Ti-containing mesoporous silica packed microcolumn separation/preconcentration combined with inductively coupled plasma-mass spectrometry for the determination of trace Cr, Cu, Cd and Pb in environmental samples

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Supplemented materials

Synthesis of Ti-containing mesoporous silica

Briefly, 2.0 g of CTAB was dissolved in the mixed solutions of 30 mL 1 mol L^{-1} HCl and 15 mL water under the condition of 40 ^{o}C water bath. Then 3.95 g TEOS was added to the above prepared solution with violent stirring for 2 h and solution A was obtained. 0.057 g $TiCl_4$ and 0.2 g TBOB were dissolved in 8 mL isopropanol under the condition of 40 ^{o}C water bath and solution B was formed after violent stirring for 0.5 h. Solution B was added slowly to solution A and the gel was produced after stirring for 22 h. The gel was transferred into PTFE vessel and the PTFE vessel was loaded in autoclave with hydrothermal treatment for 24 h at 100 ^{o}C. The solid product was obtained by filtration of the product after hydrothermal treatment. After washed with high purity deionized water several times, the solid product was vacuum dried at 80 ^{o}C for 2 h, and then calcined in muffle furnace at 450 ^{o}C for 10 h. After that, the surfactant was removed and the Ti-containing mesoporous silica was obtained.

Figure S1 shows the SEM images of the self-prepared Ti-containing mesoporous silica at different magnifications. It can be seen that the self-prepared Ti-containing

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mesoporous silica presents irregular thin sheet structure.

The TEM images of the self-prepared Ti-containing mesoporous silica are shown in Fig. S2. It can be seen that there are many worm-like pores on the surface of the materials, which increase the surface area of the materials and enhance mass transfer for the analytes during the extraction process.

Figure S3 shows XRD patterns of the self-prepared Ti-containing mesoporous silica. As can be seen, there is one big diffraction peak that shows the materials are amorphous.

Figure S4 is the UV-Vis spectra of the Ti-containing mesoporous silica. It can be seen that there is a strong absorption peak at 195 nm, which demonstrated that Ti and Si were coordinated through the silicon oxygen tetrahedron, without forming separate TiO_2 crystal. The result of UV-Vis spectra was in accordance with that of XRD.

The FT-IR spectra of the self-prepared Ti-containing mesoporous silica are shown in Fig. S5. It can be seen that the absorption bands at 1080 cm^{-1} and 790 cm^{-1} are attributed to the vibration frequency of Si-O-Si. The absorption bands at 3460 cm^{-1} and 1630 cm^{-1} are ascribed to the vibration frequency of Si-O-H. The characteristic absorption bands of Ti-O-Si appeared at 960 cm^{-1}.

Figure Captions

Fig. S1 SEM images of Ti-containing mesoporous silica

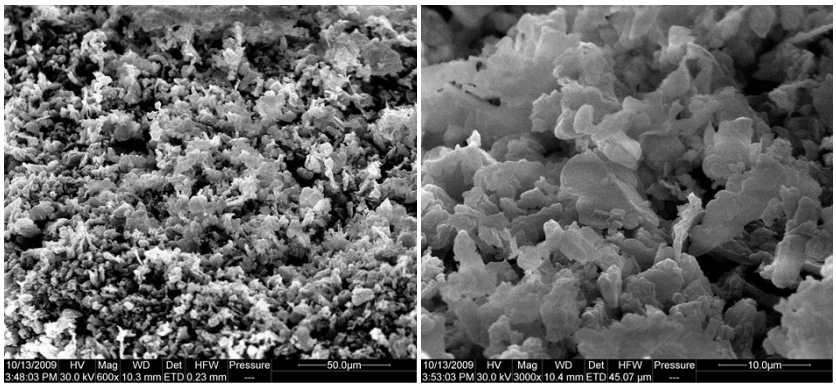
Fig. S2 TEM image of Ti-containing mesoporous silica

Fig. S3 XRD spectra of Ti-containing mesoporous silica

Fig. S4 UV-Vis diffuse reflectance spectra of Ti-containing mesoporous silica

Fig. S5 FT-IR spectra for (a) Ti-Si mesoporous material and (b) metal ions loaded Ti-Si mesoporous material

Fig. S1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3:48:03 PM 30.0 kV 600x 10.3 mm ETD 0.23 mm ---
10/13/2009 HV Mag WD Det HFW Pressure 10.0µm
3:53:03 PM 30.0 kV 3000x 10.4 mm ETD 45.07 µm ---

