis, separation, bio-imaging, and drug delivery (1–21). Besides non-covalently encapsulating guest materials (encapsulation method) (8–9), chemical functionalization is widely used to turn the chemically inert surface of mesoporous silica into desired reactive surfaces for various applications. Consequently there have been significant basic science efforts to functionalize the surface of mesoporous silica (1–7) (10–21). The approaches to functionalize mesoporous silica can be generally divided into co-condensation (one-pot synthesis) (22–25) and grafting (post-synthesis modification) (15–17) according to the modification procedure before or after mesoporous silica formation. The choice of the functionalization method depends on the desired properties for a particular application (19).

In addition to the surface chemistry of the functional groups, the engineered forms and morphologies of mesoporous silica are important for enabling the required performances (20) in applications such as separation. For example, mesoporous nanoparticles with specific surface functional groups are of great interest for selectively sequestering various aqueous radionuclide and metal ions from groundwater and wastewater (26–29). The high ionic selectivity, large sorption site density, fast sorption kinetics, and stable silicate structure yield a potentially efficient material for capturing metal and radionuclide ions from contaminated groundwater. At the same time, materials with appropriate particle sizes can be used to monitor the transport of the material in natural and engineered environments to assess the fate and transport of contaminants and colloidal particles in subsurface environments, if optical labels can be attached to these particles (30–34).

A great deal of effort has recently been devoted to the controlled synthesis of mesoporous silica with specific morphologies, particle sizes, and pore structures (35–40). For example, Cai et al. have reported a route for synthesizing mesoporous silica with various morphologies at the nanometer (average size of 100 nm) and micrometer (average size of 1 μm) scales by varying the concentration of surfactant and tetraethyl orthosilicate (TEOS) (38). Ordered mesoporous silica with radially-oriented mesochannels has been prepared using anionic surfactants (N-lauroylsarcosine sodium) as templates (39). And the group of Thomas Bein has synthesized mesoporous silica nanoparticles in the form of stable colloidal suspensions with 50 to 100 nm particle sizes.
sizes from concentrated precursor solutions with high yields by using triethanolamine (TEA) as a substitute for the more commonly used hydrolysis initiators NaOH or NH₄OH (40). Additionally, a wide range of functionalized mesoporous materials has been studied for selective binding of radioactive elements (20,41,42). However, there has been no report of a controlled synthesis of fluorescent mesoporous nanoparticles or their application based on simultaneous selective binding and optical tracking.

In this paper, we developed a one-pot method for synthesizing fluorescent functionalized mesoporous silica (FMS) with a uniform particle size and ordered pore structure for binding and potentially monitoring radionuclides. The FMS structure and the integration of functional molecules into the silica host matrix were characterized by transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), and infrared (IR) spectra, etc. The strong fluorescence and adsorption affinity toward radionuclide ions such as U(VI) (K_d value of 10^5 mL/g) of the FMS were demonstrated by fluorescence and adsorption measurements. We therefore conclude that FMS can be used as a simultaneous fluorescent tracking and remediation reagent to extract the radionuclide U(VI) from contaminated sediments.

EXPERIMENTAL SECTION

Chemicals

All chemicals were used directly without further purification, including salicylic acid (SA, minimum 99.8%, Sigma-Aldrich), N, N-dimethylformide (DMF, anhydrous, 99.8%, Sigma-Aldrich), 1,1'-carbonyldiimidazole (CDI, reagent grade, Aldrich), aminopropyltriethoxysilane (APTES, 99%, Sigma-Aldrich), ethanol (anhydrous, Sigma Aldrich), cetyltrimethylammonium chloride solution (CTAC, 25 wt% solution in water, Aldrich), TEOS (Fluka), TEA (minimum 98%, Sigma), and deionized (DI) water. Hydrochloric acid (HCl, 37%, A.C.S. Reagent, Sigma-Aldrich) and ethanol were used for template extraction.

Material Synthesis

Fluorescent mesoporous silica nanoparticles were synthesized by combining Fryxell’s method of activation of SA (18) and Bein’s synthesis of a colloidal suspension of nanosized mesoporous silica (40,44,45). FMS was synthesized by controlling the hydrolysis of TEOS using organic amine. SA is activated by CDI in DMF solution and then linked to APTES for further functionalization of FMS. Detailed synthesis is as below.

