Supporting Information

Polysulfide chalcogels with ion-exchange properties and highly efficient mercury vapor sorption

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1. EXPERIMENTAL PROCEDURE

Synthesis of starting materials. K_2S_x (x = 3-6) precursors were used to provide poly sulfide anions, Sx2-, to react with platinum ions in order to construct the platinum poly sulfide frameworks. Liquid NH_3 reactions were used to prepare potassium tri-, tetra-, penta-, and hexasulfide. An amount of 7.82g (0.2 mol) of potassium and a stoichiometric amount of sulfur--9.62 g (0.3 mol) for K_2S_3, 12.83 g (0.4 mol) for K_2S_4, 16.03 g (0.5 mol) for K_2S_5, and 19.24 g (0.6 mol) for K_2S_6—were placed in a 500 mL round bottom flask with a magnetic stir bar. All materials were handled in a nitrogen atmosphere. The round bottom flask was connected to a condenser with a keck-clamp and bar clamp, and was purged with nitrogen for 15 min. Then, liquid NH_3 was slowly added to the round bottom flask while the bottom of flask was kept in a dry ice-acetone bath. When ~150 mL NH_3 was added to the round bottom flask, stirring was initiated, and the addition of NH_3 was stopped after a total of ~350 mL had been added. The dry ice-acetone bath was then removed and the NH_3 solution slowly warmed to room temperature in order to reflux. During this process, potassium polysulfide slowly formed. The NH_3 solution refluxed under steady stirring until no trace of unreacted potassium (blue metallic appearance on the flask wall) was seen. The total reaction time varied (3-5h) and depended on the total amount of reactants present in the reaction. Once the reaction was complete the remaining NH_3 was boiled off by stirring at room temperature. When the NH_3 level was ~150 mL, stirring was stopped, and evaporation was continued until no liquid remained. The flask was flushed with nitrogen for 30 min, and was dried under vacuum overnight. The yields of final products were 87-95%.

Synthesis of platinum polysulfide aerogels. K_2PtCl_4 (Aldrich, 98%) was used as a platinum ion precursor and K_2S_x (x = 3-6) as a polysulfide precursor to construct platinum polysulfide aerogels. An amount of 41.51 mg (0.1 mmol) K_2PtCl_4 was dissolved in 2.5 ml of formamide (Sigma-Aldrich, >99.5%) and mixed with another 2.5 ml formamide solution containing 0.1 mmol of K_2S_x (17.44 mg of K_2S_3, 20.65 mg of K_2S_4, 23.86 mg of K_2S_5, and 27.62 mg of K_2S_6). The mixture of platinum and polysulfide precursors yielded bright orange colloidal suspensions instantly and slowly changed to deep red solutions. The viscosity of the solution increased and eventually solidified into a monolithic deep brown wet gel in a minimum of 2d. When the polymerization of inorganic build blocks (Pt^{2+} and S_x^{2-}) completed, the monolithic wet gel retained its mechanical integrity and hold its shape from gentle movements in the formamide solution. After the gelation process, the remaining formamide solution was decanted and the wet gel was soaked in $EtOH/H_2O$ (3:1) for 7 d, then with EtOH for 7 d. During this solvent exchange process, old solvent was exchanged with a fresh solvent every 24h to remove any dissolved counter ions and unreacted precursors. The solvent-exchanged wet gel was dried with a supercritical dryer (A Tousimis Autosamdri-815B Series A) using CO2 as a drying medium. A wet-gel dried under ambient conditions lost its porosity due to the surface tension produced during the drying process, however the supercritically dried sample yielded a highly porous structure. The final product was a brittle dark brown powdery solid with low density.

Mercury capture experiments. Potassium platinum polysulfide chalcogel samples were tested for elemental mercury capture in a closed vial set up. An amount of 200 mg of Hg was placed at the bottom of glass vial and 20 mg of chalcogel was placed above, supported by conical shaped filter paper at the top of the vial. The vial was capped, wrapped with Teflon tape, and put inside a bigger glass vial filled with sand. This double glass vial set up was used to prevent the leakage of mercury vapor from inside, and sand was used to transfer heat to the inner glass vial. Vials containing each chalcogel were placed in the sand bath where the temperature was kept between 80 and 140 °C for 24h. The sand bath was cooled to room temperature and chalcogel samples were collected to evaluate the amount of mercury captured during the experiment. The weight of chalcogel before and after the mercury capture experiment was measured to estimate the amount of mercury present within the sample, and ICP and EDS analysis were used to confirm the presence of mercury inside the chalcogels and other samples.

