Functionalized Monolayers on Ordered Mesoporous Supports

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Mesoporous silica materials containing functionalized organic monolayers have been synthesized. Solid-state nuclear magnetic resonance suggests that a cross-linked monolayer of mercaptopropylsilane was covalently bound to mesoporous silica and closely packed on the surface. The relative surface coverage of the monolayers can be systematically varied up to 76 percent. These materials are extremely efficient in removing mercury and other heavy metals from both aqueous and nonaqueous waste streams, with distribution coefficients up to 340,000. The stability of these materials and the potential to regenerate and reuse them have also been demonstrated. The surface modification scheme reported here enables rational design of the surface properties of tailored porous materials and may lead to the synthesis of more sophisticated functionalized composites for environmental and industrial applications.

The synthesis of mesoporous silica has greatly expanded the possibilities for the design of open pore structures (*1*, *2*). Because of their large surface area and well-defined pore size and pore shape, these materials have great potential in environmental and industrial processes. However, many applications (such as adsorption, ion exchange, catalysis, and sensing) require the materials to have specific attributes such as binding sites, stereochemical configuration, charge density, and acidity (*3*). Here, we report the formation of organic monolayers within ordered mesoporous silica and show that these functionalized layers confer specific adsorption behavior for heavy metal ions.

Functional groups (thiol groups in this case) were introduced to the pore surface of mesoporous silica as the terminal groups of organic monolayers. The hydrocarbon chains aggregated and formed close-packed arrays on the substrate. The siloxane groups then underwent hydrolysis and ultimately became covalently attached to the substrate and cross-linked to one another. This material, called functionalized monolayers on mesoporous supports (FMMS), can efficiently remove mercury and other heavy metals (such as lead and silver) from contaminated aqueous and organic solutions. The distribution coefficient, K_d, has been measured to be as high as 340,000. [K_d is defined as the amount of adsorbed metal (in micrograms) on 1 g of adsorbing material divided by the metal concentration (in micrograms per milliliter) remaining in the treated waste stream.]

Mesoporous silica materials were synthesized in cetyltrimethylammonium chloride/hydroxide (CTAC/OH), silicate, and mesitylene solutions (*1*, *4*). The calcined mesoporous silica has a surface area of 900 m^2 g^{-1} and an average pore size of 55 Å, as determined by the gas adsorption technique and transmission electron microscopy (TEM). To prepare the FMMS material, we mixed tris(methoxy)mercaptopropylsilane (TMMPS) with mesoporous silica in an appropriate solvent (*5*). We selected TMMPS because it has been used previously to make functionalized monolayers (6) and the thiol groups have a high affinity for binding metals. The stoichiometry was based on the measured surface area (900 m^2 g^{-1}) and the assumption of 5×10^{18} molecules per square meter in a fully dense monolayer coverage, as indicated by previous solid-state nuclear magnetic resonance (NMR) studies (*7*). This mixture was stirred at room temperature overnight and then heated to reflux for 4 hours. After cooling to room temperature, the mixture was filtered, washed copiously with 2-propanol to rinse away any surplus TMMPS, and then dried under vacuum.

The population density and the quality of the functionalized monolayers on the mesoporous materials are greatly affected by two factors: the population of silanol groups and the number of adsorbed water molecules on the mesoporous silica surface. The silanols anchor the organic molecules to the silica surface. However, the calcining step used in preparing mesoporous silica dehydrates the silica surface and removes most of the silanols, which results in poor surface coverage (*8*). A proper amount of adsorbed surface water is also important because the hydrolysis reaction is one of the critical first steps in the process of building the monolayer. Ideally, just enough water for the siloxane hydrolysis would be associated with the surface. The presence of free water is detrimental to the efficient formation of a clean monolayer because of polymerization of TMMPS in solution (*9*).

