Selective Surfaces: High-Surface-Area Zinc Tin Sulfide Chalcogels

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Supporting Information

ABSTRACT: Porous zinc tin sulfide aerogel materials were constructed by metathesis reactions between Zn(acac)2•H2O and tetrahedral thiostannate cluster salts containing discrete [SnS4]4-, [Sn2S6]4-, and [Sn4S10]4- units. Self-assembly reactions of the Zn2+ linker and anionic thiostannate clusters yielded polymeric random Zn/Sn/S networks with gelation properties. Supercritical drying of the gels and solvent/counterion removal resulted in a metal sulfur framework. Zn2Sn(SnS4)x (x = 1, 2, 4) aerogels showed high surface areas (363–920 m2/g) and pore volumes (1.1–1.5 cm3/g), and wide bandgap energies (2.8–3.2 eV). Scanning and transmission electron microscopy studies show the pores are micro- (d < 2 nm), meso- (2 nm < d < 50 nm), and macro- (d > 50 nm) regions. The zinc chalcogenide aerogels also possess high affinities toward soft heavy metals and reversible absorption of strong electron-accepting molecules.

KEYWORDS: porous materials, gas absorption, gas separation, chalcogenides, heavy metal removal

INTRODUCTION

Aerogels are a unique class of porous materials that are largely composed of randomly interconnected nanoparticles. Aerogels possess low density and high internal surface area, which lead to potential applications such as catalysis,1–5 separations,6 sensing devices,7,8 and charge storage.9 The majority of aerogel studies are based on oxide materials, such as SiO2, Al2O3, and TiO2 or carbon-based materials.10 However, nonoxide counterparts also merit strong interest, because of the unique combination of accessible open frameworks, high surface areas, surfaces with soft Lewis basicities, and more-attractive electronic properties that are relevant for photocatalysis,11 photoconductivity,12 photovoltaic cells,13,14 electroluminescence,15–18 and water remediation.19,20

The field of nonoxide aerogels is relatively unexplored, and only limited studies have been reported. This may be partially because of the difficulties in preparing and handling precursors, the complexities of synthesis, and the ability to obtain gels.15,17,21–26

Chalcogenide cluster-based aerogels, nicknamed chalcogels, are a new class of porous materials and have been made using a simple metathesis reaction between cationic transition-metal linkers and anionic chalcogenide clusters.19,20,27,28 This strategy offers a direct synthetic method for obtaining monolithic porous semiconducting aerogels with advantages in device adaptation and reproduction. The platinum-based chalcogel system, Pt[M(Q=Sn)2] (where M = Ge, Sn; Q = S, Se, Te; and x = 1, 2, 4), uses germanium or tin chalcogenide clusters as anionic building blocks and platinum ions as a linking metal.20 The platinum-based chalcogels display tunable electron bandgap energies, depending on the choice of cluster units. The synthesis of chalcogels derived from Sn3+ and Sn2+ linkers and [Sn4S10]4- and [Sn4S10]4—building blocks has also been reported with the mixed-metal Pt/Sh/Ge/Se10 chalcogel exhibiting high gas selectivity toward CO2/C2H6 over H2.29

EXPERIMENTAL SECTION

Synthesis of Starting Materials. Na4SnS4•14H2O. Na4SnS4•14H2O was used as a precursor to provide [SnS4]4— anions when dissolved. An amount of 28.89 g (120 mmol) of Na4S•9H2O (Aldrich, 99%) was dissolved in 100 mL of H2O with stirring. Then, 7.8 g...
(30 mmol) of SnCl₂·5H₂O (Aldrich, 98%) was dissolved in H₂O and added dropwise to the Na₄S·9H₂O solution with continuous stirring. The solution was kept at 45 °C for 8 h and then added to 400 mL of methanol and stored in a refrigerator for 48 h. Precipitated white crystals of Na₄SnS₄·1H₂O were washed with EtOH and dried under vacuum for 24 h. The final product yield was 73%, based on SnCl₂·5H₂O.

Na₄SnS₄·1H₂O, Na₄SnS₄·1H₂O was used as a source of [Sn₄S₁₀]⁴⁻ chalcogenide clusters during the metathesis reaction. To synthesize Na₄SnS₄·1H₂O, a similar method was adopted. A 3:1 ratio of Na₂S·9H₂O (14.4 g; 60 mmol) and SnCl₂·5H₂O (5.2 g; 20 mmol) was reacted in 100 mL of H₂O for 8 h and the resulting solution was added to 300 mL of acetonitrile. With vigorous stirring, a light yellow emulsion was formed in solution and resulted in a white precipitate. The solution was kept in a refrigerator for 48 h and the resulting white crystals of Na₄SnS₄·1H₂O of were filtered, washed with acetonitrile, and dried in a vacuum oven for 24 h yielding 65% of total product.