2. CHARACTERIZATION

Elemental analysis of pristine and Hg^o-laden chalcogels. The elemental composition of the platinum chalcogenide aerogel was determined to confirm the reaction between platinum and polysulfide precursors, and to estimate the amount of mercury captured by the chalcogel. A Hitachi S-3400N-II scanning electron microscope was used for energy dispersive spectroscopy (EDS) with a 20.0 kV acceleration voltage and a 100 sec acquisition time. A thin slice (1mm) of chalcogel was cut and mounted on top of carbon taped on metal stub for both scanning electron microscope (SEM) imaging and EDS analysis.

Inductively coupled plasma-atomic emission spectroscopy was used to confirm the relative ratio between platinum and mercury and to evaluate the amount of mercury capture per gram of chalcogel used. A Varian VISTA-MPX Inductively Coupled Plasma (ICP) spectrometer was used for this characterization. An amount of 20 mg of platinum polysulfide chalcogel was dissolved with 5 mL of aqua regia (HNO_3 : HCl = 1 : 3) at 50 °C for 24h. The aqua regia solution was diluted with deionized water up to 25 ml and re-diluted to fit into the range of calibration standard solutions (K : 0-1 ppm, Pt : 0-10 ppm, Hg : 0-15 ppm). Six standard solutions including a blank were prepared using diluted 1000 mg/L commercial solutions (Aldrich or GFS chemicals) of K, Pt, and Hg.

Nitrogen adsorption isotherm measurements. The nitrogen adsorption/desorption isotherm of each chalcogel was measured using a Micromeritics Tristar II system at 77K to estimate the porosity preserved after critical point drying of the wet gel. Chalcogel samples were degassed at 345 K under vacuum for 12 h before the porosimetry measurements. The nitrogen adsorption isotherm from 0.05-0.30 relative pressure was used to fit with the Brunauer-Emmett-Teller (BET) model to calculate the surface area.

Powder X-ray diffraction. The X-ray diffraction pattern was measured to identify any long range ordering or crystallinity present in the potassium platinum polysulfide chalcogels. A STOE IPDS II (50kV, 40 mA) diffractometer equipped with graphite monochromatized Mo Kα (λ = 0.71073 Å) radiation source and Image Plate (IP) detector was used to obtain diffraction intensity data from 0 to 60° in 2θ. Chalcogels were finely ground, packed in a 0.5 mm glass capillary tube, and vacuum sealed for the sample preparation.

Raman spectroscopy measurements. The Raman spectra were measured and used to identify the presence of polysulfide ligands in chalcogels. Raman spectra were collected on a DeltaNu Advantage NIR spectrometer using 785nm radiation from a diode laser and equipped with a CCD detector. A max power of 60 mW and beam diameter of 35 um was used. The spectrum was collected using an integration time of 5s. For sample preparation, each chalcogel was ground, packed inside of pyrex capillary tube, and sealed to protect the sample from oxygen and moisture. All manipulation for sample preparation before sealing were done in a nitrogen filled glove box.

Infrared spectroscopy measurements. The characteristic vibration and rotational modes of the polysulfides and platinum sulfide was studied with infrared (IR) spectroscopy. Spectra in the far-infrared (Far-IR) region (200-600 cm^{-1}) were collected with a computer-controlled Nicolet 750 Magna-IR series II spectrometer equipped with a TGS/PE detector and silicon beam splitter in 2 cm^{-1} resolution. Samples were diluted with CsI and pelletized to be used for transmittance mode under nitrogen atmosphere.

Thermal stability analysis. Chalcogel samples were analyzed using a thermal gravimetric analyzer (TGA) to confirm the stability of each chalcogel at the flue gas releasing temperature where common mercury vapor waste is found (140 °C). A Shimadzu TGA 50 was used for the analysis with an aluminum pan as a sample holder. For each samples, an amount of 10-20 mg of chalcogel was used for the thermal analysis. Any weight change in the sample during the heating profile (from room temperature to 200 °C) was collected.

Electron microscope imaging. The porous structure of each chalcogel was observed with a scanning electron microscope (SEM) and transmission electron microscope (TEM). A Hitachi S-3400N-II was used with a 10-15 kV acceleration voltage and a 60 sec acquisition time for SEM imaging. A Hitachi H-8100 TEM was used with a 200 kV accelerating voltage and 50K-80K magnification for image capture. For SEM samples, the same procedure used to prepare EDS samples was applied. To prepare TEM samples, a drop of EtOH solution (20 µL) containing finely ground chalcogel was placed on a copper grid and was dried at room temperature.