To optimize reaction conditions for depositing alkoxysilane-based monolayers on mesoporous silica, we carefully rehydrated the silica surface, controlled the amount of surface adsorbed water, and used the proper solvent. Benzene and toluene were found to be optimum both for forming organic monolayers and for removing excess water through an azeotrope. Excess silane (at least fivefold) was used relative to the available surface area and the reaction mixture was boiled. The relative surface coverage was estimated on the basis of (i) the surface area of the support, (ii) the weight change after the functionalized monolayers were attached, and (iii) the ideal loading density that could be achieved on flat surfaces. These results were also verified by electron energy-dispersive spectroscopy (EDS). We systematically varied the population densities of functional groups on the mesoporous materials from 10 to 76% of full surface coverage. Because we used short chain alkane thiols to avoid blocking the pore channels, a monolayer coverage of 76% on mesoporous silica is considered a good result. Shorter molecules pack less efficiently than do longer molecules because of reduced van der Waals interactions between the pendant chains (*10*). A systematic illustration of the FMMS material is shown in Fig. 1, with each functional group binding one metal ion.

The FMMS material is a useful environmental remediation agent because it has a high affinity for binding mercury and other heavy metals. As shown by a TEM micrograph of FMMS with 76% coverage after

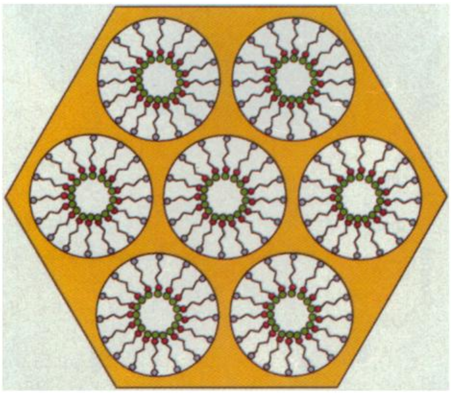

Fig. 1. Schematic drawing of FMMS. One end group of the functionalized monolayers is covalently bonded to the silica surface and the other end group can be used to bind heavy metals or other functional molecules.

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contact with a solution containing mercury ions (Fig. 2A), the ordered porous structures were preserved in the chemical treatment processes for attaching the functionalized monolayers. Although most mercury was evaporated under the electron beam and therefore was not visible in the TEM image, some mercury was detected in the EDS spectrum (Fig. 2B). The EDS also detected sulfur from the thiol group. Compositional analysis indicates that the relative concentration for sulfur and silica is 5.2 mmol per gram of silica, which is in excellent agreement with the gravimetric estimate (5.6 mmol per gram).

The structure of the functionalized monolayers and the chemical bonding can be studied by solid-state NMR experiments (*11*). A Chemagnetics NMR spectrometer was used for the NMR experiments (*12*). Single-pulse (SP) ^{13}C NMR spectra and peak assignments [Si-CH2(3)-CH2(2)-CH2(1)-SH] for samples with 25%, 76%, and mercury-laden 76% coverage of functionalized monolayers on mesoporous silicates, respectively, are shown in Fig. 3. For 25% coverage (Fig. 3A), the peak at 12.8 parts per million (ppm) was attributed to the methylene carbon group C3, directly bonded to the Si atom. The peak at 28.3 ppm was attributed to the other two methylene carbons (C2 and C1). An additional peak at 24.7 ppm (Fig. 3B) was observed for 76% coverage. This peak was assigned to the methylene carbon (C1) next to the -SH group on the basis of the chemical shifts reported for $CH_3(CH_2)_7SH$ (*11*).

The difference between Fig. 3A and Fig. 3B is attributable to a different molecular conformation for the organic monolayers at different coverages. At low surface coverage, the carbon chains can adapt a wide range of conformations; therefore, the peaks for C2 and C1 cannot be distinguished because of conformational heterogeneity. At higher population densities, all of the carbon chains are near one another and have a more upright orientation with respect to the silica surface. The molecules have a higher degree of ordering that narrows the linewidths in the ^{13}C spectrum and allows better resolution of the peaks for all three carbons.

