Porous Amorphous Chalcogenides as Selective Adsorbents for Heavy Metals

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SUPPORTING INFORMATION

Powder X-ray Diffraction (PXRD). The samples were examined by PXRD for identification purposes and to assess phase purity. Powder patterns were obtained by using a CPS 120 INEL X-ray powder diffractometer with a graphite monochromated Cu K α radiation operating at 40 kV and 20 mA. Samples were ground and spread on a glass slide.

Raman Spectroscopy. The DeltaNu Raman system with a 785 nm CW laser and a spectral range from ~ 200 to 2000 cm⁻¹ was used. Samples were loaded in capillary tubes. The 785 nm laser was chosen as a compromise between optimizing sensitivity and avoiding fluorescence, which overwhelms the Raman system.

Elemental Analysis. Powders were imaged by a scanning electron microscope (SEM) and the relative atomic composition was determined with energy dispersive spectroscopy (EDS). A Hitachi S-3400N-II system was used with 25.0 kV acceleration voltages, a 60 s acquisition time and the ESED II detector for elemental analysis. Carbon and oxygen content from EDS data were excluded from the calculation of relative elemental composition ratios for accuracy.

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron studies were performed using a Thermo Scientific ESCALAB 250 Xi spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) and operated at 300 W. Samples were analyzed under vacuum (P < 10^{-8} mbar), whereas survey scans and high-resolution scans were collected using pass energy of 50 eV. Binding energies were referred to the C 1s binding energy at 284.6 eV. A low-energy electron flood gun was employed for charge neutralization. Prior to XPS measurements, powders of amorphous and porous amorphous chalcogenides were attached on copper foil, mounted on stubs, and successively put into the entry-load chamber to pump.

Differential Thermal Analysis (DTA). DTA experiments were performed on Shimadzu DTA-50 thermal analyzer. Typically, a sample (~40 mg) of ground material was sealed in a quartz ampoule under vacuum. A similar ampoule of equal mass filled with Al_2O_3 was sealed and placed on the reference side of the detector. The heating rate was 10° C min⁻¹ under a 30 ml min⁻¹ flow of N₂.

Band Gap Measurements. UV/vis/near-IR diffuse reflectance spectra were obtained at room temperature on a Shimadzu UV-3010 PC double beam, double monochromator spectrophotometer in the wavelength range of 200-2500 nm. BaSO₄ powder was used as a reference (100% reflectance) and base material on which the powder sample was coated. The reflectance data were converted to absorption using the Kubelka-Munck function, and the band edge for each sample was estimated from the intercept of the line extrapolated from the high-energy end of the absorption to the baseline.

Inductively Coupled Plasma-Mass Spectroscopy [ICP-MS] analyses. Accurate determination of Hg²⁺, Pb²⁺ and Cd²⁺ in solutions after ion-exchange was performed by ICP-MS. Quadrupole ICP-MS is capable of identifying elements from ppt-ppb levels. To accurately determine the amount of Hg²⁺, Pb²⁺ and Cd²⁺, a computer-controlled Thermo Elemental (Waltham, MA) PQ ExCell Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with a quadrupole setup was used. Isotopes ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰²Hg, ²⁰⁶Pb, ²⁰⁷Pb, ¹¹¹Cd were analyzed. Nine standards of Hg²⁺, Pb²⁺ and Cd²⁺ in the range of 1-40 ppb were prepared by diluting commercial (Aldrich or GFS chemicals) 1000 ppm solutions. To accurately measure the extremely low level of (<1 ppb) Hg²⁺, Pb²⁺, Cd²⁺ concentrations of some solutions, seven standards in the range 0.1-2 ppb were prepared and used for the determination of the Hg²⁺, Pb²⁺ and Cd²⁺ content of these solutions. All samples (including standards and a blank solution) were prepared in a 3% nitric acid solution with 1 ppb ¹⁵³Eu internal standard in order to correct for instrumental drift and matrix effects during analysis^[11] To help stabilize Hg²⁺ in solution and avoid contamination of the plasma by trace mercury amounts, solution of Au (with ~ 10 times higher in concentration than Hg) was added to the standards and the Hg²⁺-containing samples.^[2,3]

References:

 Moens, L.; Dams, R., NAA and ICP-MS: A comparison between two methods for trace and ultra-trace element analysis. *J. Radioanal. Nucl. Chem.* 1995, *192*, 29-38.
Gerlach, R. W.; Gustin, M. S.; Emon, J. M. V., On-Site Mercury Analysis of Soil at Hazardous Waste Sites by Immunoassay and ASV. *Appl. Geochem.* 2001, *16*, 281-290.
Fatemian, E.; Allibone, J.; Walker, P. J., Use of gold as a routine and long term preservative for mercury in potable water, as determined by ICP-MS. *The Analyst* 1999, *124*, 1233-1236.



Figure S1. PXRD pattern (before soaking in water) and SEM images (after soaking in water: exsolution) of compound 1.



Figure S2. SEM images and EDS analyses of the amorphous chalcogenide $K_{2x}Sn_xSb_{3-x}S_6$, $Cs_{2x}Sn_xSb_{3-x}S_6$, $K_{2x}Sn_xSb_{3-x}Se_6$ (*x*=0.8-1; 1, 2, and 3 respectively).



Figure S3. X-ray photoelectron spectra of " $K_2SnSb_2S_6$ " with K (A), Sn (B), Sb (C) and S (D). The hatched line is experimental and the solid lines are calculated.



Figure S4. X-ray photoelectron spectra for " $Cs_2SnSb_2S_6$ " of Cs (A), Sn (B), Sb (C) and S (D). The black line is experimental and the colored solid lines are calculated. A weak peak generated at about 532.5 eV in (C) is likely from adventitious oxygen 1s energy.



Figure S5. DTA thermograms of amorphous chalcogenides 1, 2, and 3.



Figure S6. EDS analysis, SEM image, PXRD pattern, and photo image of the crystalline phase of **3**, K₄Sn₃Se₈.



Figure S7. SEM images and EDS analyses of the porous chalcogenide glasses of 1 and 2. K^+ , and Cs⁺ are partially exchanged with A^+ from the corresponding inert salt (A=Na, K).



Figure S8. X-ray photoelectron spectra for " $Cs_{2-x}K_xSnSb_2S_6$ " of Cs (A), K (B), Sn (C), Sb (D) and S (E). The black line is experimental and the colored solid lines are calculated.



Figure S9. X-ray photoelectron spectra for "Na_{2-x} K_x SnSb₂S₆" of K (A), Na (B), Sn (C), Sb (D) and S (E). The black line is experimental and the colored solid lines are calculated.



Figure S10. (A) TGA of sample obtained after soaking porous $Na_{2-x}K_xSnSb_2S_6$ in an aqueous solution with a pH~4 for 18 hours. The weight loss corresponds to water loss. (B) IR spectra of the sample obtained after soaking porous $Na_{2-x}K_xSnSb_2S_6$ in an aqueous solution of pH~4 for 18 hours (before and after TGA). The IR absorption feature at 2430 cm⁻¹ is attributed to the S-H stretching vibration.



Figure S11. Absorption spectra of as synthesized amorphous $K_2SnSb_2S_6$ and porous amorphous $Na_{2-x}K_xSnSb_2S_6$ at various aqueous pH values.