Ion-exchange reactions. One of the potassium platinum polysulfide chalcogels ($KPtS_3$-CG) was tested as a potential ion-exchange material by immersing it in an aqueous solution of CsCl (Sigma-Aldrich, 99.9%). An amount of 20 mg of $KPtS_3$-CG (~ 0.05 mmol) was placed in a 3 mM CsCl solution with stirring for 12h. The chalcogel sample was filtered and subsequently washed with 20 mL of EtOH (Fluka, > 99.8%) 9 times, 20 mL of diethyl ether (Sigma-Aldrich, anhydrous, > 99.0%), and then dried in a vacuum oven for 12 h at 75 °C. The Cs-ion-exchanged chalcogel sample was analyzed by EDS to confirm the results of the ion-exchange reaction. The Cs-ion-exchanged chalcogel was reacted with a 5 mM aqueous KCl solution to test the reversibility of the ion-exchange. The same washing, drying and EDS analysis procedure was used for this second ion-exchanged chalcogel.

3. SUPPLEMENTARY FIGURES

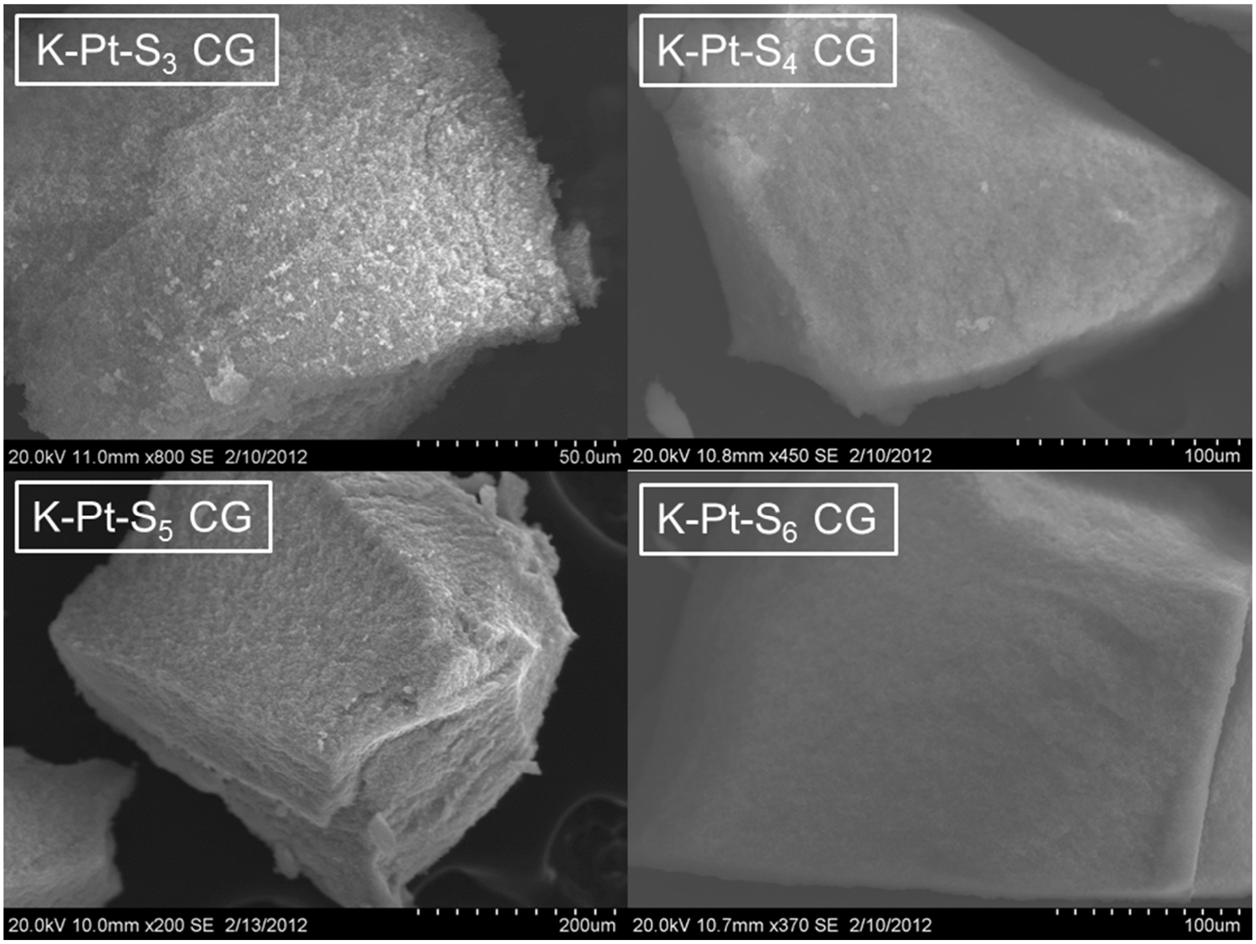

Figure 1S. Scanning electron microscopy (SEM) images of K-Pt-S_x shows fluffy features throughout the micron sized specimens, indicating a porous structure of these materials.