[(CH₃CH₂)₄N]₄Sn₄S₁₀ was used as a source of [Sn₄S₁₀]⁴⁻, which is an adamantane tetrahedral cluster. In an evacuated fused silica tube, 220 mg (2 mmol) of K₂S, 474 mg (4 mmol) of Sn, and 256 mg (8 mmol) of S were reacted by a direct flame (500 °C for 10 d). As the polymerization size in the chalcogels, elastic scattering of X-rays at small angles was used to characterize the chalcogenide framework, as described earlier. 19,20,27,33

Thermogravimetric Analysis. Thermal stability of chalcogel samples were measured using a Shimadzu Model TGA-50 system with handheld platinum foil basket. The temperature range was 25—600 °C, and the heating rate was 10 °C/min. Thermal analysis was conducted under a nitrogen atmosphere with a flow rate of 40 mL/min.

Synthesis of Zinc Tin Sulfur (ZTS) Wet Gel. An amount of 2 mmol (520 mg) of Zn(acetylacetonate)·H₂O (Sigma—Aldrich, 99.995%) was dissolved in 10 mL of formamide and 1 mmol of the corresponding tin sulfide precursor (Na₄SnS₄·1H₂O, ~590 mg; Na₄SnS₄·1H₂O, ~770 mg; [(CH₃CH₂)₄N]₄Sn₄S₁₀, ~925 mg) was added to 10 mL of formamide in a separate vial. The zinc precursor solution was added slowly into the tin sulfide precursor solution with stirring, yielding a cloudy suspension. Slight heating and vigorous stirring were required to obtain a clear solution. When the precursor salts were completely dissolved, the solution was transferred to a clean glass vial and placed in a sand bath (60 °C) for 5—10 d. As the polymerization occurred, the viscosity of the solution increased, which eventually solidified to a monolithic gel. The remaining formamide was decanted and the gel was soaked in an EtOH/H₂O solution (3:1) for 3 d and then in 100% EtOH for 7 d, to remove byproducts and impurities. A fresh supply of soaking solvent (EtOH/H₂O and EtOH) was provided every 24 h.

Supercritical Drying of Wet Gels. A Tousimis Autosamdri-815B Series A supercritical fluid dryer was used to perform supercritical drying of the wet gel. The wet gel was transferred into the supercritical drying chamber inside of a custom-built metal basket. Liquid CO₂ was introduced at a temperature of 31 °C and gaseous CO₂ was bled at a rate of 100 s⁻¹. 31 A load of 1350 psi for 4 min, and gaseous CO₂ was bled at a rate of 100—150 psi/min to minimize pore collapse during evaporation of the CO₂ from the gel system.

X-ray Diffraction and Pair Distribution Function Analysis. An Inel CPS 120 (40 kV, 20 mA) powder diffraction equipped with graphite monochromatized Cu Kα (λ = 1.541 Å) radiation was used in asymmetric reflection mode to obtain diffraction intensity data from 10° to 100° in 2θ. The finely ground powder samples of aerogel were placed on top of a microscope slide for PXRD measurement. Pair distribution functions (PDF) were obtained using a high-energy synchrotron beam source of 58 keV (λ = 0.2128 Å) with the sample packed in a 1 mm Kapton capillary tube in transmission geometry. A MAR3450 image plate detector was used for the acquisition of the diffraction data, and a NIST silicon standard was used to calibrate the detector-to-sample distance. The Fit2D software was used for the reduction of the two-dimensional (2D) diffraction patterns to intensity vs 2θ profiles. PDFgetX2 software was used to obtain the total scattering structure function, 32 which takes into account of the measured scattering intensity (I(q)), the atomic concentration (Cᵢ), and the X-ray atomic form factor (fᵢ). The function F(Q) (F(Q) = [S(Q) − 1]) was Fourier-transformed to G(r), which provides the probability of finding two atoms separated by a radial distance r. 33

G(r) = \frac{2}{\pi} \int_{0}^{Q_{\text{max}}} Q[S(Q) − 1] \sin(Qr) dQ

G(r) was then used to evaluate the local structure of the chalcogenide framework, using the Barrett–Joyner–Halenda (BJH) model. 34

Electron Microscopy Imaging and Elemental Analysis. The aerogel microstructures were imaged by scanning electron microscopy (SEM), and the relative atomic composition of the chalcogels was determined using energy-dispersive spectroscopy (EDS). A Hitachi Model S-3400N-II system was used with acceleration voltages of 20.0 kV, an acquisition time of 100 s, and the ESED II detector for elemental analysis. The samples were ground and positioned on a carbon-taped metal stub for image capture and elemental analysis. Carbon and oxygen content from EDS data were excluded from the calculation of relative Zn:Sn:S composition ratio accuracy. Transmission electron microscopy (TEM) was used to view higher-resolution images of the zinc chalcogels, using a Hitachi Model H-8100 TEM instrument with an accelerating voltage of 200 kV and a 50k—80k magnification for image capture.

A Bruker S4 Explorer system was used for X-ray fluorescence (XRF) to attain the elemental compositions of the zinc chalcogels. The XRF data provided result complementary to the EDS data. The chalcogel samples were ground and pelletized in Kapton film for measurement. Analysis of the lighter elements (C, H, N, O) was performed by Midwest Micro Lab, Inc., to determine the presence of residual organic solvent (formamide) and acac ligand within the chalcogel framework. CHN and oxygen analysis was performed via combustion of chalcogel samples at 990 and 1200 °C, respectively, and gravimetric determination of the thermochemical decomposition was performed.