Activation of SA by CDI and Binding with APTES

The reaction equation of SA activation is shown in Fig. 1a. SA (2.76 g, 20 mmol) was dissolved in 50 mL of DMF. Then CDI (3.243 g, 20 mmol) and 12 mL of DMF were added to the above solution. This mixture was stirred under nitrogen for 1 h until the evolution of CO₂ ceased. Then APTES (4.68 mL, 20 mmol) was added into the mixture to link with activated SA (Fig. 1b). The final clear solution was stirred under nitrogen for 16 h and denoted as APTES-SA.

Synthesis of FMS

Fluorescent mesoporous silica nanoparticles were prepared with a modified method based on Bein’s approach (40,44,45). In the typical preparation of fluorescent mesoporous silica nanoparticles (e.g., molar ratio of TEOS: TEA = 1:4, reaction time 3 h, and molar ratio of APTES-SA: TEOS = 1:10), water (6.4 mL), ethanol (1.05 mL), and CTAC (1.04 mL, 25 wt% CTAC solution) were mixed and stirred at room temperature for 30 min. TEA (1.85 g) was subsequently added to the mixture and the solution was stirred for 1 h until it dissolved. TEOS (0.692 mL) and APTES-SA (1.05 mL) were also added into the mixture and stirred for 3 h at room temperature. Figure 1c shows a cartoon of the synthesized FMS in which SA molecules were bonded to the wall through a co-condensation reaction. The amounts of TEA, TEOS, and APTES-SA as well as the reaction time were varied to investigate their effects on the properties of particles. In the following descriptions, the samples were labeled to reflect the molar ratio of TEOS to TEA, the reaction time, and the molar ratio of TEOS to APTES-SA. For example, S4-0.5-0.1 stands for a TEOS: TEA ratio of 1:4, a reaction time of 0.5 h, and an APTES-SA: TEOS ratio of 1:10. The synthesis may also be done using biodegradable and inexpensive block copolymer templates (46).

Extracting surfactant templates from the fluorescent mesoporous silica nanoparticles proceeded as follows: Ethanol (30 mL) was added into the translucent, colloidal...
aqueous suspension of the mesoporous materials. The resulting precipitates were washed by repeated centrifugation at 10,000 rpm for 10 min and then re-dispersed in ethanol/DI H$_2$O (1:1) under sonication. Concentrated hydrochloric acid (3 mL) in ethanol (240 mL) was used for template extraction. Usually, the sample (1.0 g) was stirred in a 100 mL extraction solution at room temperature for more than 6 hours. This procedure was repeated three times. Subsequent washing was performed by repeated centrifugation at 10,000 rpm for 10 min and re-dispersion in DI H$_2$O under sonication. All products were suspended and stored in DI H$_2$O for further characterization and use.

Samples for absorbance and fluorescence measurements were prepared by diluting stock solutions of the different samples and then separating the solid from DI H$_2$O by centrifuging with Amicon Ultra-4 centrifugal filter devices (low-binding Ultracel membranes [30 K Dalton]) at 5,000 rpm for 10 min. The supernatant was discarded.

**Characterization**

TEM analysis was performed on a JEOL JSM-2010 TEM microscope operated at 200 kV. The surface area was determined using Quantachrome Autosorb Automated Gas Sorption Systems. The Brunauer-Emmett-Teller (BET) surface area was obtained with the single-point adsorption method. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted with a TGA/DSC 1 (Mettler Toledo) thermogravimetric analyzer in argon at a scan rate of 10°C/min from room temperature to 800°C. Absorbance and fluorescence measurements were performed on a Tecan Safire$^2$ Microplate reader system equipped with ultraviolet-visible (UV-Vis) fluorescence and an absorbance reader ($\lambda_{\text{ex}} = 304$ nm, $\lambda_{\text{em}} = 436$ nm). Uranyl ion adsorption onto the material was measured with UV-Vis recording spectrophotometry (UV-2501 PC, Shimadzu Scientific Instruments, Columbia, MD). FTIR spectra were recorded with a Nicolet iS10 spectrometer (Thermo Scientific) at a resolution of 1 cm$^{-1}$ or higher, employing a diamond Smart ITR accessory.