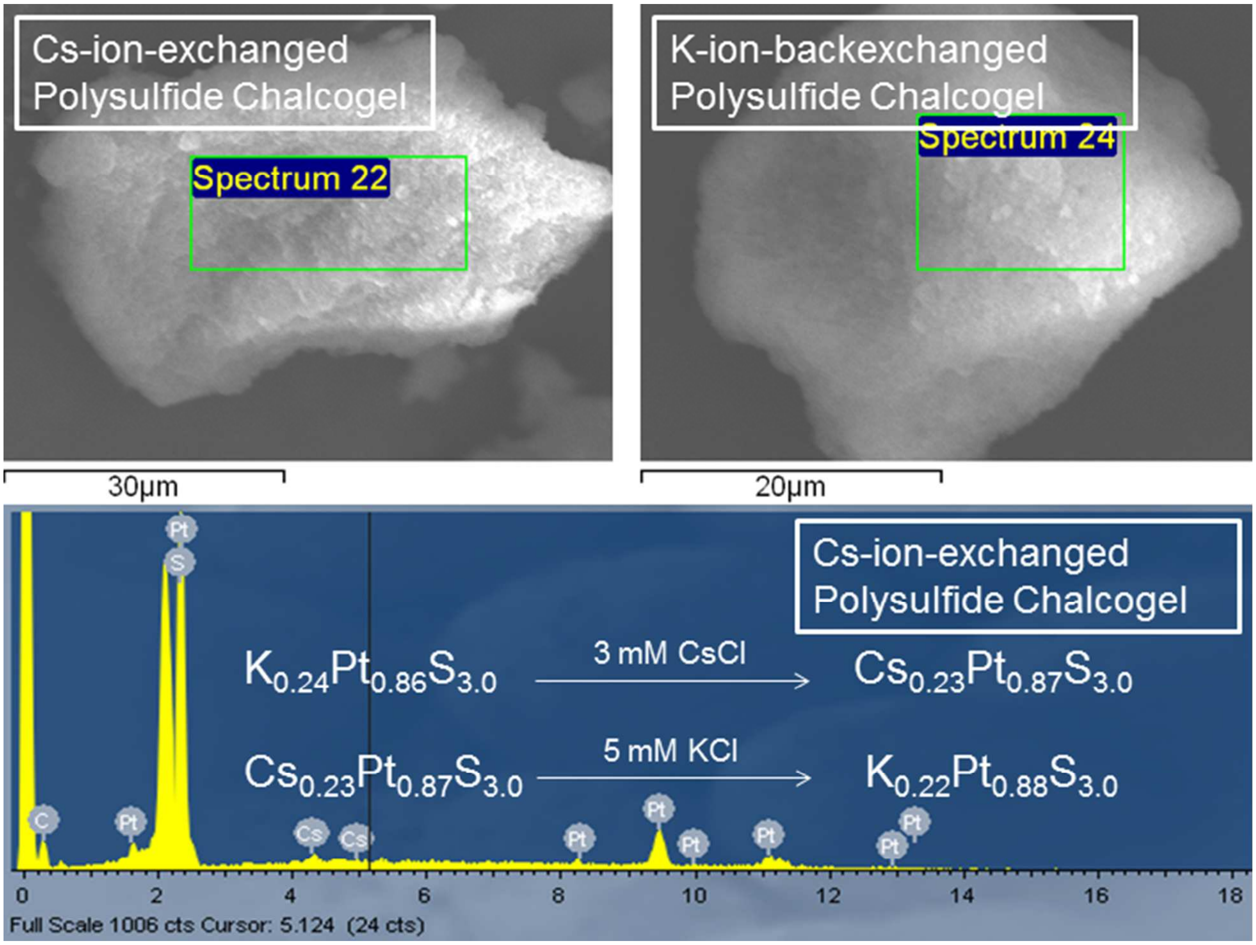

Figure 2S. Ion-exchange results of polysulfide chalcogel with 3mM CsCl solution show complete replacement of potassium with cesium. This Cs-exchanged chalcogel is capable of re-ion-exchange with a solution of 5 mM KCl as confirmed by EDS analysis.

