Heavy Metal Sequestration Using Functionalized Monolayers on Mesoporous Supports

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Functionalized Monolayers on Ordered Mesoporous Supports

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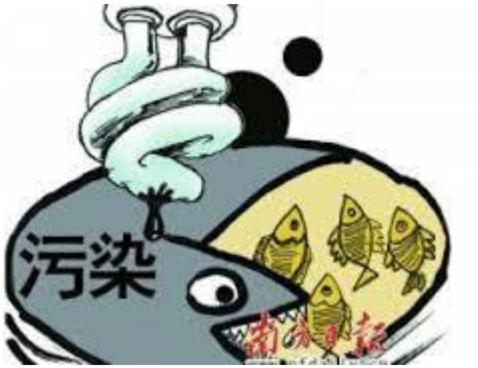
Mesoporous silica materials containing functionalized organic monolayers have been synthesized. Solid-state nuclear magnetic resonance suggests that a cross-linked monolayer of mercaptopropylsilane was covalently bound to mesoporous silica and closely packed on the surface. The relative surface coverage 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.

Background

Energy Saving Lamp



Batteries

Mercury Thermometer

Minamata Disease in Japan in 1950s

Smoke Pollution

Mercury pollution exists everywhere, which brings pain and disaster to people all over the world.

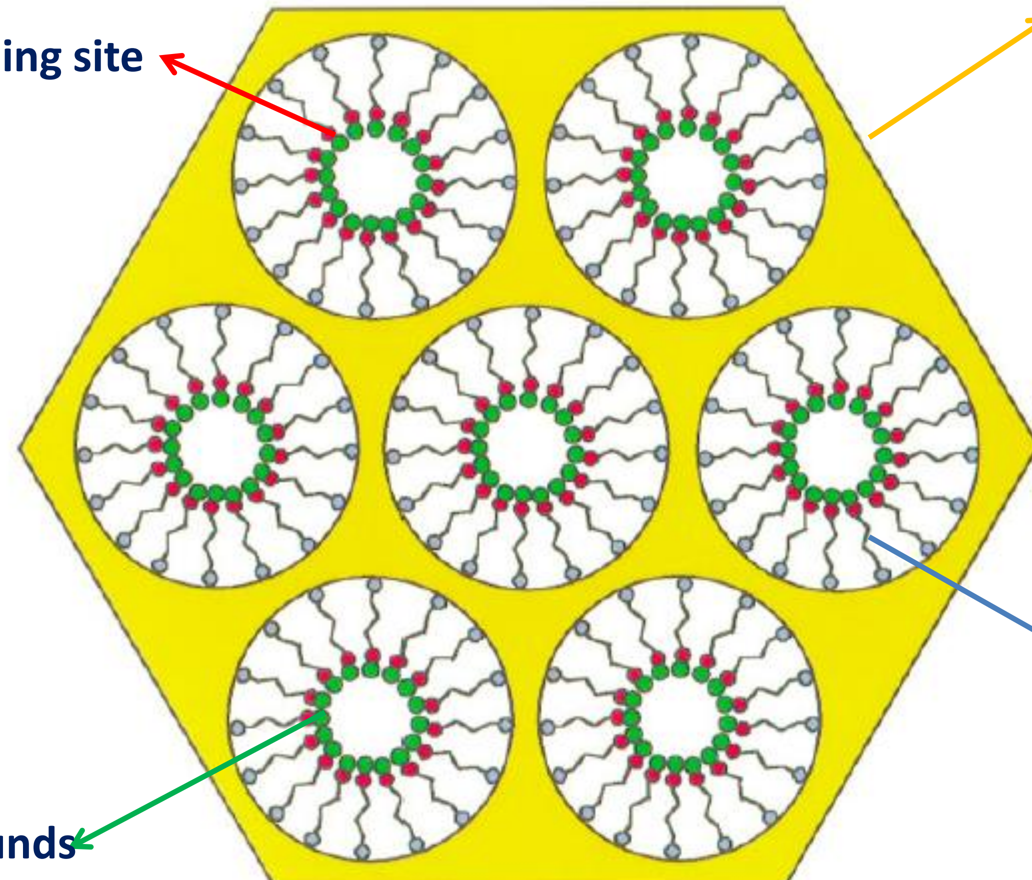
What?

This paper combines ordered mesoporous structures and functionalized monolayers for the removal of Hg contamination.

