Supporting Information

Ion-exchangeable Cobalt Polysulfide Chalcogel

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1. Experimental procedures

Starting material: All operations were performed in a N_2-glovebox. For critical point drying, the gel was taken out of the glovebox and briefly exposed to ambient atmosphere. K_2S_5 was prepared by heating a stoichiometric mixture of K_2S and S for 4h at 500°C in an evacuated sealed quartz tube. *Attention*: In order to avoid a spontaneous start of the exothermic reaction the quartz tube must be cooled with liquid nitrogen during sealing. Shaking of the sealed tube can also initiate the reaction.

Gel preparation: 0.05 g (0.2 mmol) $[Co(OAc)_2 \cdot 4H_2O]$ was dissolved in 1 mL H_2O, 1 mL 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 formamide. After one week the resultant black gel was solvent exchanged by soaking the gel in a 50:50 EtOH:H_2O solvent mixture for ca. 12 hours. This procedure was repeated 5-6 times. Then the black gel was 4-5 times with EtOH over the course of a week. The black gel pieces were subsequently dried with supercritical CO_2.

Ion-exchange experiment: The gel was tested for reversible ion-exchange of the potassium ions with caesium ions. 0.076 g of the xerogel was treated for 17 h with 10 mL of a 0.1 M aqueous CsCl solution. The gel was then filtered through a small Büchner funnel and then washed nine times with 10 mL of deionized water. The ion-exchanged gel was finally washed with 10 mL of EtOH and 10 mL of Et_2O and dried under reduced pressure. The reversibility of the ion exchange was checked by repeating the procedure using 0.058 g of the Cs-containing chalcogel and repeating the procedure with a 0.1M KCl solution. The resulting dried solids were investigated by SEM/EDS.

2. Characterization

Supercritical drying. Critical point drying of the chalcogels was done with a Autosamdri – 815B (tousimis) instrument. Depending on the amount of gel, the soaking time and exchange time vary. A black aerogel was obtained after supercritical drying at 40ºC.

Density measurements. The skeletal densities of the aerogel materials were measured by a Micromeritics AccuPyc 1340 gas pycnometer (1cc model) using ultra high purity (UHP) helium gas.

SEM/EDS. Scanning electron microscopy images of the aerogel samples were taken with Hitachi S-3400N VP-SEM. Powdered aerogel samples were placed on carbon tape.

Infrared spectroscopy. Infrared spectra of solid samples were obtained on a Thermo Nicolet 6700 FT-IR spectrometer. Spectra were obtained on fine powders in diffused reflectance mode under nitrogen atmosphere and averaging 256 interferograms with resolution of 2 cm^{-1}.

UV/VIS spectroscopy. UV/vis diffuse reflectance spectra were recorded at room temperature with a Shimadzu model UV-3101PC double-beam, double monochromator spectrophotometer.

TEM images. TEM samples were prepared by suspending the aerogel sample in ether and then casting on holey carbon coated Cu grid. High-resolution transmission electron micrograph (TEM) was obtained with a JEOL 2100F instrument (field emission) operating at 200 kV. The simulation of the diffraction pattern was carried out using the programme MacTempasX v. 2.3.15.

CHN-Analysis. CHN analysis was performed by Midwest MicroLab LLC. C 0.27, H 1.14, N 0.74 %. Because of the low percentages of the elements present and the error of the measurement, no further information (content of formamide or other solvents) can be obtained.

Thermogravimetric analysis (TGA). The TGA measurements were performed on a Shimadzu TGA-50 thermogravimetric analyzer in aluminum boats under Ar flow (30 mL/min).

Nitrogen physisorption measurements. Nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 system. For each measurement, about 200 mg of samples were taken. Before measurement, samples were degassed at 348 K under vacuum ($<10^{-4}$ mbar) for overnight. Low pressure incremental dosing of 3 cc/g STP and 45 s equilibration were applied as analysis conditions. BET transform plot was

obtained in the 0.05 to 0.35 relative pressure (P/Po) regions and correlation coefficient of 0.99999 was obtained in every case.

Powder Diffraction. The diffraction pattern was recorded on a Scintag XDS2000 automated diffraction system, with four-circle pole-figure and GeLi solid-state detector. Cu-Kα radiation was used. The sample was prepared by spreading out the aerogel on a low-background sample holder using a few drops of EtOH. The diffraction patterns (raw data) were compared to the phases in the International Centre for Diffraction Data (ICDD, release 2009, JADE 9.0) powder diffraction file (PDF).