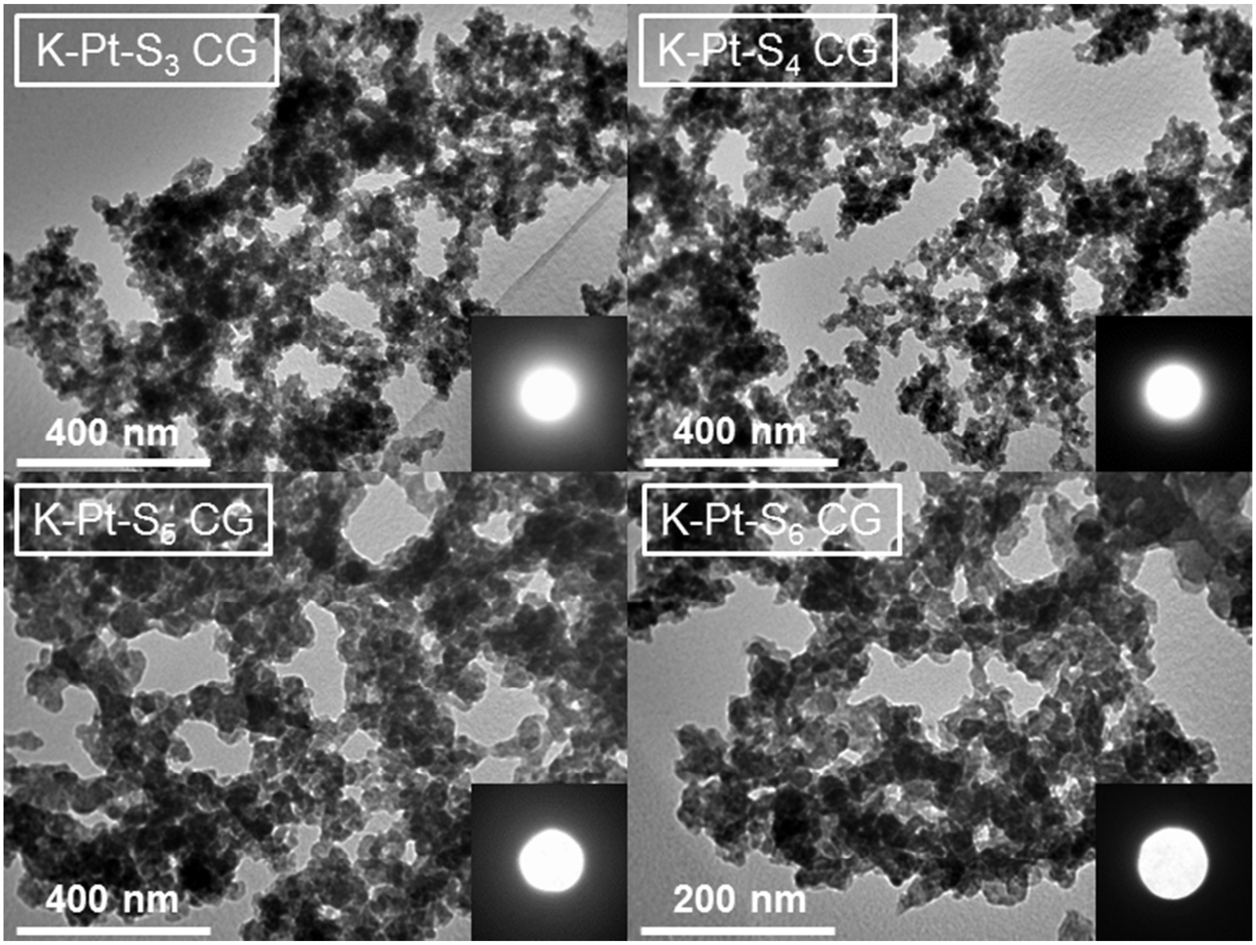

Figure 3S. Transmission electron microscopy (TEM) images show a nano-scale porous structure of K-Pt-S_x chalcogels. Random aggregation of nanoparticles form disordered three dimensional porous structures with broad size and shape. Electron diffraction images only show a diffuse ring indicating the amorphous nature of these chalcogels.