Thiols: Binding site

Ordered Mesoporous Supports

- Surface area: 900 m^2g^{-1}
- Pore size: 5.5 nm



Short hydrocarbon chains

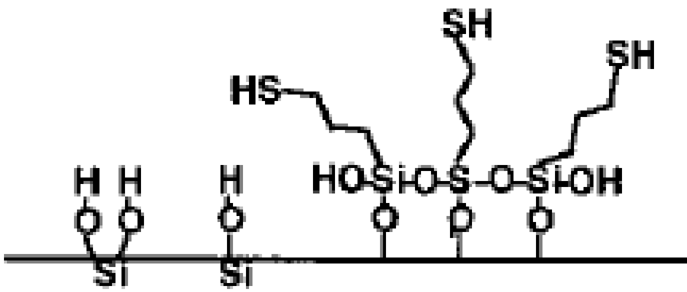
- Avoid blocking the channels

Hg compounds

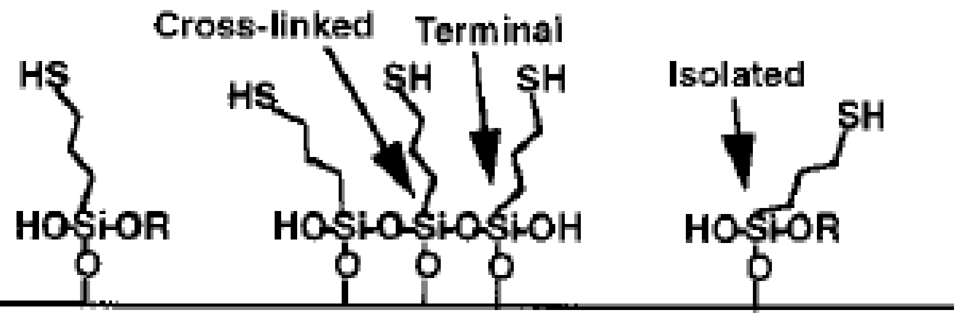
- Metallic, inorganic, organic, charged, and neutral compounds

Why?

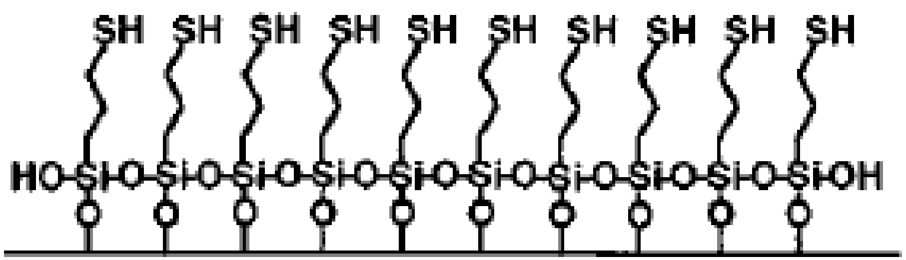
Disordered molecules



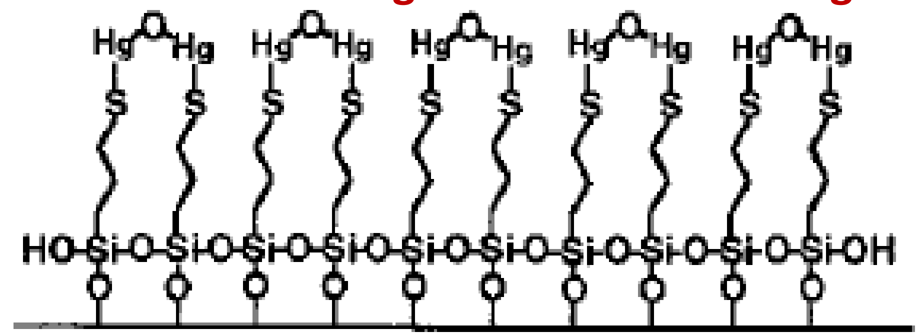
Chemical bonding between monolayers and supports



Ordered monolayers



Chemical bonding between thiol and Hg



How?

Challenges for preparation of the materials

- Enough Si-OH on the substrate for anchor of thiols;

- Enough water for hydrolysis of siloxane groups in thiols;

- Removal of free water to avoid polymerization of thiol layers.