The close-packed conformation of the carbon chains is also evident in ^{29}Si NMR results (Fig. 4). Relative peak intensities in ^{29}Si cross-polarization magic angle spinning (CP-MAS) are not strictly quantifiable because of differences in relaxation behavior. Therefore, we used the Bloch-decay pulse sequence (single-pulse excitation) with long recycle times to obtain data that allowed us to quantify the molecular composition of these materials. The large peak at −111 ppm is from the silica support. In Fig. 4A, three additional peaks from −50 to −80 ppm are identified for 25% coverage, corresponding to three different environments for the siloxane groups in the functionalized monolayers (*13*): (i) isolated groups that are not bound to any neighboring siloxanes, (ii) terminal groups that are only bound to one neighboring siloxane, and (iii) cross-linked groups that are bound to two neighboring siloxanes. Among the three, the most dominant peak comes from the terminal group. For 76% coverage (Fig. 4B), the molecules are closer to one another, and the most predominant peak corresponds to the cross-linked siloxane group; the isolated siloxane group is absent. The transition from disordered conformation at low surface coverage to close-packed conformation at high coverage is illustrated in Fig. 5.

The ^{13}C spectrum for 76% coverage with mercury (Fig. 3C) shows that the three resonances corresponding to the C1, C2, and C3 methylene carbons observed in Fig. 3B are still discernible but become much broader. A new broad peak appears at 37 ppm, and the peak at 24.7 ppm markedly decreases in height. This result suggests strong chemical bonding between the mercury and thiol group, which causes the shift of the peak corresponding to C1 attached to the thiol group. The next C2 group is also affected, but to a lesser degree. The continued presence of the peak at 24.7 ppm indicates that the thiol groups are not yet saturated with mercury.

The chemical bonding between mercury and the thiol group was further confirmed by extended x-ray absorption fine structure (EXAFS) studies. A schematic of the proposed structure is shown in Fig. 5C (*14*). When the mercury binds to the thiol group, the Hg–S and Hg–O bond lengths are 2.4 ± 0.01 Å and 2.14 ± 0.01 Å, respectively. The mercury atoms on the two adjacent thiol groups are linked by the same oxygen atom, with a Hg-Hg separation of 3.99 ± 0.05 Å, and the bond angle of Hg–O–Hg is calculated to be 137°.

The ability of FMMS materials to remove mercury and other heavy metals from

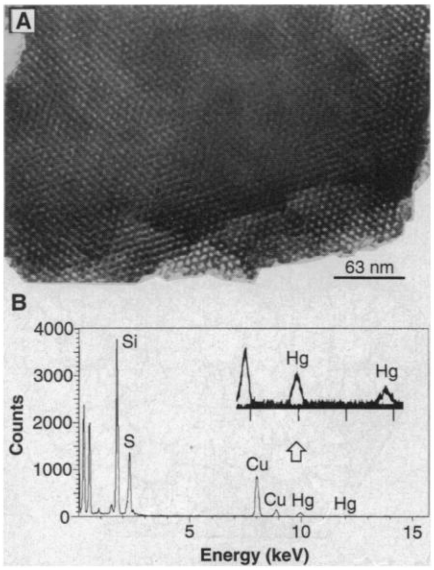

Fig. 2. A TEM micrograph (**A**) and EDS spectrum (**B**) of the mercury-laden FMMS. Mercury and sulfur on the organic layers can be observed on the EDS spectrum.

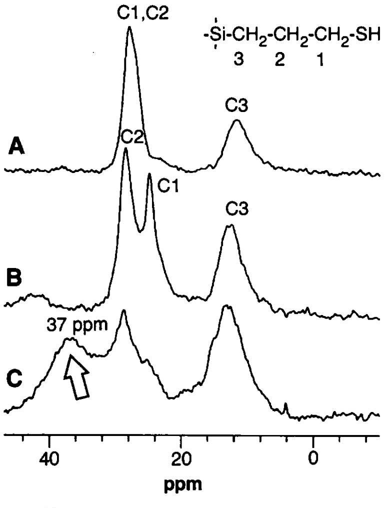

Fig. 3. ^{13}C NMR spectra of organic monolayers on mesoporous silica with the peak assignments. (**A**) At 25% coverage, C1 and C2 cannot be separated because of conformational heterogeneity. (**B**) At 76% coverage, C1 and C2 are clearly resolved, suggesting a more homogeneous environment. When the functionalized groups bind to mercury, all the peaks become broadened, and the original C1 peak almost disappears. (**C**) A new peak is observed at 37 ppm for C1 because of the mercury thioalkoxide.