**RESULTS AND DISCUSSION**

The morphology of the synthesized FMS changes with the ratio of TEOS:TEA, the reaction time, as well as with the ratio of APTES-SA:TEOS (Fig. 2). The FMS (S4-3-0.1) sample obtained under typical conditions (TEOS: TEA ratio of 1:4, a reaction time of 3 h, and an APTES-SA: TEOS ratio of 1:10) exhibits a spherical morphology with a uniform particle size of about 230 nm and a radially aligned, pore structure (Fig. 2a). The inset in Fig. 2a is a higher resolution image showing the pores packed in this radial configuration. The molar ratio of TEOS: TEA was varied from 1:4 to 1:1 to investigate its effect on the particle size of fluorescent mesoporous silica. Small mesoporous silica particles of about 120 nm were obtained by decreasing the TEOS: TEA ratio to 1:1 while keeping all other conditions the same (Fig. 2b). The trend of decreasing particle sizes with increasing TEOS:TEA ratios is consistent with the results observed for the pure mesoporous silica nanoparticles synthesized by Möller et al. (38). However, the variation of the amount of TEA did not significantly affect the pore size of the mesoporous nanoparticles (Fig. 3).

We also studied the influence of the reaction time on the formation of FMS to study the growth process of the fluorescent mesoporous silica nanoparticles. The TEM image of S4-0.5-0.1 (Fig. 2c) and S4-24-0.1 (Fig. 2d) show the morphology of the sample obtained after 0.5 h and 24 h of reaction time while all other conditions were kept the same. Silica particles began to form after the mixture was stirred at room temperature for 0.5 h, but at this stage no individual spheres could be detected, the formed silica particles...
were fused together (Fig. 2c). Typically, the complexation of silicon species with TEA resulting in silatranes requires reaction times of several hours. The agglomeration observed is probably due to the fast hydrolysis and condensation of TEOS (38). When the mixture had been allowed to react for 3 h, silica particles became separated with a particle size of 230 nm (Fig. 2a). The particle size of FMS increases to about 400 nm for a reaction time of 24 h (Fig. 2d).

The effect of the amount of APTES-SA was also investigated. The mesoporous structure of FMS did not change significantly when the amount of APTES-SA was small (Figs. 2a, b, d), but the particle size decreased to about 100 nm when only one fifth of the normal amount of APTES-SA was used (Figure 2e). The synthesized product, however, no longer displayed the mesoporous structure or spherical morphology when the ratio of APTES-SA:TEOS was higher than 1:2.5 (Fig. 2f). Large pieces of irregular particles resulted instead of mesoporous spheres. It was further found that adding APTES, a hydrophilic organosilane, in the co-condensation reaction caused the particle sizes of silica to increase (23).

To prove the existence of mesoporosity, the material was precipitated with ethanol from the reaction solution, washed with ethanol/HCl, and dried for a N$_2$ sorption measurement (Fig. 3). Figures 3a and 3c are the typical isothermal curves for samples S4-3-0.1 and S1-3-0.1. The calculated surface area according to the BET theory was 719 m$^2$/g for sample S4-3-0.1, with a pore volume of 1.12 cm$^3$/g. For S1-3-0.1, the BET surface area was 824 m$^2$/g with a pore volume of $\sim$1.05 cm$^3$/g. The average mesopore diameter for samples S4-3-0.1 and S1-3-0.1, according to the Barrett-Joyner-Halenda (BJH) model, was 4.3 nm and 3.5 nm, respectively (Figs. 3b and d). These results indicate that the FMS indeed have a large surface area and porous structure.

We carried out TGA and IR analyses on sample S4-3-0.1 to confirm the existence of SA molecules. The sample was heated to 900°C in air at a heating rate of 10°C/min. The weight loss curve (Fig. 4a) showed a 1% weight loss at about 100°C, which was likely caused by the evaporation of residual water in the sample. There was about another 4% weight loss from around 200°C to 400°C, which was attributed to the removal of surfactant residue (37), even though no CH groups were detectable in the IR spectra (Fig. 4b).
The 9% weight loss after 400°C was attributed mainly to the organic parts of SA and APTES. Assuming that the reactions were complete, the theoretical weight loss calculated from the molar SA-APTES:TEOS ratio of 1:10 was ~20%. These results suggested that about half of the SA-APTES molecules were immobilized on the silica surface. IR spectra (Figs. 4b, c, and d) of sample S4-3-0.1 also confirmed the incorporation of SA-APTES molecules. The vibration seen at around 1050 cm⁻¹ in Fig. 4c could be indexed as the stretch of C-O in SA. The IR bands at around 1650 cm⁻¹ and 1550 cm⁻¹ (Fig. 4d) could be indexed as C=O stretching and N-H bending vibrations of an amide (Fig. 1b).

