A new thioether functionalized organic–inorganic mesoporous composite as a highly selective and capacious Hg²⁺ adsorbent†

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A new thioether functionalized organic–inorganic ordered mesoporous composite as a highly selective and capacious Hg²⁺ adsorbent was synthesized by one-step co-condensation of (1,4)-bis(triethoxysilyl)propane tetrasufide (BTESPTS, $(CH_3CH_2O)_3Si(CH_2)_3S–S–S–S(CH_2)_3Si(OCH_2CH_3)_3$) and tetraethoxysilane (TEOS), with tri-block copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) $EO_{20}PO_{70}EO_{20}$ as template.

Removal of heavy metal ions from wastewater has been an extensive industrial research subject. Various materials, such as ion exchange resins, activated charcoal and ion chelating agents immobilized on inorganic supports,[1] have been used as heavy metal adsorbents. However, these materials show many drawbacks because of their wide distribution of pore size, heterogeneous pore structure, low selectivity and low loading capacities for heavy metal ions. Research on environmental application of mesoporous silicas as novel heavy metal adsorbents has also been carried out recently.[2–12] In this article, a thioether functionalized organic–inorganic mesoporous composite as a highly selective and capacious Hg²⁺ adsorbent is reported for the first time.

Mercier and coworkers used 3-mercaptopopyltrialkoxysilane (MPTS) to modify HMS and MSU mesoporous silica samples by either post-grafting or co-condensation methods.[6,8] Those samples showed good selectivity to Hg²⁺ and the Hg²⁺ adsorption capacity was proportional to the thiol content. Liu and coworkers[2,4] used mercaptopropylsilyl functionalized large pore MCM-41 as an absorbent and obtained a remarkable adsorption capacity of 600 mg Hg g⁻¹. Dai *et al.*[7] improved the adsorption selectivity of specific cations by a novel surface imprinting method, but this suffered from high cost and poor regenerability. Lee *et al.*[10] synthesized a new types of bi-functional porous silicas *via* the co-condensation of TEOS, MPTS and 3-aminopropyltrimethoxylsilane (APTS). This absorbent was also highly selective for Hg²⁺ but the existence of amino groups decreased the metal adsorption capacities. Most recently, a propylthiourea modified mesoporous silica for mercury removal was reported.[11] Thioethers have the same

affinity for heavy metal ions as thiols, but no reports can be found to load them into mesoporous materials as adsorbents.

A procedure similar to that of mesoporous silica SBA-15[13] was used to prepare thioether functionalized mesoporous composite. With the tri-block copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) $(EO_{20}PO_{70}EO_{20})$ as template, samples were synthesized by the one-step co-condensation of tetraethoxysilane (TEOS) and different proportions of (1,4)-bis(triethoxysilyl)propane tetrasufide (BTESPTS, $(CH_3CH_2O)_3Si(CH_2)_3S–S–S–S(CH_2)_3Si(OCH_2CH_3)_3$), which were mixed in advance. When 4 g of $EO_{20}PO_{70}EO_{20}$ was used, the molar composition of each mixture was x TEOS : $(0.041 - x)$ BTESPTS : 0.24 HCl : 8.33 H_2O, where x = 0.041, 0.0402, 0.0385, 0.0376, 0.0368, 0.0354, 0.0347 corresponding to BTESPTS molar concentrations of 0, 2, 6, 8, 10, 12, 15%, respectively. The template was removed by ethanol reflux (1 g of as-synthesized powder per 100 ml ethanol). The samples were dried at 100 °C and denoted as S0, S2, S6, S8, S10, S12 and S15 corresponding to the BTESPTS molar concentrations, respectively.

The samples were investigated by X-ray diffraction (XRD). They all showed an obvious XRD reflection peak in the range 2θ 0.8–1.25° (Fig. S1, ESI†). With more organic content being introduced into the framework of the mesoporous SBA-15, the peak intensity decreased and broadened, and the peak shifted to higher angle. These indicated that the structural ordering of the organic and inorganic mesoporous composite suffered some disturbance at high loading level of BTESPTS, the pore diameter decreased and the pore size distribution became wider.

HRTEM images and electron diffraction (ED) patterns for sample S15 (Fig. 1) revealed a hexagonal structure with images parallel and perpendicular to the pore channels. TEM evidence of the hexagonal structure was also observed for sample S2. This proved that the hexagonal ordering of the samples synthesized at higher organosiloxane contents could still be maintained. The single peak of the XRD pattern displayed the (100) reflection of the hexagonally ordered materials.

