Ion-Exchangeable Cobalt Polysulfide Chalcogel

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S *Supporting Information*

ABSTRACT: We present a promising approach in synthetic chalcogel chemistry that is extendable to a broad variety of inorganic spacers. Polychalcogenide aerogels with ion-exchange properties are demonstrated in cobalt polysulfide. The new materials show a broad range of pore sizes and high surface area of 483 m^2/g.
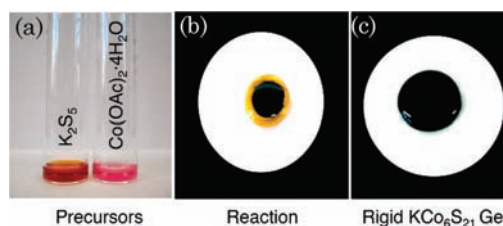
Figure 1. Precursor solutions in formamide/water (a), combinations of the solutions and immediate reaction (b), and the rigid wet gel of KCo_6S_{21} (c).

In addition to the well-established aerogels made from metal oxides,[1] low-density porous materials composed of metal chalcogenides have recently come into focus.[2] Such systems could be capable of combining the electronic properties of chalcogenides with internal porosity. By replacement of O^{2-} in porous materials with S^{2-}, Se^{2-}, or Te^{2-}, a logical progression in the research of aerogels is made.[3] In particular, there is a distinct attraction in moving from oxides to chalcogenides because of the increased covalency (and decreased band gap) in the semiconducting phases.[2b] Aerogels based on aggregated binary nanocrystals (e.g., CdS, CdSe) and on amorphous GeS_2 have been reported.[2b,4] These chalcogenide gels by virtue of their more polarizable metal-chalcogenide surface promise new applications beyond those of conventional aerogels, including remediation of heavy metals, energy conversion, chemoselective absorption of molecules, and catalysis.[2a,5]

The preparation of chalcogenide gels has been achieved by three different synthetic routes: Thiolysis (e.g., LaS_x, WS_x, ZnS, and GeS_x),[6] nanoparticle condensation (e.g., ZnS, CdS, CdSe, PbS),[7] and metathesis reactions between soluble chalcogenide clusters and salts of linking metal ions (e.g., $Pt_2[M_4Q_{10}]$, M = Ge, Sn, Q = S, Se).[8] Thiolysis of alkoxides, thiolates, silylamides, and metal alkyl precursors in nonaerobic conditions in the presence of hydrogen sulfide have been shown to yield metal sulfide gels or precipitates. The use of the thiolysis route is limited due to the scarcity of suitable precursors and difficulties in handling and syntheses. Nanoparticle based aerogels have been prepared by applying the oxidative condensation of preformed metal chalcogenide nanoparticles to three-dimensional networks. Also the sol−gel assembly of nanoparticles into metal chalcogenide aerogels is limited to nanoparticles with established syntheses and to compositions that are robust to gelation conditions. For the metathesis approach, up until now alkali metal salts of molecular building blocks, such as adamantane $[Ge_4Q_{10}]^{4-}$ or $[Sn_2Q_6]^{4-}$ clusters (Q = S).[8] In the case of the reaction of thiomolybdate with cobalt salts, polymeric networks (chalcogels) are constructed from $[MoS_4]^{2-}$ units.[9]

Because metathesis reactions have been demonstrated to be particularly useful for the preparation of new compositions of gels, we wanted to alter the anions and focus on the use of ditopic linear polychalcogenido anions. The long polychalcogenide ligands would act as struts and bridge metal centers and introduce openness and porosity into metal polychalcogenide networks. Only a few metal-polyselenide open networks have been described, but they lack porosity.[10]

In the present study, we report the preparation and characterization of a porous cobalt polysulfide that was obtained from the reaction of K_2S_5 with cobalt acetate. K_2S_5 was prepared by heating a stoichiometric mixture of K_2S and S for 4 h at 500 °C in an evacuated sealed quartz tube.[11] A total of 0.05 g (0.2 mmol) of $[Co(OAc)_2 \cdot 4H_2O]$ was dissolved in 1 mL of H_2O, and 1 mL of formamide was added to it. The pink solution of cobalt acetate was slowly added to an orange solution of 0.048 g (0.2 mmol) K_2S_5 in 1.5 mL of formamide (Figure 1a). After keeping the reaction undisturbed for 1 week, a black gel was obtained (Figure 1c) and solvent exchanged with 50:50 ethanol,water 5−6 times. Treatment of the gel then involved 4−5 washings with ethanol over a week followed by supercritical CO_2 drying. This process removes the majority of the solvent from the pores retaining the gel network. After critical point drying, the obtained aerogel consists of very fluffy particles and larger chunks of up to 0.5 cm in diameter. The scanning electron micrograph (Supporting Information, Figure S1) of the obtained chalcogel showed the spongy nature of the gel for which a skeletal density of 3.02 g·cm^{-3} was determined.