Particle Size Measurements. Small-angle X-ray scattering (SAXS) analysis was performed in order to estimate the average particle size in the chalcogels. Elastic scattering of X-rays at small angles (0.1°—10°) was used to provide information about the particle size.
Assuming a spherical shape, the average particle size of chalcogel was calculated based on scattering intensity using the Guinier approximation. The scattering intensity \( I \) can be expressed in relation to the scattering vector \( q \) and the radius of gyration \( R_G \), which is the mean square distance from the center of gravity of the outermost electron shell of the analyte. 

\[
I(q) = I_0 \exp \left( -\frac{1}{3} q^2 R_G^2 \right)
\]

When the natural logarithm \( \ln \) is applied, the relationship between \( R_G \), \( I \), and \( q^2 \) can be expressed as

\[
\ln(I) = \ln(I_0) - \frac{1}{3} q^2 R_G^2
\]

Thus, when the natural logarithm of the scattering intensity \( I \) is plotted over the \( q^2 \) parameter, the slope of the fitting should be proportional to \( R_G \). When the values of \( R_G \) are below 10 Å, the radius of gyration can be converted to an average particle diameter, using the following relationship to find the particle size:

\[
D = 2 \sqrt{\frac{R_G^2}{3}}
\]

Finely ground aerogel samples were held in a custom-built cell composed of a Kapton window (ca. 4 mm width) and zirconium foil (40 μm thick) for the measurement. A Bruker Hi-star 2-D wire detector with Cu rotating anode at 40 kV and 13 mA operating condition (0.04 Å⁻¹ < \( q < 0.6 \) Å⁻¹) was used for the SAXS measurements. The sample-to-detector distance was measured using a Ag-behenate standard (\( d_{001} = 58.38 \) Å), 2D diffraction images were integrated into a one-dimensional (1D) diffraction pattern, as a function of \( q \) and the scattering intensity \( I \) with the FIT2D program. The sample exposure time to the X-ray was 2 h for each sample.

**Density Measurements.** The skeletal density of the chalcogel samples was measured using a Micromeritics Model AccuPyc1340 system. A calibration standard of 0.718 cm³ was used prior to the SAXS measurements. The density was calculated from the weight of the sample divided by the measured volume.

**Heavy-Metal Removal Experiments.** Aqueous solutions of \( \text{Hg}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Pb}^{2+} \), \( \text{Fe}^{3+} \), and \( \text{Zn}^{2+} \) (100 mg/L) were prepared by the addition of \( \text{HgCl}_2 \), \( \text{Cd(CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O} \), \( \text{Pb(CH}_2\text{COO})_2 \cdot 3\text{H}_2\text{O} \), \( \text{FeCl}_3 \cdot \text{Cu(CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O} \), and \( \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) to 100 mL of \( \text{H}_2\text{O} \). An amount of 10 mg of the \( \text{Zn}^{2+} / \text{SnS}_4^{4-} \) chalcogel was suspended in 100 mL of each stock solution and stirred for 24 h. The resulting heavy-metal removal capacity of the chalcogels. The target metal ion concentration, counterions, basicity, and solvent. Zinc coordination complexes with the bidentate ligand acetylacetonate (acac) were used as precursors to obtain slower reactions with anionic thiosulfate clusters and prevent precipitation. Other zinc precursor salts with weakly bound monodentate ligands, such as acetate and nitrate, resulted in precipitation. The reaction temperatures also affect the reaction rate and polymerization processes. For example, at room temperature, more than one month of gelation time was required to observe rigid gels that were strong enough to withstand solvent exchange and critical point drying. When the temperature was adjusted to 60 °C, the polymerization and gelation processes were completed within 5 d. Metathesis reactions occurring at temperatures of >60 °C yielded precipitation or shrinkage of the gel volume, leading to smaller pore volumes and lower internal surface areas of the aerogels. Under the proper conditions, the polymerization process eventually led to rigid gels within 7–10 d: 

\[
\text{Zn}^{2+} / \text{SnS}_4^{4-} \rightarrow \text{Zn}_2\text{SnS}_4 \quad (\text{eq 8})
\]

formed a cream-colored gel within 7 d, 

\[
\text{Zn}^{2+} / \text{SnS}_6^{4-} \rightarrow \text{Zn}_2\text{SnS}_6 \quad (\text{eq 9})
\]

formed a light yellow gel within 7 d, and 

\[
\text{Zn}^{2+} / \text{SnS}_{10}^{4-} \rightarrow \text{Zn}_2\text{SnS}_{10} \quad (\text{eq 10})
\]

formed a light gray gel within 10 d. 