Magnetic Measurements. Magnetic susceptibility measurements were made on powder samples using a Quantum Design MPMS SQUID magnetometer. Temperature dependent susceptibility measurements were made with an applied field of 2000 Oe from 2 to 300K with both field cooled and zero field cooled modes.

3. Supplementary Figures

Element	1st analysis, atomic%	2nd analysis atomic%	3rd analysis atomic%	Average of atomic%
S	75.58	71.71	76.79	74.69
K	3.38	4.02	3.19	3.53
Co	21.03	24.27	20.01	21.77

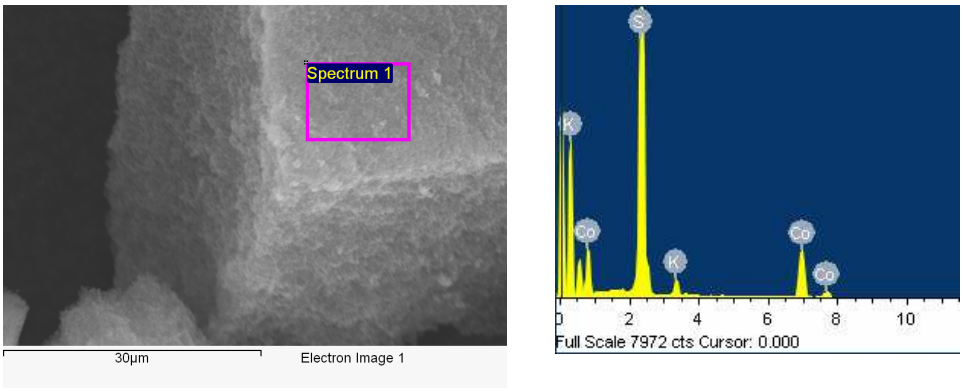
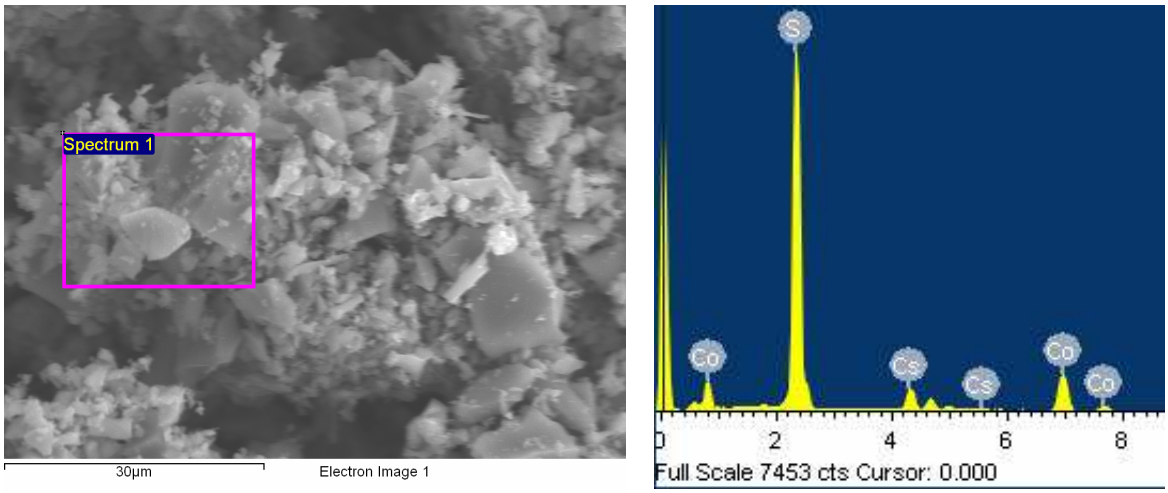


Figure S1: SEM/EDX analysis of the KCo_6S_{21} aerogel. Analyses were performed on several sample gel pieces and powdered gel pieces giving the listed average composition. The images illustrate the sometimes surprisingly regular faces of larger gel particles and spongy nature of the low-density cobalt polysulfide.