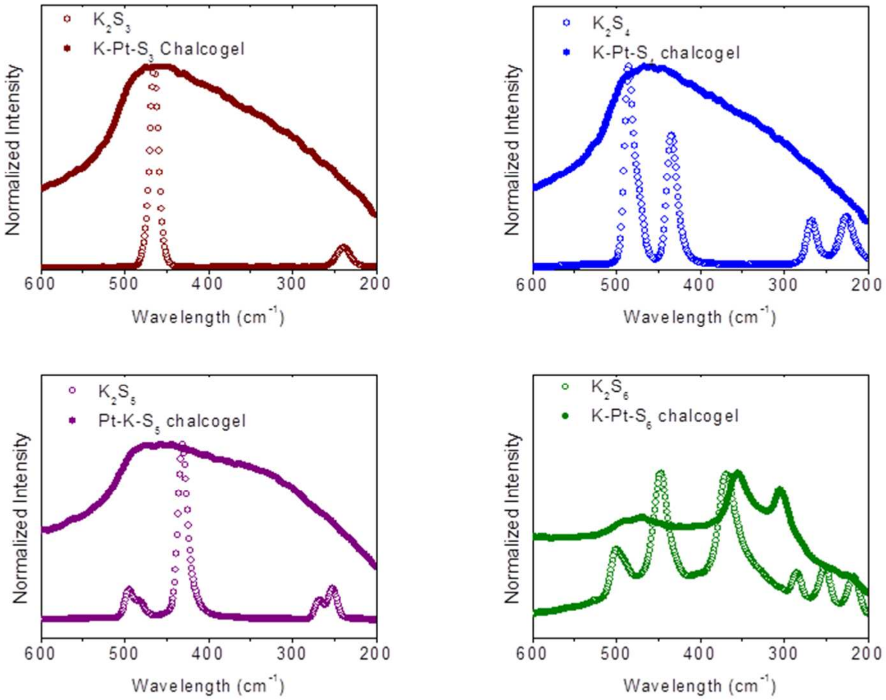

Figure 4S. Raman spectra of polysulfide chalcogels show broad bands which corresponds to the presence of S-S vibration from polysulfide ligands.

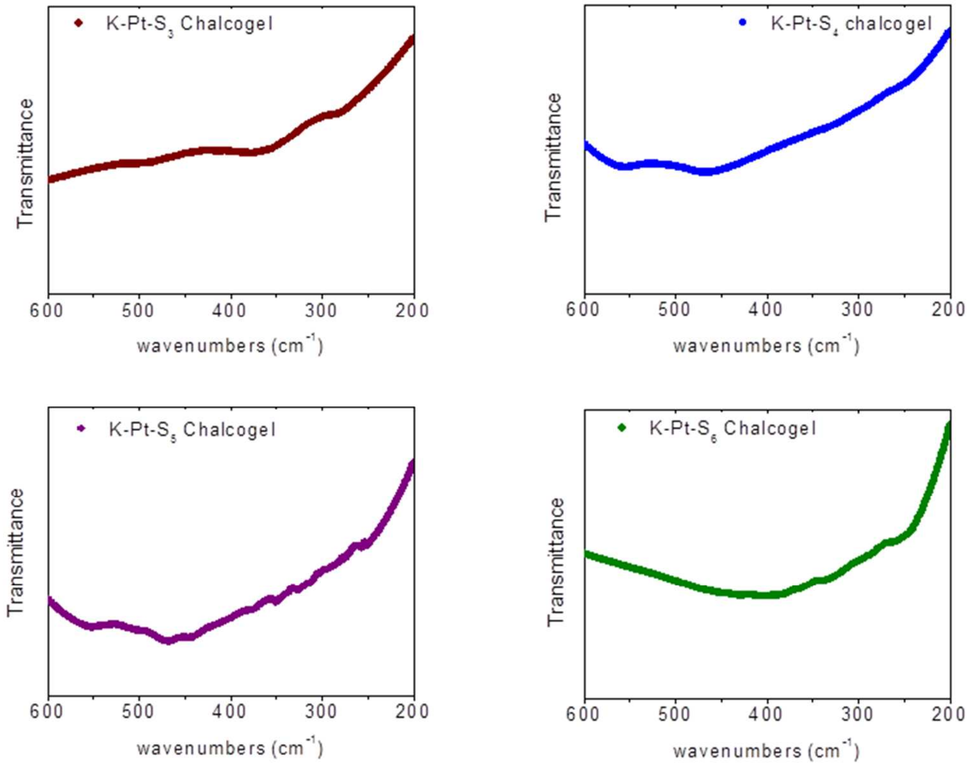

Figure 5S. Infrared spectrum of chalcogels featuring broad absorption peaks between 300-500 cm^{-1} region.