SA incorporated in the FMS produces fluorescence and has an excellent metal coordination capability that can be used to track FMS in the environment (41) and to remediate radionuclide metal ions in wastewater and contaminated groundwater. The fluorescence and UV-Vis absorption spectra were recorded using a diluted FMS suspension after the reactant had been removed reactant by repeated centrifugation filtration and washing. The incorporated SA in the FMS showed fluorescence at around 430 nm when excited at 310 nm (Fig. 5a). The SA density in the sample is ~9 wt. % (functional group/silica) estimated from the fluorescent spectra. The filtrate after washing displayed very little fluorescence (data not shown), indicating that the fluorescent group was stable and covalently linked to the mesoporous structure. SA is a well-known ligand with a strong affinity towards metal ions (18). With its large surface area and pore structure, the SA-FMS showed excellent selectivity and a good capacity to extract radionuclide ions from contaminated solutions. Using U(VI) as an example, the equilibrium U(VI) adsorption (Fig. 5b) follows the Langmuir adsorption model

\[
\frac{C_{\text{ads}}}{C_{\text{eq}}} = \left( \frac{C_{\text{max}}K_{\text{d}}}{C_{\text{eq}}K_{\text{d}} + 1} \right) \frac{1}{C_{\text{eq}} + \frac{1}{C_{\text{max}}}}
\]

where \(C_{\text{ads}}\) is the amount of metal ion U(VI) adsorbed at equilibrium per gram of adsorbent, FMS. \(C_{\text{eq}}\) is the equilibrium concentration of aqueous U (VI), \(C_{\text{max}}\) is the maximum number of surface sites per gram of FMS, and \(K_{\text{d}}\) is commonly referred to as the Langmuir constant, is the equilibrium constant of the sorption reaction here. The loading capacity \(C_{\text{max}}\) that was determined from the isotherm was 3333.3 µg U(VI)/g FMS, \(K_{\text{d}}\) was 37.5 mL/µg, and at low concentration range, a distribution coefficient, \(K_{\text{d}} (\text{mg/L})\), was as high as 10⁻⁵ mL/g. This demonstrated the strong affinity of the SA-FMS towards U(VI) in the synthetic ground water, that has the same chemical composition as the groundwater at the US Department of Energy’s Hanford site with a pH 8.2 and an ionic strength of 6.3 mM, under typical groundwater U(VI) concentrations. The \(K_{\text{d}}\) value is four orders of magnitude higher than the U(VI) affinity toward most sediments in natural environments (47–49). This result implied that the here synthesized FMS is an efficient remediation material to capture radionuclides, such as U(VI), from contaminated groundwater and sediments at U(VI)-contaminated sites.

The saturation loading capacity is determined by the reactions of the uranyl U(VI) ions with other ionic species in the simulated ground water according to the reaction below at the specific pH 8.3 (50).

\[
>\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 \rightarrow \text{SOUO}_2\text{HCO}_3^- + 2\text{H}^+
\]

where >SOH denotes the adsorption site and SOUO₂HCO₃⁻ is adsorbed U(VI). The loading is limited by the HCO₃⁻ concentration and is much lower than heavy metals such as Hg.

**CONCLUSION**

In summary, we have synthesized a fluorescent FMS material with a narrow particle size distribution and ordered pore structure using a one-pot, co-condensation reaction. The synthesized FMS may be used as a reagent for simultaneous fluorescent tracking and radionuclide capture.
remediation. The material has a $K_d$ value of $10^5$ (mL/g) toward U(VI) adsorption, which is four orders of magnitude higher than the U(VI) adsorption to most sediments in natural environments. This opens the way for a new approach using large-surface-area mesoporous materials with desired functional molecules for synergistic environmental monitoring and remediation in contaminated sediments.

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