a b

Fig. S2

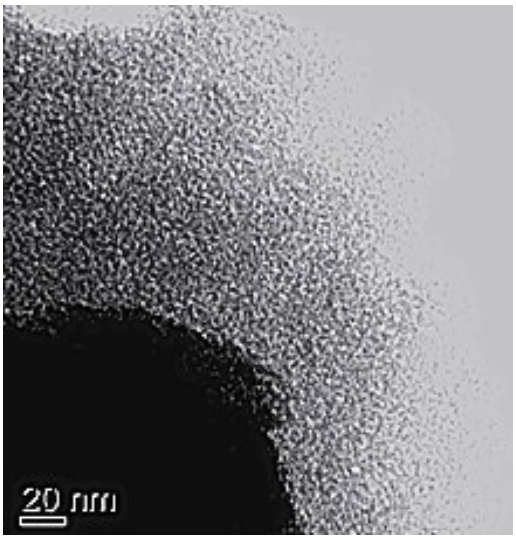

Fig. S3

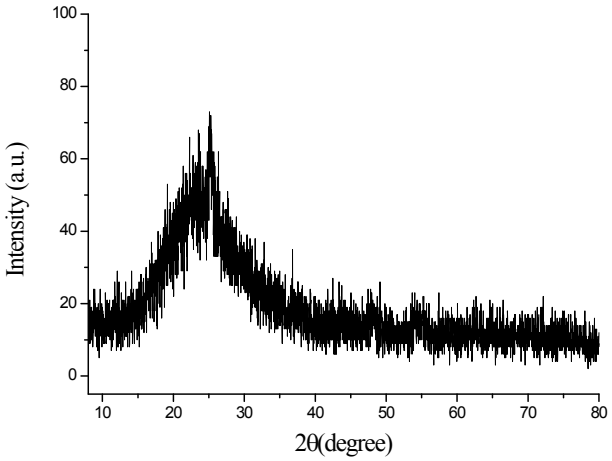

Fig. S4

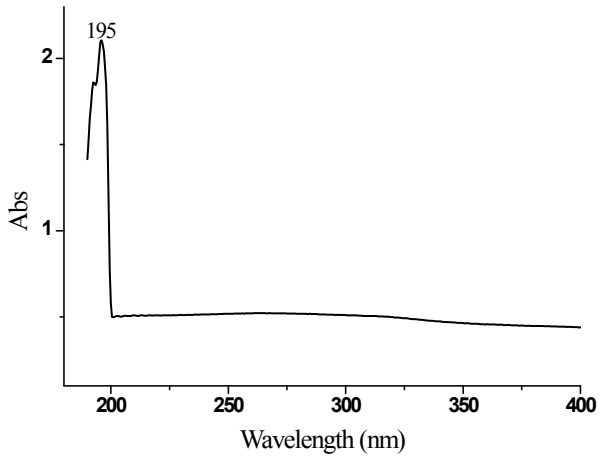

Fig. S5

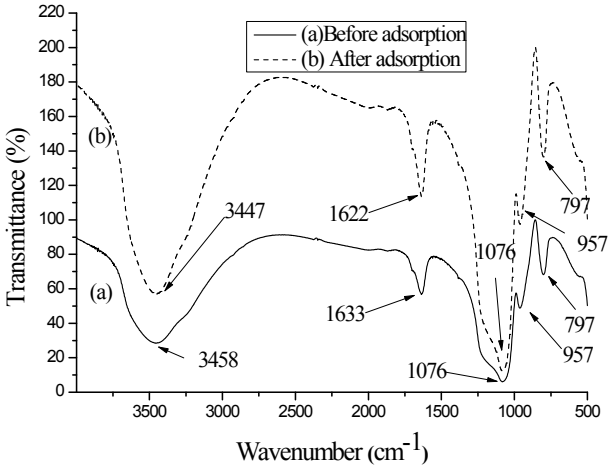
(a)Before adsorption
(b) After adsorption
Transmittance (%)
Wavenumber (cm-1)
(b)
(a)
3447
1622
1076
797
957
1633
3458
797
957
1076

Table S1 The binding energy of elements before and after adsorption by XPS

Element	Peak	Binding energy (eV)	
		Before adsorption	After adsorption
O	1S	533	532
Si	2P	104	103
Ti	$2P_{3/2}$, $2P_{1/2}$	459, 464	459, 465
Cr	$2P_{3/2}$, $2P_{1/2}$	574, 583	576, 585
Cu	$2P_{3/2}$, $2P_{1/2}$	932, 954	935, 943
Cd	$3d_{5/2}$, $3d_{3/2}$	405, 412	406, 412
Pb	$2f_{7/2}$, $2f_{5/2}$	137, 141	139, 144

Exciting source: Mg

The details of Synthesis of Ti-containing mesoporous silica

Briefly, 2.0 g of CTAB was dissolved in the mixed solutions of 30 mL 1 mol L^{-1} HCl and 15 mL water under the condition of 40 ^{o}C water bath. Then 3.95 g TEOS was added to the above prepared solution with violent stirring for 2 h and solution A was obtained. 0.057 g $TiCl_4$ and 0.2 g TBOB were dissolved in 8 mL isopropanol under the condition of 40 ^{o}C water bath and solution B was formed after violent stirring for 0.5 h. Solution B was added slowly to solution A and the gel was produced after stirring for 22 h. The gel was transferred into PTFE vessel and the PTFE vessel was loaded in autoclave with hydrothermal treatment for 24 h at 100 ^{o}C. The solid product was obtained by filtration of the product after hydrothermal treatment. After washed with high purity deionized water several times, the solid product was vacuum dried at 80 ^{o}C for 2 h, and then calcined in muffle furnace at 450 ^{o}C for 10 h. After that, the surfactant was removed and the Ti-containing mesoporous silica was obtained.