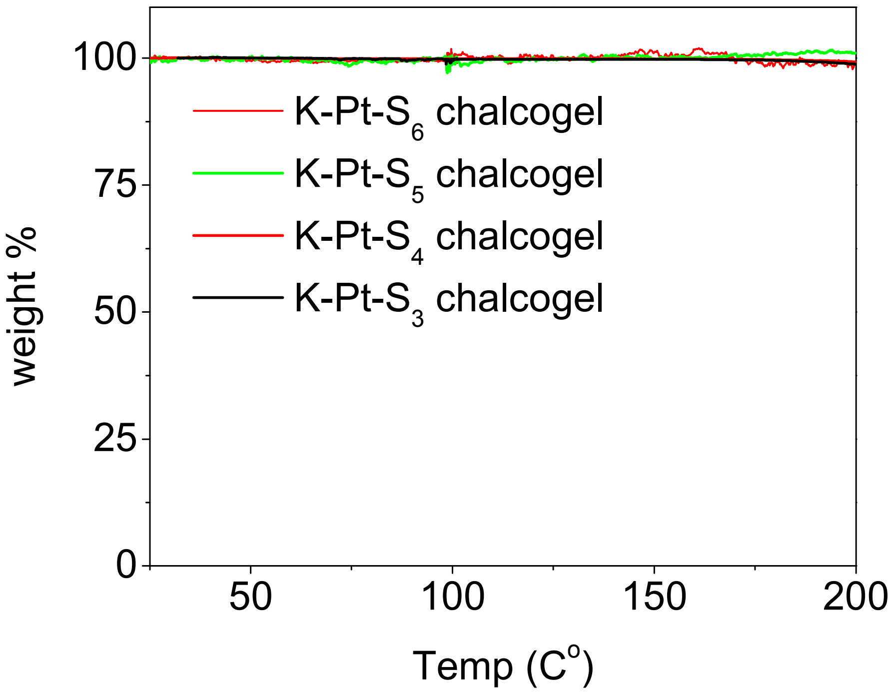

Figure 6S. Thermal gravimetric analysis (TGA) of polysulfide chalcogels shows no significant weight change up to 200 °C in both nitrogen and air atmosphere. This indicates that these materials do not undergo decomposition or partial oxidation in this temperature range.

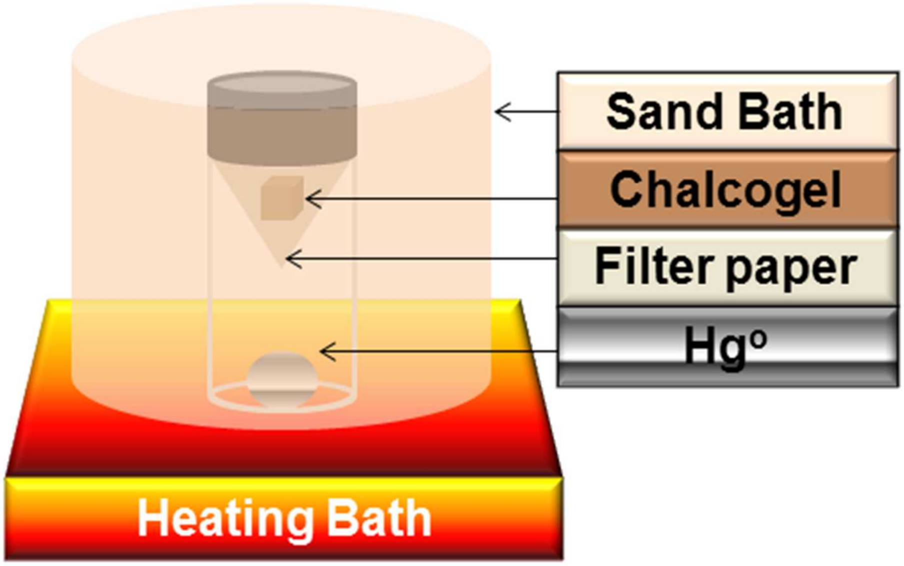

Figure 7S. Schematic representation of mercury capture experimental set up.