Techniques

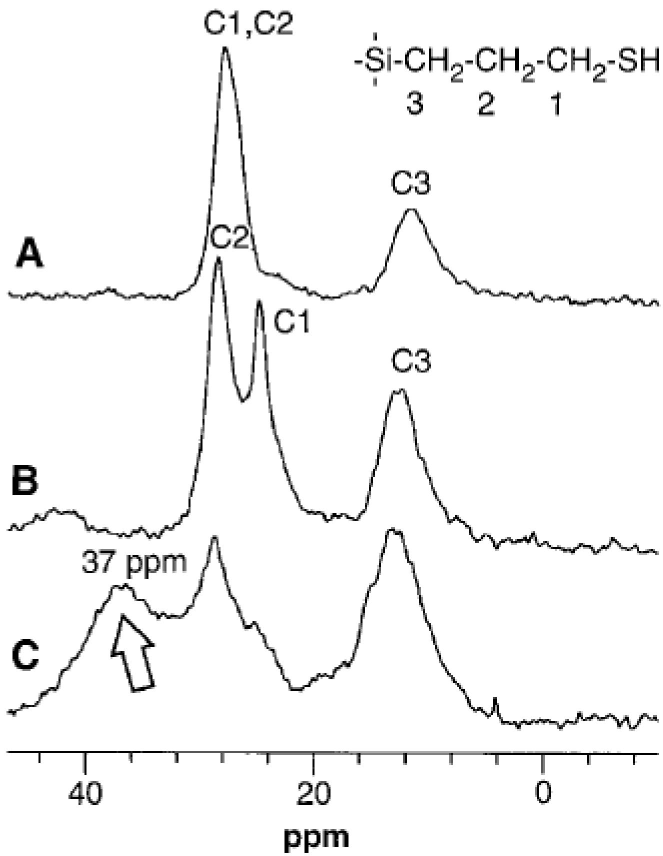
- Carefully rehydrated the silica surface;
- Controlled the amount of surface adsorbed water;
- Solvent: Benzene and toluene were optimum;
- Excess silane (at least fivefold);
- Systematically varied the population densities of functional groups on surface;

The Ability to Remove Heavy Metals

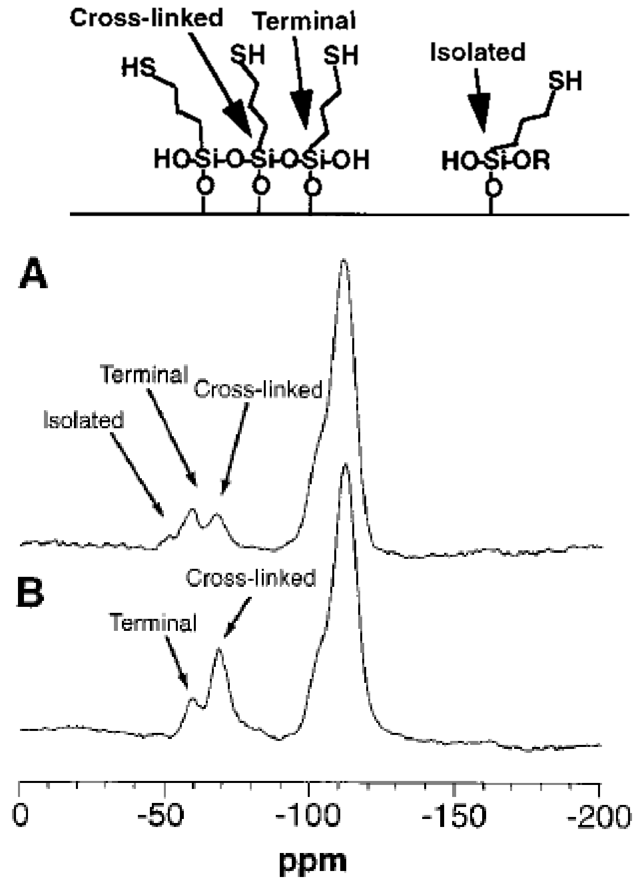
Table 1. Analyzed concentrations of toxic metal contaminants regulated under the Resource Conservation and Recovery Act in waste solutions before and after FMMS treatment.