**RESULTS AND DISCUSSION**

**Metathesis Reactions and Chalcogel Formation.** The metathesis reactions that give rise to the gelled chalcogenide networks are sensitive to the solution conditions, such as temperature, concentration, counterions, basicity, and solvent. Zinc coordination complexes with the bidentate ligand acetylacetonate (acac) were used as precursors to obtain slower reactions with anionic thiosulfate clusters and prevent precipitation. Other zinc precursor salts with weakly bound monodentate ligands, such as acetate and nitrate, resulted in precipitation. The reaction temperatures also affect the reaction rate and polymerization processes. For example, at room temperature, more than one month of gelation time was required to observe rigid gels that were strong enough to withstand solvent exchange and critical point drying. When the temperature was adjusted to 60 °C, the polymerization and gelation processes were completed within 5 d. Metathesis reactions occurring at temperatures of >60 °C yielded precipitation or shrinkage of the gel volume, leading to smaller pore volumes and lower internal surface areas of the aerogels. Under the proper conditions, the polymerization process eventually led to rigid gels within 7–10 d: 

\[
\text{Zn}^{2+} / \text{SnS}_4^{4-} \rightarrow \text{Zn}_2\text{SnS}_4 \quad (\text{ZTS-cg1})
\]

(8) 

\[
2\text{Zn}^{2+} / [\text{SnS}_6^{4-}] \rightarrow \text{Zn}_2\text{SnS}_6 \quad (\text{ZTS-cg2})
\]

(9) 

\[
2\text{Zn}^{2+} / [\text{SnS}_{10}^{4-}] \rightarrow \text{Zn}_2\text{SnS}_{10} \quad (\text{ZTS-cg3})
\]

(10)
A schematic representation of the metathesis chalcogel reaction for the Zn$_2^{2.1}$/[Sn$_{5.2}$S$_{3.8}$]$_{4-}$ system is summarized in Figure 1.

An optimized Zn$_2^{2.1}$/[Sn$_{5.2}$S$_{3.8}$]$_{4-}$:formamide molar ratio of 2:1:500 was used for all three Zn/Sn/S chalcogel syntheses. Higher concentrations of precursors (Zn$_2^{2.1}$/[Sn$_{5.2}$S$_{3.8}$]$_{4-}$:formamide molar ratio of 2:1:1000) increased the gelation time and reduced the mechanical strength of the wet gels. Given the proper reaction temperature and concentration, the metal-chalcogenide solutions transformed to a thick and viscous sol state, where the chalcogenide

Figure 1. Schematic representation of the formation of Zn$_{2.2}/$[Sn$_{5.2}$S$_{3.8}$]$^{4-}$ (ZTS-cg2) chalcogel via the metathesis route.

local structure of the chalcogel networks. In the PXRD patterns of all zinc chalcogels, broad peaks were observed (Figure 2A), which indicates the lack of long-range order within the chalcogel structure. This is similar to previously reported chalcogels. However, we observed that the Zn-chalcogel sample, when exposed to an X-ray beam for more than 8 h, began to show a more-distinct nanocrystalline ZnS phase (see Figure S 1 in the Supporting Information). This is the first example of X-ray sensitivity that has been observed in the chalcogel family.

PDF analysis of the total X-ray scattering pattern can provide useful information about the particle size in the chalcogel family. PXRD patterns of samples exposed to the X-ray beam for several hours using a Cu Kα source or for 90 s to a high-energy synchrotron X-ray beam (58 keV/λ = 0.2128 Å) appear to develop nanocrystalline ZnS within the amorphous network (Figure 2B). Because the Zn−S, S−S, and Zn−Zn distances in the ZnS phase closely matches with the thiostannate interatomic distance of Sn−S and S−S, it is difficult to determine the source of the major vectors at 2.4, 3.8, 4.5, 5.8, 10.0 Å. However, these relative atomic vectors are very similar to meso-structured zinc tin sulide materials, e.g., (CP)$_x$Zn$_y$Sn$_z$S$_w$ (where “(CP)” represents cetylpyridinium), here, the cetylpyridinium acts as a structure-directing agent. Since ZTS-cg1 (Zn$_{2.1}$/[Sn$_{8.2}$S$_{5.2}$]$^{4-}$) and ZTS-cg2 (Zn$_{2.1}$/[Sn$_{8.2}$S$_{5.2}$]$^{4-}$) have very similar PDF patterns, they likely have similar local structures, which are defined mainly by tetrahedral ZnS$_4$ and SnS$_4$ units.

Small-angle X-ray scattering (SAXS) is a powerful technique for probing materials with void space and nanosized features, and it can provide useful information about the particle size in the chalcogels. SAXS patterns are only observable when there is a divergence in electron density within the structure. For the ZTS-cg series, the scattering occurs at 0.063–0.065 nm$^{-1}$, and the average distance between particles ($d = 2/q$) is 96 nm. This seemingly large distance between particles accounts for the random aggregation of primary particles during the metathesis reaction and is associated with the large pores present in the ZTS-cg chalcogels. Based on the scattering intensity obtained from SAXS, the radius of gyration ($R_g$) was calculated for ZTS-cg1 (1.70 nm), ZTS-cg2 (2.01 nm), and ZTS-cg3 (1.92 nm), which reflects the spatial measure of a particle. Using Guinier’s

Figure 2. (A) Powder X-ray diffraction (XRD) patterns using a Cu Kα beam source on zinc chalcogels, showing broad diffraction peaks, which are indicative of an absence of an extended lattice structure for all three chalcogel samples. (B) Pair distribution function based on high-resolution XRD (58 keV, λ = 0.213 Å) of zinc chalcogel samples, showing various correlation vectors corresponding to the Zn−S, Sn−S nearest-neighbor and Zn···Sn and S···S next-nearest-neighbor distances.