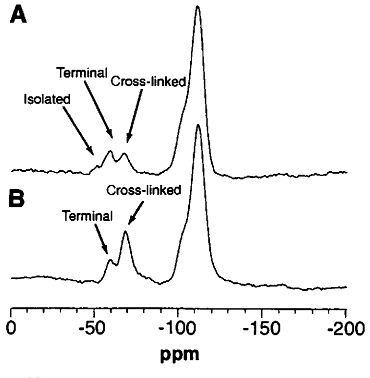

Fig. 4. ^{29}Si NMR spectra of FMMS with 25% and 76% coverage. The peak at −111 ppm is from the silica support. (**A**) At 25% coverage, three additional peaks from −50 to −100 ppm are observed, corresponding to isolated, terminal, and cross-linked conformations. Among the three, the largest peak is from the terminal silanol group. (**B**) At 76% coverage, the peak from the isolated silanol group disappears and the largest peak is from the cross-linked siloxane group.

contaminated solutions was tested under a wide range of conditions. Mercury and heavy metal contamination is a serious problem at waste-contaminated sites (*15*). Industrial and civilian sources deposit up to 10,000 tons of mercury into the environment every year (*16*). Table 1 shows the ion concentrations of several simulated contaminated solutions before and after treatment with FMMS with 10% and 25% surface coverage. The solutions simulated Savannah River Site (SRS) radioactive wastes in holding tank L or nonradioactive vacuum pump oil waste from the SRS tritium facilities (*17*). A single treatment with FMMS reduced the mercury concentration to well below U.S. Environmental Protection Agency elemental limits for hazardous wastes and even drinking water standards. The silver concentrations also were reduced below the detection limit.

Similar results were obtained for lead (except at pH 3). These tests also showed that background ions, such as sodium, barium, and zinc, do not bind to FMMS, and FMMS remains effective in the presence of high concentrations of such ions. As a test of thermal and hydrolytic stability, we heated mercury-loaded FMMS in air and in water. In situ NMR experiments indicated that the bonding between mercury and FMMS and the structure of the organic monolayers are stable up to 125°C. The hydrolytic stability was demonstrated by heating the mercury-loaded FMMS in water at 70°C for 24 hours. Only a very small amount of mercury was released during this process. To regenerate the used FMMS materials, we washed mercury-loaded FMMS with a concentrated HCl (12.1 M) solution. This resulted in 100% removal of the loaded mercury. The regenerated materials retained a loading capacity of 210 mg of Hg per gram of FMMS. The FMMS materials remained effective even after several regeneration and reuse cycles.

Compared with conventional remediation technologies for heavy metals (*18*), the FMMS materials have (i) high metal loading capacity because of the densely populated thiol groups on the large surface area mesoporous oxides, and (ii) high selectivity of heavy metals against background electrolytes. FMMS should bind metallic, inorganic, organic, charged, and neutral mercury compounds and can be used in a variety of media such as water, oil, and gas. The mercury-loaded FMMS should also have good long-term durability as a permanent waste form. The small pore size (<20 nm) should prevent bacteria (at least 2000 nm in size) from solubilizing the bound mercury and forming deadly methyl mercury (*16*).

Beyond its immediate applications in environmental cleanup, FMMS provides a unique opportunity to introduce molecular binding sites and to rationally design the surface properties (for example, wettability and charge density distribution) of mesoporous materials. In addition, functionalized monolayers have been widely investigated in materials synthesis (*19–21*). Specific groups in the functionalized monolayers can be used to attach new functional groups (*20*) or to stimulate mineral deposition (*21*). We believe the combination of ordered mesoporous structures and functionalized monolayers can play a pivotal role in the development of a new generation of hierarchical structures and functionalized composites.