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

Structure and Binding Study



^{13}C NMR spectra

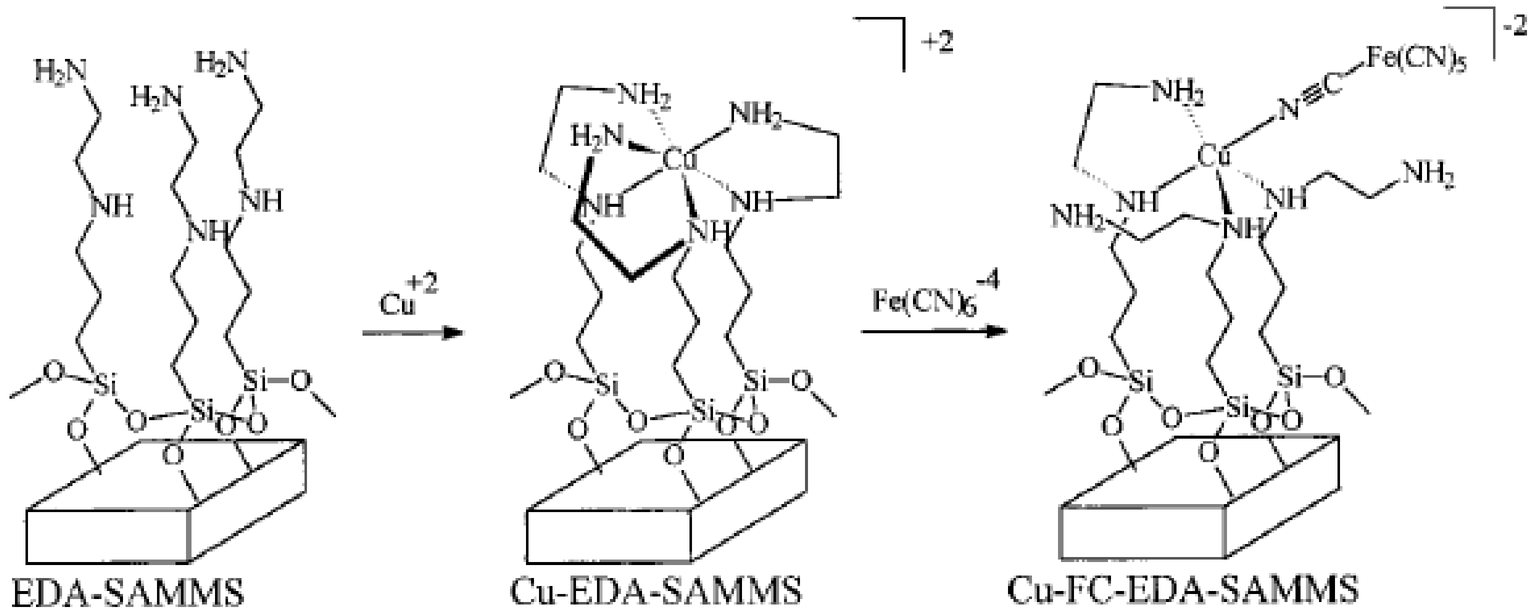


^{29}Si NMR spectra

A: 25% coverage
B: 76% coverage
C: Binding with Hg

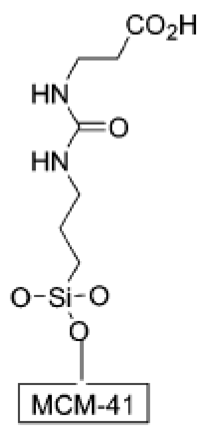
A: 25% coverage
B: 76% coverage

Cs Selective FMMS

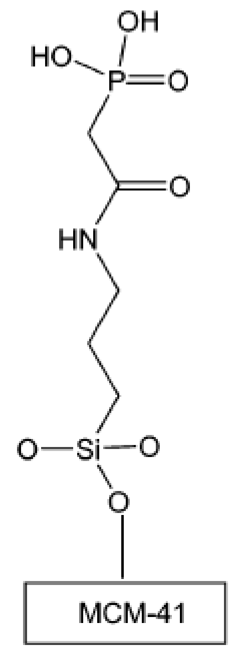


Lin, Y.; Fryxell, G. E.; Wu, H.; Engelhard, M., *Environmental science & technology* **2001**, 35 (19), 3962-3966.

Actinide Sequestration



Gly-UR-SAMMS



Ac-Phos Acid SAMMS

Fryxell, G. E.; Lin, Y.; Fiskum, S.; Birnbaum, J. C.; Wu, H.; Kemner, K.; Kelly, S., Environmental science & technology **2005**, 39 (5), 1324-1331.

Thanks For Your Listening!