PXRD, PDF, and SAXS Analysis. PXRD and PDF measurements were performed to investigate the long-range as well as the

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approximation\textsuperscript{47,48} and calculated $R_g$ values, the average particle size of the chalcogel samples was estimated to be $4.4 \pm 0.5$ nm for ZTS-cg1, $5.2 \pm 0.6$ nm for ZTS-cg2, and $5.0 \pm 0.5$ nm for ZTS-cg3 (see Figure 3). By comparison, the particle size ($D$) and the average pore diameter ($d$) of [MoS$_4$]$^{4-}$-based chalcogels\textsuperscript{27} are $5.2$–$23.2$ nm and $24.6$–$45.8$ nm, respectively.

**Transmission and Scanning Electron Microscopy Analysis.** Transmission electron microscopy (TEM) images of the ZTS chalcogels show amorphous aggregations of randomly shaped nanoparticles forming random porous networks with pore diameters of $5$–$100$ nm (see Figures 4A–C). Darker areas indicate multilayer stacks of nanoparticles. The pore spaces represent the presence of formamide and other counterions during the metathesis reaction before the solvent exchange process. The absence of structure-directing agents allows particle aggregation of the inorganic species around the solvent molecules, yielding a random network. Electron diffraction patterns of these gels show diffuse rings proving the amorphous nature of the network. SEM images showed overall aggregation of particle growth at the micrometer scale (Figure 4D). The morphology of the chalcogels was consistent throughout the series, regardless of the size of the thiosilanate clusters used to construct them.

**Measurement of Optical and Chemical Properties.** UV–vis diffuse reflectance spectroscopy shows bandgap energies at $2.89$ eV
(430 nm) for ZTS-cg1, 3.14 eV (395 nm) for ZTS-cg2, and 3.23 eV (384 nm) for ZTS-cg3. (See Figure S 2 in the Supporting Information.) The absence of an observable absorption edge at 3.6 eV indicates that the different ZTS-cg chalcogels contain very little ZnS (e.g., <2%–4%). The elemental and optical properties of the chalcogels are summarized in Table 1. The difference in bandgap energy between ZTS-cg1 (Zn$^{2+}$/[SnS$_4$]$^{4-}$, 2.9 eV) and Chalcogel-6 (Pt/SnS$_4$, 1.4 eV)$^{49,50}$ is consistent with the general trend where the bandgap energy increases as the mean atomic number of the constituent atoms becomes smaller.$^{49,50}$

**Nitrogen Adsorption and Surface Area.** The new chalcogel series described here features very high internal surface areas, large pore volumes, and a broad distribution of pore sizes. (See Table 1.) All three zinc chalcogels showed very similar nitrogen adsorption isotherm patterns: that is, minor adsorption at very low pressures ($P/P_0 < 0.05$), and major adsorption at higher pressures ($0.7 < P/P_0 < 1.0$), with a small hysteresis loop (see Figure 5). Both micropores ($d < 2$ nm) and slits between particles are expected to contribute to minor adsorption at lower pressures, whereas mesopores ($2 < d < 50$ nm) and macropores ($d > 50$ nm) play an active role in major adsorption at higher pressures. The presence of the small hysteresis loop indicates the slower desorption rate of nitrogen, compared to the adsorption rate, because of the percolation effect of random porous networks.$^{49,50}$

The presence of pores within the materials is supported by the high BET surface areas (363–520 $m^2/g$) and large total pore volumes (1.2–1.6 $cm^3/g$) of the ZTS chalcogels. These surface areas correspond to 955–1965 $m^2/g$ when normalized to the surface area of SiO$_2$ for the same number of atoms. BJH pore size distribution analysis shows a wide distribution of pore sizes, consistent with the absence of long-range order in the chalcogels. (See Figure SD.) The average pore diameter of the chalcogels is within the range of 11.7–14.3 nm, as calculated from the surface area and total pore volume (assuming that the pore shape can be roughly approximated as being cylindrical. The skeletal densities of the zinc chalcogels are 3.30 ± 0.02 g/cm$^3$ for ZTS-cg1, 3.31 ± 0.02 g/cm$^3$ for ZTS-cg2, and 3.27 ± 0.03 g/cm$^3$ for ZTS-cg3, which explains the less-dense structure of the chalcogels, compared to the bulk ZnS (4.09 g/cm$^3$) and SnS$_2$ (4.50 g/cm$^3$).$^{51}$