(a)

Element	Weight%	Atomic%
S	56.38	75.32
Co	26.26	19.09
Cs	17.36	5.59



(b)

Element	Weight%	Atomic%
S	62.57	77.52
K	1.90	1.93
Co	26.45	17.83
Cs	9.08	2.71

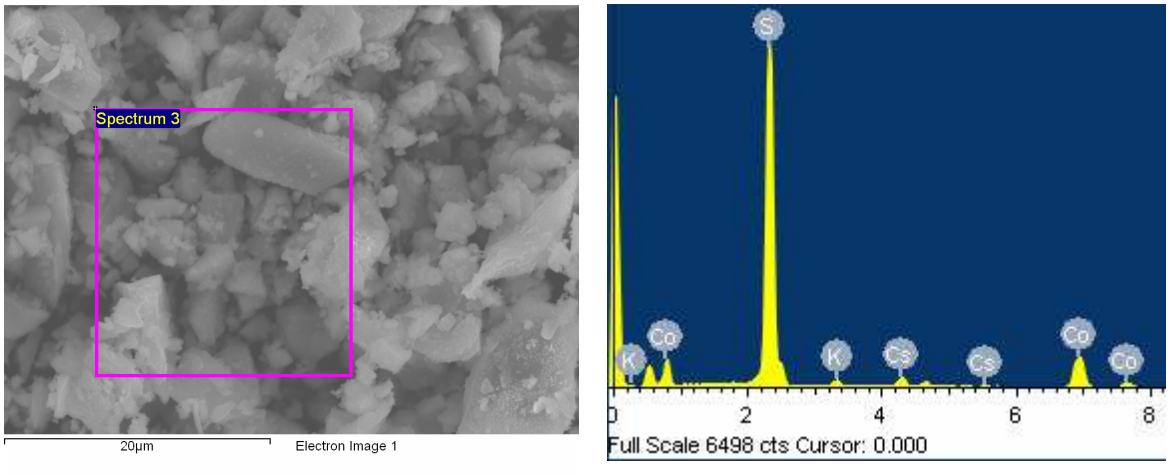


Figure S2: SEM/EDS analysis of the gel (a) after ion exchange with CsCl solution. (b) Partial reversibility of the ion-exchange was observed when the Cs ions are exchanged for potassium ions.