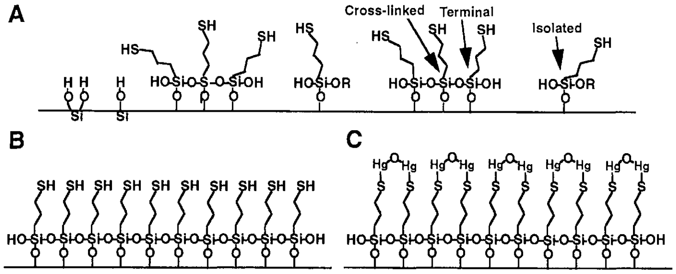

Fig. 5. Schematic conformations of functionalized monolayers on the surface under different conditions. (**A**) Disordered molecules at 25% surface coverage. (**B**) Close-packed at 75% surface coverage. (**C**) Containing mercury at 75% surface coverage.

Table 1. Analyzed concentrations of toxic metal contaminants regulated under the Resource Conservation and Recovery Act in waste solutions before and after FMMS treatment.

Solution	Concentration (ppm)							K_d of Hg
	Hg	Ag	Cr	Pb	Ba	Zn	Na	
				No treatment				
WW, pH 3	6.20	1.80	1.79	7.22	7.18	3.96	2220	
WW, pH 7	6.00	0.45	1.13	5.25	7.12	2.75	2212	
WW, pH 9	6.35	1.04	0.58	2.90	7.15	1.32	2222	
Oil	12.10							
				After treatment, 10% FMMS				
WW, pH 3	0.0108	<0.005	1.45	1.66	7.60	3.93	2236	55,670
WW, pH 7	0.0064	<0.005	0.70	0	7.35	2.23	2202	90,974
WW, pH 9	0.0056	<0.005	0.71	0	7.40	1.41	2218	110,056
Oil	0.635							1,806
				After treatment, 25% FMMS				
WW, pH 3	0.0008	<0.005	1.67	2.26	8.64	5.06	2185	290,588
WW, pH 7	0.0008	<0.005	0.07	0	8.21	1.54	2114	281,213
WW, pH 9	0.0007	<0.005	0	0	8.82	1.19	2201	340,141
Oil	0.06							3,467

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4. Mesoporous silica materials were synthesized according to (*1*). Typically, CTAC/OH solution was prepared by batch contact of 29 weight % CTAC (Carsoquat CT-429, Lonza Inc.) with strongly basic ion exchange resin (DOWEX-1, Sigma; 0.2 g of resin per gram of 29 weight % CTAC solution). In order, 13 g of colloidal silica (Hi-Sil 233, PPG Industries), 51 g of tetramethylammonium silicate (10% SiO_2, TMA/Si molar ratio 0.5, SACHEM Inc.), and 28 g of mesitylene (Eastman Kodak) were added to each 100 g of CTAC/OH solution. The mixture was sealed in a Teflon-lined vessel and heated at 105°C for 1 week. The product was recovered by suction filtration, dried at ambient temperature, and calcined at 540°C for 12 hours under flowing air.
5. For synthesis of 10% FMMS samples, 2.0 ml of TMMPS was mixed with 1.288 g of mesoporous silica in 100 ml of chloroform. This mixture was stirred at room temperature for 5 days and then filtered. The collected solid was washed copiously with chloroform to rinse away any surplus mercaptan and then dried under vacuum. For synthesis of 25% FMMS samples, 4.32 g of mesoporous silica was suspended in 125 ml of reverse osmosis (RO) water and taken to reflux for 4 hours. After cooling to room temperature, the sample was centrifuged down, the water was decanted off, and the silica was air-dried for 5 days. This hydrated mesoporous silica was then suspended in 250 ml of toluene, treated with 30 ml of TMMPS, and taken to reflux for 4 hours. After cooling to room temperature, the reaction mixture was filtered. The solid was washed copiously with chloroform and dried under vacuum. For synthesis of 75% FMMS samples, 3.5 g of mesoporous silica was suspended in 100 ml of RO water and heated to reflux to 3 hours. The mixture was cooled and filtered. The wet product was placed in a round-bottom flask along with 250 ml of benzene. The flask was fitted with a Dean-Stark trap and the mixture was heated to reflux. The wet product was heavily aggregated for about the first half of the azeotropic distillation, and then it dispersed nicely. The Dean-Stark distillation was continued until 4.5 ml of water had been removed. This left ~2.0 ml of water dispersed across