**Thermal Analysis.** The ZTS materials were studied using thermogravimetric analysis (TGA) to evaluate the thermal stability of the samples at elevated temperature under nitrogen. All Zn$^{2+}$/[Sn,S$_{2x+2}$]$^{4-}$ ($x = 1, 2, 4$) aerogel samples were dried in nitrogen at 100 $^\circ$C to remove any adsorbed molecules before the measurement. Based on elemental analysis of the as-synthesized and dried samples, no degradation of the inorganic framework occurred during the drying process. No samples showed any weight loss until 180 $^\circ$C, and then a gradual weight loss was observed as the temperature increased from 180 $^\circ$C to 600 $^\circ$C. At 600 $^\circ$C, the samples lose 26%–30% of their weight (see Figure 6A), because of the loss of sulfur from the chalcogel framework, as confirmed by EDS analysis. (See Figure S 3 in the Supporting Information.)
Table 1. Elemental Composition, Optical Bandgap Energy, Pore Network Properties, and Density of Zn Chalcogels (ZTS-cg)

<table>
<thead>
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<th>aerosol</th>
<th>ZTS-cg1</th>
<th>ZTS-cg2</th>
<th>ZTS-cg3</th>
</tr>
</thead>
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<tr>
<td>rel. atomic ratio (EDS)</td>
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<td>Zn1.6Sn3.9</td>
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<tr>
<td>rel. atomic ratio (XRF)</td>
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<td>Zn1.6Sn3.6</td>
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<td>3.2–3.3</td>
</tr>
<tr>
<td>surface area BET (m²/g)</td>
<td>503–520</td>
<td>413–415</td>
<td>363–393</td>
</tr>
<tr>
<td>( S_{\text{BET}} ) SiO₂ equiv. (m²/g)</td>
<td>955–995</td>
<td>1219–1221</td>
<td>1815–1965</td>
</tr>
<tr>
<td>tot. pore vol. (cm³/g)</td>
<td>1.5–1.6</td>
<td>1.1–1.3</td>
<td>1.3–1.4</td>
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<tr>
<td>avg. pore diameter (nm)</td>
<td>12.2–12.4</td>
<td>11.6–11.8</td>
<td>14.2–14.4</td>
</tr>
<tr>
<td>skeletal density (g/cm³)</td>
<td>3.30 ± 0.03</td>
<td>3.31 ± 0.02</td>
<td>3.27 ± 0.03</td>
</tr>
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Figure 5. (A, B, C) Nitrogen adsorption and desorption isotherms of the ZTS-cg chalcogels (A) ZTS-cg1, (B) ZTS-cg2, and (C) ZTS-cg3, showing type II isotherms with minor adsorption at low relative pressure and major adsorption at high relative pressure. (D) Consistent with the nature of aerogels, the BJH pore distribution of ZTS-cg1 \( (\text{Zn}^{2+}/\text{[SnS}_{6}^{4-}) \) shows no specific distribution of pore size in the meso-macro pore size region (20–100 nm).

Comparison to the as-synthesized ZTS-cg2 sample shows that the ZnS phase becomes more distinct at 200 °C, but the overall amorphous structure remains. The amorphous chalcogel network appears to persist up to 400 °C, but crystalline SnO₂ and ZnO begin to appear, along with ZnS. As the temperature reaches 600 °C, the aerogel structures are completely destroyed and decompose to ZnO (space group \( \text{P}6\text{mc} \)), SnS (space group \( \text{P}6\text{mc} \)), and SnO₂ (space group \( \text{P}4\text{2} / \text{mmm} \)). (See Figure 6B.) The bound acetylacetonate ligand within the inorganic framework is believed to be a source of oxide, even in a flowing nitrogen or argon environment at higher temperature.

**Experiments Involving the Removal of Heavy-Metal Ions.** The wide sulfidic surfaces of the \( \text{Zn}^{2+}/\text{[SnS}_{6}^{4-}) \) \( (\text{ZTS-cg}) \) chalcogels make them ideal candidates for studying the selective removal of soft heavy-metal ions from aqueous solution (see Table 2). During the suspension of the ZTS-cg chalcogel in the metal-ion solution, the sulfur sites act as soft Lewis bases and attract heavy transition-metal ions, which act as soft Lewis acids. As a result, heavy-metal ions such as \( \text{Hg}^{2+} \) replace the zinc from the ZTS-cg network through an ion-exchange reaction (eq 11):

\[
2\text{Hg}^{2+} + \text{Zn}_{2}\text{SnS}_{6} \rightarrow \text{Hg}_{2}\text{SnS}_{6} + 2\text{Zn}^{2+}
\]

The strong affinity of \( \text{Hg}^{2+} \) toward the sulfidic surfaces of the aerogels is emblematic of the hard soft acid–base theory proposed by Pearson.\(^{52} \) The ZTS-cg1 system showed high distribution coefficient \( (K_d) \) values: 1.62 \( \times 10^5 \) mL/g for \( \text{Hg}^{2+} \), 1.02 \( \times 10^6 \) mL/g for \( \text{Pb}^{2+} \), and 3.13 \( \times 10^6 \) mL/g for \( \text{Cd}^{2+} \) solution. Chalcogels composed of larger clusters such as \( \text{[SnS}_{6}^{4-}) \) and \( \text{[Sn}_{10}^{4+} \) exhibited greater affinities for heavy-metal ions. For instance, ZTS-cg2 and ZTS-cg3 exhibited \( K_d \) values of 2.80 \( \times 10^6 \) mL/g and 1.10 \( \times 10^8 \) mL/g, respectively, toward \( \text{Hg}^{2+} \) solution.