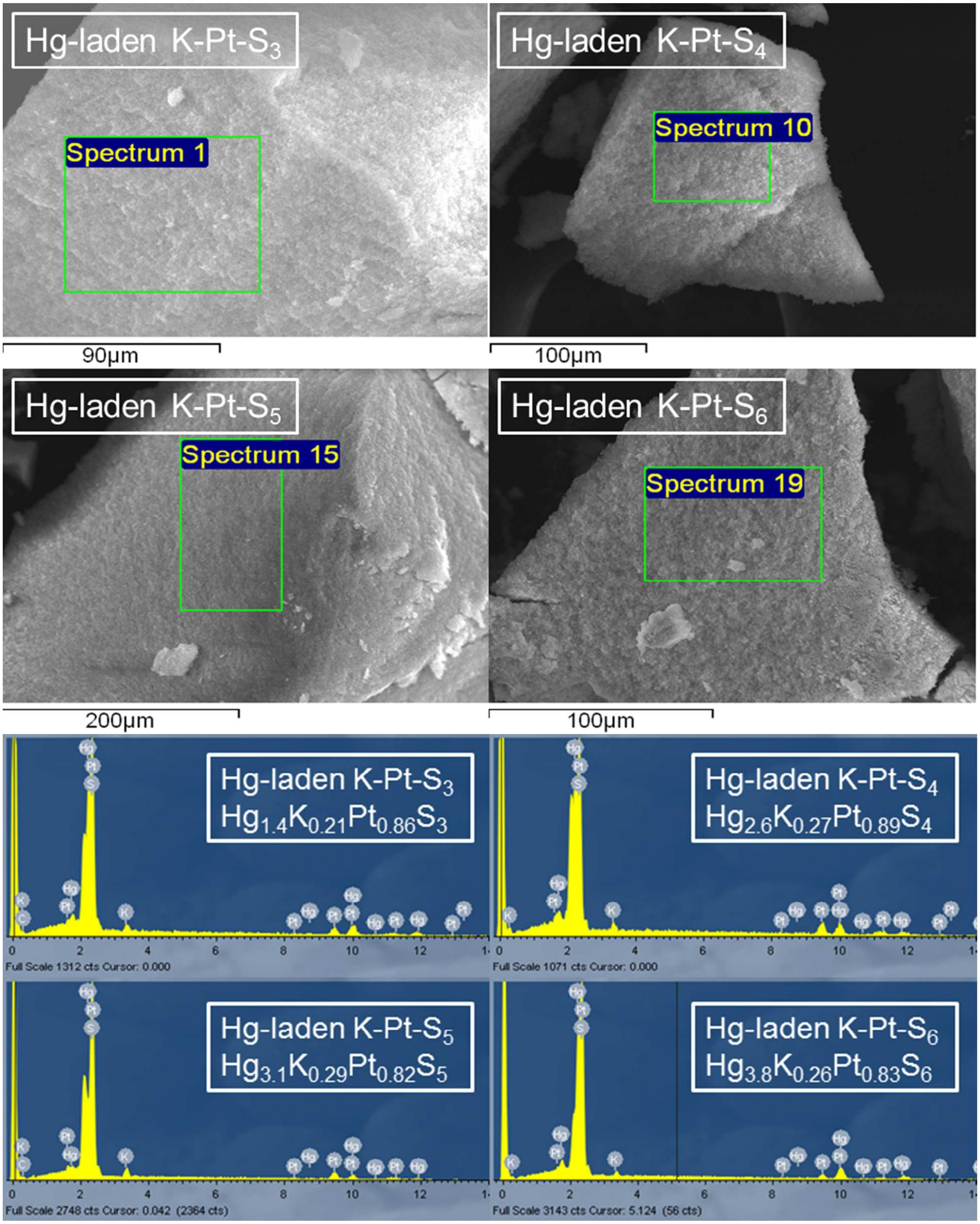

Figure 8S. Scanning electron microscopy (SEM) and energy dispersive analysis (EDS) of Hg-laden polysulfide chalcogels reveal the amount of mercury adsorbed on the surface.

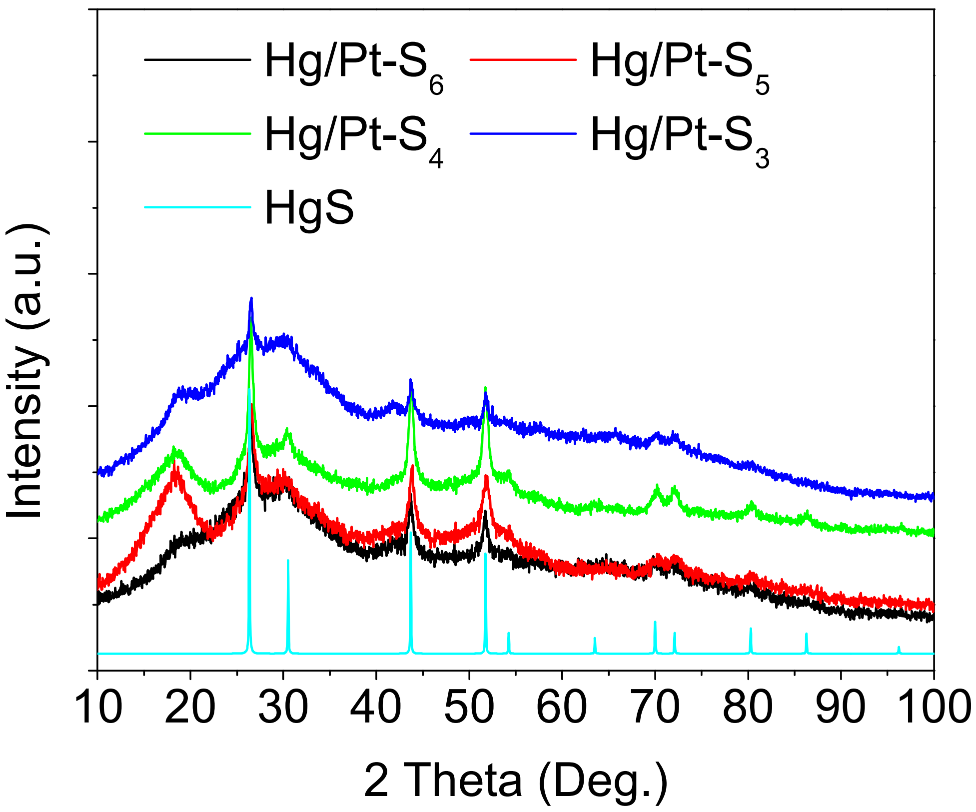

Figure 9S. Hg-laden polysulfide chalcogels shows the presence of HgS within the gel structure from the powder X-ray diffraction pattern.