The obtained gel was initially characterized by energy dispersive X-ray spectroscopy (EDS) which confirmed that most of the potassium ions were washed out during solvent exchange. In the dried gel, the elements Co, S, and K are present with an average ratio Co/S/K of 1:3.5:0.17 (S1). The average composition of the aerogel can be written as "KCo_6S_{21}" (Figure S1). This indicates that the Co^{2+} ions do not fully neutralize the polysulfide chains and the Co/S_x network has a residual anionic charge which is balanced by K^+ ions. The K^+ ions are thus part of the materials and are located within the pores of the network. These ions are
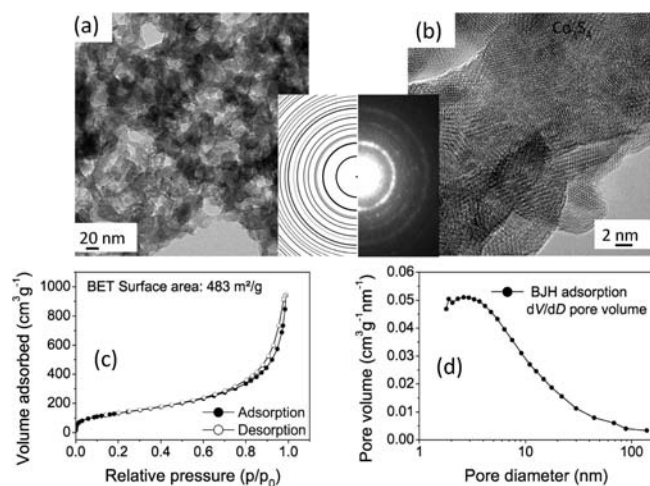
Figure 2. Characterization and properties of the K/CoS_x gel. (a) Low magnification image showing amorphous porosity in most regions, (b) high magnification image depicting some of the few crystalline nanoparticles present. They were identified as Co_3S_4 by electron diffraction together with simulation (inset). (c) Nitrogen adsorption–desorption isotherm. (d) Pore-size (V–D) distribution plot calculated from the adsorption isotherm by the BJH method.

accessible and can be exchanged fully and reversibly with Cs^+ ions. (Supporting Information Figure S2, eq 1). Confirmation for the K/Cs exchange and back again comes from EDS analysis of the materials.

$$KCo_6S_{21} + Cs^+ \rightleftharpoons CsCo_6S_{21} + K^+ \qquad (1)$$

KCo_6S_{21} is the first example of an ion-exchangeable chalcogel and underscores a new functional property for this class of materials. This finding suggests that a Co/S_x network has formed with an overall negative charge that is likely to be the result of polysulfide ligands with a terminal negative charge and a K^+ counterion $[Co–(S)_x–S^-K^+, (x = 0–4)]$. Polysulfide ligands can also chelate the metal atoms in KCo_6S_{21} similar to S^{2-}, $(S_3)^{2-}$, and $(S_4)^{2-}$ ligands in the molecular at-complex $(NH_4)_2[Re_2S_{16}]$.[12] The lower S/Co ratio in KCo_6S_{21}, however, suggests that here the majority of polysulfide ions coordinate Co atoms in bridging mode. Polysulfide ions are in fact the essential ingredient for the high-porosity aerogel to form.

The phase and crystallinity of the xerogel and the aerogel were investigated by powder diffraction. Whereas the xerogel was amorphous, the final aerogel features a poorly resolved diffraction pattern with high noise level and nonlinear background due to the amorphous character of the gel. The presence of weak broad crystalline peaks is due to the presence of the cobalt sulfides Cattierite CoS_2 and Linnaeite Co_3S_4 (Figure S3). The presence of tiny amounts of crystalline Co_3S_4 in the amorphous framework was also confirmed by transmission electron microscopy (TEM) (Figure 2a,b). The morphology of the aerogel was studied by TEM showing a broad range of pores extending from the meso- (2–50 nm) into the macro- (>50 nm) porous region (Figure 2a). The pores are arranged irregularly and do not seem to form channels throughout the aerogel. Instead, a random porous interconnected network is observed that is typical for aerogel structures. The infrared spectrum of the final gel showed some remaining adsorbed solvent after critical point drying. It also confirmed the presence of polysulfide chains with observed $\nu(S–S)$ bands at 570 (br) and 461 cm^{-1} that are characteristic

for polychalcogenide anions of the type $(S_2)^-$, $(S_3)^{2-}$, and S_4^{2-} (Figure S4).[13] In the thermogravimetric analysis (TGA), continuous weight loss is observed upon heating (Figure S8). EDS analysis of the residue after TGA gave an average composition of $Co:S:K = 6:1:1$ (S5). From the electronic absorption spectrum the bandgap of the gel was determined by diffuse reflectance showing a value of ca. 0.7–1.1 eV (S8).

The nitrogen adsorption–desorption isotherm of the aerogel exhibits a type-IV adsorption branch with a combination of H1 and H3 hysteresis loops characteristic for a predominantly mesoporous system (Figure 2c).[14] The Barrett–Joynes–Halenda (BJH) plot of pore size distribution shows a characteristic broad range of pores (1.8–138 nm) with an average pore diameter of 12 nm (Figure 2d). The intraparticle microporosity of 15% was determined using the Dubinin–Radushkevich model (Table S6). The BET surface area (S_{BET}) of 483 m^2/g, to the best of our knowledge, is one of the largest reported so far for chalcogenide gels. When compared on a per mole basis, the silica equivalent is 810 m^2/g which is comparable to porous silica prepared by wet methods.[15]

The $K/Co/S_x$ gel is the first example of an ion-exchangeable chalcogel. This opens the path for functionalizing these materials for a variety of uses and enables efforts directed toward the synthesis of functional chalcogels that have already been shown to have interesting applications, for example, in the catalysis of hydrodesulfurization reactions.[9] The preparation of the $K/Co/S_x$ gel by the reaction of an alkali metal polysulfide (inorganic spacer) with a transition metal salt expands the series of gel preparations. Introducing porosity in such a straightforward manner marks the end of the paradigm that surfactants, bulky organic cations, templates, or preformed clusters or nanoparticles are necessary for the preparation of porous chalcogenide frameworks.

■ ASSOCIATED CONTENT

S **Supporting Information.** Experimental details and characterization of the KCo_6S_{21} gel. This material is available free of charge via the Internet at http://pubs.acs.org.

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