N_2 adsorption and desorption isotherm curves (Fig. S2, ESI†) of the samples showed that the sharp increase of nitrogen adsorption shifted to lower P/P_0 with more BTESPTS was incorporated into the framework, which indicated the decrease
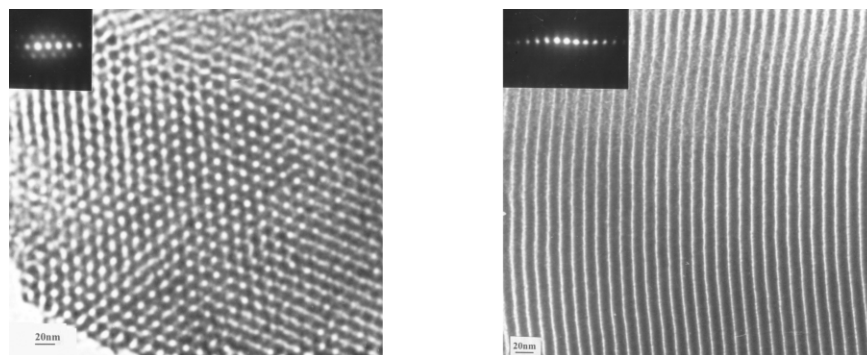
Fig. 1 TEM images and ED patterns of sample S15 with the incident electron beam parallel (**left**) and perpendicular (**right**) to the pore channels.

of the pore size. This is consistent with the XRD results. The sharp increase of N_2 adsorption almost disappeared for sample S15, and the isotherms tend to show the feature of microporous materials. In addition, the hysteresis loop changed from type H1 to H2, which showed the pore shape changes from cylindrical to ink-bottle ones.[14] Their pore size distributed over a very narrow range (Fig. S2, ESI†), and the centered pore size decreased from 5 nm for S2 to 2 nm for S15.

Thermogravimetric analysis of sample S2 (Fig. S3, ESI†) was conducted under atmospheric conditions. At a temperature up to 150 °C, the physisorbed water on the surface of the sample was desorbed, resulting in weight loss and an endothermic peak. In the range from 300 to 400 °C, the organic groups decomposed, resulting in a weight loss of 20 wt%, corresponding to the S content shown in Table. 1.

The adsorption experiment was carried out to test the adsorption selectivity and capacity of the samples. For the preparation of aqueous metal solutions, the following metal nitrates were used: $Hg(NO_3)_2 \cdot 0.5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ (see Table 2 for their concentrations). Hydrochloric acid was used to prevent the precipitation of the metal ions during the adsorption experiment (for 1 L metal ion solution, 5 ml 2 M HCl was added). 0.5 g samples and 50 ml wastewater were mixed and stirred for 20 h. Then the samples were filtered and the residual metal concentration in the solutions was measured using an atomic absorption spectrometer. Sample S0 showed no obvious adsorption of metal ions in the blank adsorption experiment.[9] The concentrations of metal contaminants in wastewater

Table 1 Physicochemical properties and Hg^{2+} adsorption capacity of the thioether functionalized organic–inorganic mesoporous composite samples

Sample	A_{BET}[a]/ m^2 g^{-1}	D_{BJH}/ nm	S content/ mmol g^{-1}	Hg adsorption capacity/ mg g^{-1}	Hg/S
S2	634	5.02	1.50	627	2.08
S6	654	3.74	2.83	1280	2.25
S8	576	3.47	3.48	1860	2.66
S10	532	3.35	3.76	2330	3.09
S12	253	3.26	4.02	2540	3.15
S15	242	3.13	4.24	2710	3.19

[a] A_{BET}, BET surface area; D_{BJH}, BJH pore diameter caculated from the desorption branch.

Table 2 The concentrations of metal contaminants in wastewater solutions before and after treatment with thioether functionalized organic–inorganic mesoporous composite samples

Solution	Hg^{2+}/ ppm	Pb^{2+}/ ppm	Cd^{2+}/ ppm	Zn^{2+}/ ppm	Cu^{2+}/ ppm
No treatment	10.76	13.07	12.43	6.79	8.78
After treatment with S2	3.80	12.85	12.35	6.76	8.75
After treatment with S6	0.34	12.64	12.32	6.76	8.74
After treatment with S12	0.23	12.47	12.23	6.51	7.16

solutions before and after treatment with the samples are shown in Table 2. It can be seen that the mercury concentration was remarkably reduced, while the samples showed little or no affinity for other metal ions. This means that the selective adsorption of the materials for Hg^{2+} was much higher than those of chelating resins with polythioethers.[1]

The Hg^{2+} adsorption capacities of the materials increased in proportion to the thioether group content in the materials. The molar ratio of Hg to S was above 2 and increased to over 3 when more organic groups was coupled into the framework of the materials (Table 1). Therefore, it is believed that the Hg^{2+} adsorption capacity of the materials is two or three times higher than that of the mesoporous adsorbents reported previously which contained equal amounts of S.[7] This could be attributed to the stereo-coordination chemistry of S with Hg^{2+}. Sample S15 showed an extraordinary high adsorption capacity up to 2700 mg Hg^{2+} g^{-1}, which is about one order higher than that of ordinary polythioether chelating resins.[1] A regeneration experiment was also conducted. The mercury-loaded sample S2 was washed with concentrated HCl (12.1 M), resulting in the complete removal of the loaded metal ions. Then this re-generated adsorbent was treated with an $Hg(NO_3)_2$ solution and a Hg loading of 240 mg g^{-1} was obtained.

In conclusion, a thioether functionalized organic–inorganic mesoporous composite has been synthesized for the first time by a one step co-condensation of TEOS and BTESPTS. The new material showed highly selective and capacious adsorption for Hg^{2+}. The adsorbent is environmentally friendly because BTESPTS is much less toxic than MPTS and the highly selective adsorption for Hg^{2+} also makes the recycling of Hg^{2+} possible. Thus the material is a new promising candidate for heavy metal adsorbents. Studies on the stability of the composite are in progress.

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