the silica surface, which is approximately equal to four monolayers of water. This suspension was then treated with 20 ml of TMMPS, stirred overnight at room temperature, and heated to reflux for 4 hours. After cooling to room temperature, the mixture was filtered and washed thoroughly with 2-propanol and dried under vacuum to yield 6.2 g of derivatized material.

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12. The 75.0-MHz ^{13}C solid-state NMR experiments were carried out with a Chemagnetics spectrometer (300 MHz, 89-mm wide-bore Oxford magnet) using a double-resonance probe. For both pure and mercury-loaded FMMS samples, SP Bloch-decay and CP methods were used with ^1H decoupling. The dried powders were loaded into 7-mm zirconia rotors and spun at 3 to 4 kHz. Spectra were collected by an SP-excitation Bloch-decay method with a 5-μs (90°) ^{13}C pulse and a 10-s repetition delay. For all experiments, 40-ms acquisition times and a 50-kHz spectral window were used. The number of transients was 1000 to 3000. The power levels of the carbon and proton channels were set so that the Hartmann-Hahn match was achieved at 55 kHz in CP experiments with contact times of 3 ms and repetition delays of 5 s. A Lorentzian line broadening of 24 Hz was used for all ^{13}C spectra. The 59.3-MHz ^{29}Si NMR spectra were also taken for both samples using the SP Bloch-decay method with ^1H decoupling. A Lorentzian line broadening of 50 Hz and a repetition delay of 30 s were used for ^{29}Si spectra. Both ^{13}C and ^{29}Si NMR chemical shifts were referenced to TMS at 0 ppm.
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Manganese Oxide Mesoporous Structures: Mixed-Valent Semiconducting Catalysts

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Hexagonal and cubic phases of manganese oxide mesoporous structures (MOMS) have been prepared by means of the oxidation of $Mn(OH)_2$. The hexagonal MOMS materials form a hexagonal array of pores with an open porous structure, thick walls (1.7 nanometers), and exceptional thermal stability (1000°C). The walls of the mesopores are composed of microcrystallites of dense phases of Mn_2O_3 and Mn_3O_4, with MnO_6 octahedra as the primary building blocks. The calcined hexagonal MOMS have an electrical conductivity of 8.13×10^{-6} per ohm·centimeter, an average manganese oxidation state of 3.55, and a band gap of 2.46 electron volts. Catalytic oxidations of cyclohexane and *n*-hexane in aqueous solutions in a batch reactor show conversions of ~10 and ~8 percent, respectively. Characterization and catalytic data suggest that MOMS systems show significant enhancement in thermal stability with respect to octahedral molecular sieve materials.

Since their discovery at Mobil Corporation in 1992, mesoporous aluminosilicate materials (designated M41S) (*1*) have attracted considerable attention. Significant advances resulting from research in this area include novel properties of these materials (*2*), new synthetic chemistry (*1*–*4*), unique structures (*5*), and synthesis of related materials (*5*).

Oxides of transition metals have some advantages over aluminosilicate materials for use in electromagnetics, photoelectronics, and catalysis because transition metal atoms can exist in various oxidation states. However, syntheses and structures of transition metal oxides can be much more complicated than oxides of main group metals because of the multitude of different coordination numbers and oxidation states. Mesoporous structures of transition metals doped into aluminosilicates [Cr (*6*)] or transition metal oxides such as Ti (*7*), V (*8*), W (*3*, *5*), Zn (*9*), Nb (*10*), and Ta (*11*) have been reported. Most of these transition metal oxide mesoporous materials are insulators with transition metals in isolated oxidation states.

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