The ZTS-cg3 sample was used to test ion selectivity in a solution containing \( \text{Hg}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}, \text{Zn}^{2+}, \) and \( \text{Fe}^{2+} \). The chalcogel showed very high efficiency in the removal of \( \text{Hg}^{2+} \) (99.9% removal, 1.12 \( \times 10^8 \) mL/g), \( \text{Cd}^{2+} \) (99.8% removal, 4.81 \( \times 10^6 \) mL/g), and \( \text{Pb}^{2+} \) (98.8% removal, 8.46 \( \times 10^5 \) mL/g), \( \text{Zn}^{2+} \) (79.8% removal, 3.98 \( \times 10^5 \) mL/g), whereas lighter and harder ions such as \( \text{Fe}^{2+} \) (6.7% removal, 7.95 \( \times 10^4 \) mL/g) showed lower affinity toward the chalcogels. The \( \text{Hg}^{2+} \) removal rate of ZTS-cg3 is comparable to materials known for their high mercury-removal efficiency, such as Chalcogel-1 (Pt/Ge\(_{10}\), \( 0.92–1.61 \times 10^7 \) mL/g),\(^{20} \) and LHMS-1 \( (\text{layered hydrogen metal sulfide}, \text{H}_3\text{MnSn}_{1–x}\text{S}_x, [x = 0.5–0.95]), 3.2 \times 10^{-5}–1.09 \times 10^{-3} \text{mL/g})\(^{53} \).

The ZTS-cg chalcogel series shows higher adsorption capacity for \( \text{Hg}^{2+} \) \( (1.40–1.69 \text{ mmol/g}) \) than the functionalized mesoporous silicas, such as MBT-SBA-15 \( (0.10–0.24 \text{ mmol/g}), \) MBT-MCM-41 \( (0.13–0.21 \text{ mmol/g}) \) (MBT = 2-mercapto-benzothiazol),\(^{54} \) and SH-EMO \( (0.32 \text{ mmol/g})\(^{55} \). This high adsorption capacity of ZTS-cg chalcogels also exists for other heavy metals, such as \( \text{Pb}^{2+} \) \( (1.53–1.63 \text{ mmol/g}) \), \( \text{Cd}^{2+} \) \( (1.94–2.85) \), and \( \text{Cu}^{2+} \) \( (3.95 \text{ mmol/g}) \), in contrast to the lower adsorption capacity of \( \text{NH}_2\text{MCM}-41\)\(^{56} \) (functionalized amino silica) for \( \text{Pb}^{2+} \) \( (0.28 \text{ mmol/g}) \) and \( \text{Cd}^{2+} \) \( (0.16–0.71 \text{ mmol/g}) \), and \( \text{SH-SBA-16}\)\(^{57} \) (thiol-functionalized silica) for \( \text{Cu}^{2+} \) \( (0.16–0.55 \text{ mmol/g}) \). These results show that the ZTS-cg can be used as a heavy-metal remediation medium for aqueous solutions without any specific functionalization.

**Absorption of Organic Molecules.** The accessible open space and wide surface areas of ZTS-cg chalcogels allow surface interaction and functionalization with guest molecules. Unlike the vast majority of porous materials that feature oxidic or carbon-based surfaces available for interaction with guest molecules, the
chalcogels have surfaces covered with softer and more-polarizable sulfide ions. Therefore, they present a new opportunity to study interactions with a variety of molecules. In this context, we tested molecules with electron-acceptor and electron-donor properties. The ZTS-cg2 chalcogel selectively absorbs TCNE, which is an electron-accepting molecule, from chloroform solution; no interaction was observed with TTF, which is a strong electron-donating molecule, or with anthracene, which is a more-inert molecule with low electron transfer ability. 57

The ZTS-cg2 sample was treated with a 1 M \( \text{SnCl}_2 \) solution and supernatant TCNE/CHCl\(_3\) solution resulting in a light brown color, and further ethanol washing and drying under nitrogen. Table 3. Summary of Infrared Spectra of TCNE, ZTS-cg2, and TCNE/ZTS-cg2,\(^a\) Recorded as KBr or CsI Pellets

<table>
<thead>
<tr>
<th>( \text{M}^{2+} ) aerogel</th>
<th>Concentration of Aqueous Metal Ions in Solution (mg/L)</th>
<th>( \text{M}^{2+} ) removal (%)</th>
<th>( q_a ) (mmol/g)</th>
<th>( K_d ) (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>ZTS-cg1</td>
<td>93</td>
<td>0.57</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>ZTS-cg2</td>
<td>112</td>
<td>0.04</td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>ZTS-cg3</td>
<td>112</td>
<td>0.01</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>MBT-SBA-15 (^c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MBT-MCM-41 (^d)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SH-ePMO (^f)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>ZTS-cg1</td>
<td>115</td>
<td>10.3</td>
<td>91.0</td>
</tr>
<tr>
<td></td>
<td>ZTS-cg3</td>
<td>113</td>
<td>1.32</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td>NH(_2)-MCM-41 (^f)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>ZTS-cg1</td>
<td>95</td>
<td>23</td>
<td>75.8</td>
</tr>
<tr>
<td></td>
<td>ZTS-cg3</td>
<td>106</td>
<td>0.22</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>NH(_2)-MCM-41 (^f)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>ZTS-cg3</td>
<td>94</td>
<td>8.52</td>
<td>91.0</td>
</tr>
<tr>
<td></td>
<td>SH-SBA-16 (^e)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>ZTS-cg2</td>
<td>112</td>
<td>8.25</td>
<td>79.8</td>
</tr>
<tr>
<td>Fe</td>
<td>ZTS-cg3</td>
<td>94.2</td>
<td>88.0</td>
<td>6.56</td>
</tr>
</tbody>
</table>

\(^a\) The metal ion absorption capacity of the chalcogel. \(^b\) An aerogel contains volume-to-mass ratio of 10 000 mL/g was used in solution. \(^c\) 2-mercaptopentahiazol (MBT) functionalized SBA-15 (mesoporous silica). \(^d\) 2-mercaptobenzothiazol (MBT) functionalized MCM-41 (mesoporous silica). \(^e\) Thiol-functionalized (bridged with ethane) periodic mesoporous organosilica. \(^f\) Amino-functionalized MCM-41. \(^g\) Thiol-functionalized SBA-16.

TCNE absorption by the ZTS-cg2 causes a red shift in its bandgap energy, as revealed by UV–vis spectroscopy. The higher the TCNE absorption, the higher the degree of bandgap shift (see Figure 7B). Namely, the bandgap of ZTS-cg2 at 3.1 eV moves to the 2.6–2.8 eV region upon adsorption of TCNE from a chloroform solution. This suggests that the incorporation of TCNE into the ZTS chalcogel network results in a donor–acceptor charge-transfer interaction where the chalcogel acts as an electron donor. The bandgap changes in the chalcogel upon TCNE absorption can be understood with an donor–acceptor interaction, where the valence band of the Zn–Sn–S chalcogel donates charge to the lowest unoccupied molecular orbital (LUMO) of TCNE. A similar phenomenon of bandgap reduction has been reported in other TCNE-incorporated materials. 39,64 In the absence of a detailed structure model for this system, however, it is difficult to explain the reduction in bandgap. The amount of TCNE absorbed by the chalcogel was calculated using the UV–vis absorbance intensity difference of a 1 \times 10^{-5} \text{M} TCNE/CHCl\(_3\) solution and supernatant TCNE/CHCl\(_3\) solution after the addition of chalcogel. Based on the absorption coefficient, the amount of TCNE absorbed in ZTS-cg2 corresponds to 0.25 equiv per formula unit.

The TCNE molecules could be desorbed from the chalcogel network by washing with ethanol. Within 48 h, the dark brown aerogel transformed to a light brown color, and further ethanol...
soaking for 24 h resulted in the original ZTS yellow color of the TCNE-free chalcogel (recall Figure 7). The supernatant ethanol solution showed a strong absorbance at 230 nm, confirming the presence of TCNE and demonstrating the reversibility of the adsorption/desorption process and the charge-transfer nature of the interaction. This result suggests that the chalcogels can discriminate among organic conjugated molecules on the basis of electronic structure and could be used as active materials for the selective absorption of a variety of electron-acceptor molecules.

**CONCLUDING REMARKS**

The reaction of $[Sn_2S_{2x+2}]^{2+}$ clusters with Zn$^{2+}$ ions coordinated with acetylacetone (acac) ligands produced in random networks that can form stable gels. Control of the metathesis conditions such as temperature, counterion, and time of polymerization greatly affects the ability to form gels and the properties of the resulting chalcogels. Metal precursors with bidentate ligands allow for a more-controlled metathesis process and provides labile self-assembly conditions that can lead to gelation. The wet gels can then sustain a supercritical drying process to yield high-surface-area aerogels. As previous chalcogels have demonstrated, the transition-metal linker greatly affects the optical and electronic properties. The zinc chalcogels feature selective absorption of a variety of electron-accepting molecules such as TCNE via charge transfer processes. The adsorption of organic acceptor molecules causes a reversible visible shift in the bandgap energy, permitting these materials to be tuned for desirable applications such as sensors, thin-film transistors, and other optical devices.

**ASSOCIATED CONTENT**

3 Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supplementary Information

Selective surfaces: High surface area zinc tin sulfide chalcogels

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Figures

Fig. S. 1 PXRD pattern of ZTS-cg2 sample exposed to x-ray beam for 8 h beginning to showing nano-crystalline ZnS phase.
Fig. S. 2 Bandgap Energy of ZTS-cg1, ZTS-cg2, and ZTS-cg3 based on UV-Vis diffusive reflectance data converted by Kubelka-Munk function. Zinc chalcogel shows wide bandgap energy of 2.9 eV (ZTS-cg1), 3.1 eV (ZTS-cg2), and 3.2 eV (ZTS-cg3)
Fig. S. 3 Relative atomic ratio change of the ZTS-cg2 composition upon heating tracked by EDS analysis