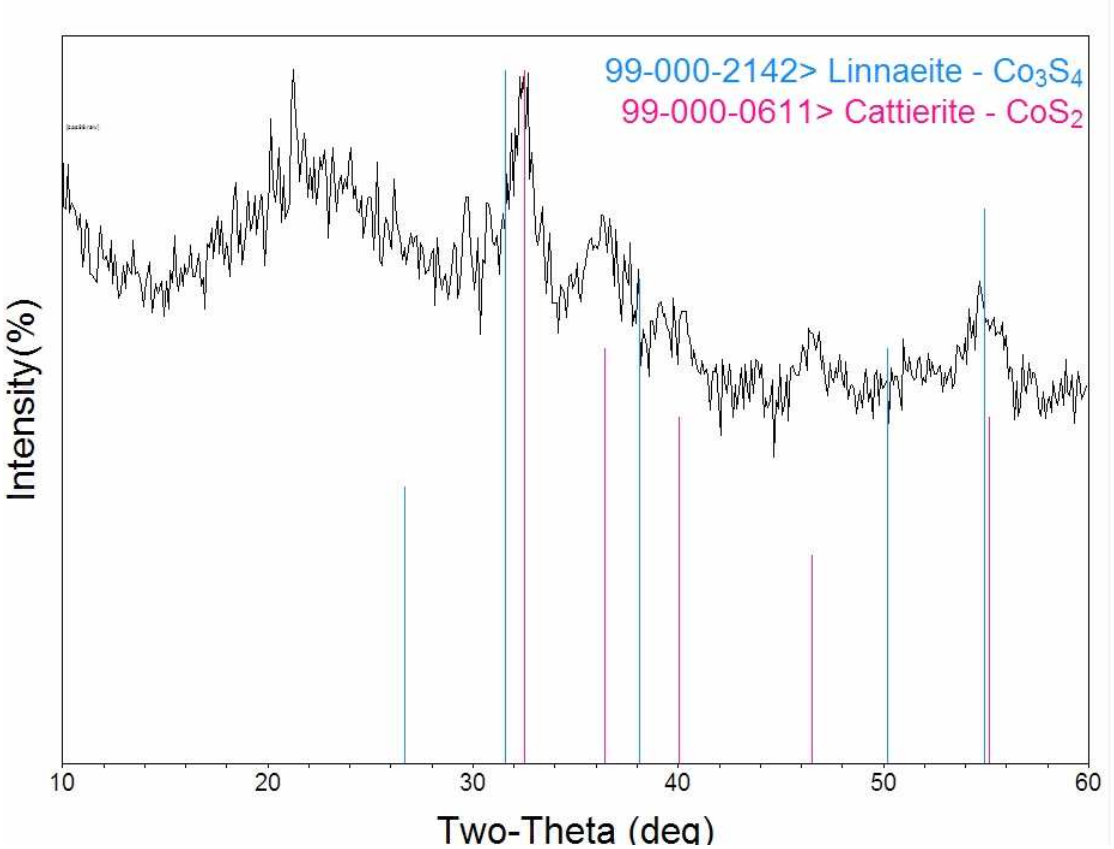


Figure S3: Poorly resolved powder diffraction pattern of the KCo_6S_{21} aerogel indicating the presence of minor crystalline particles of cobalt sulfides.

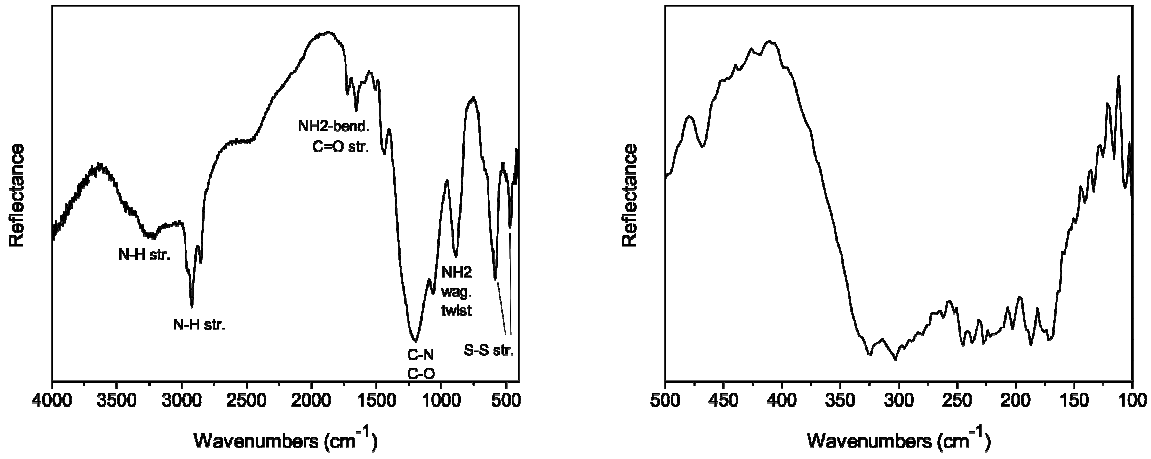
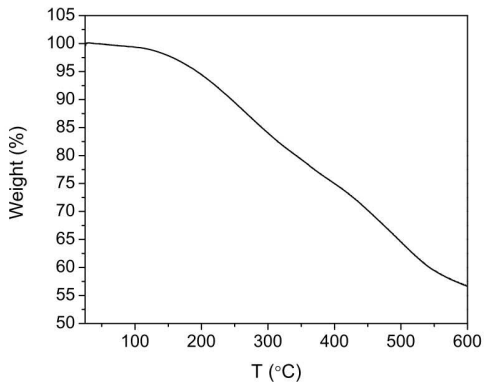
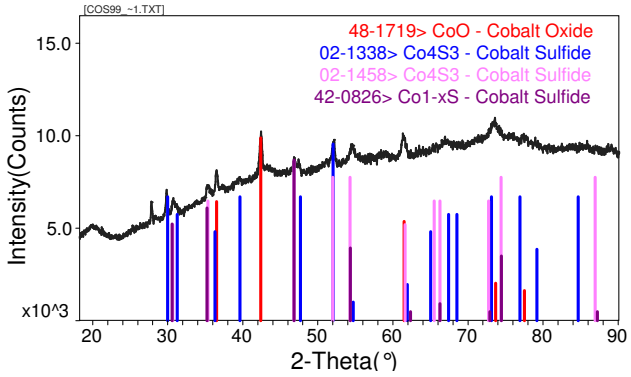


Figure S4: Infra-red spectra of KCo_6S_{21} showing the presence of moisture and formamide and possibly traces of EtOH in the NIR. The far IR spectrum characterized by a broad absorption of the gel.

(a)



(b)



(c)

Element	Weight%	Atomic%
S	7.68	12.68
K	9.71	13.15
Co	82.60	74.17

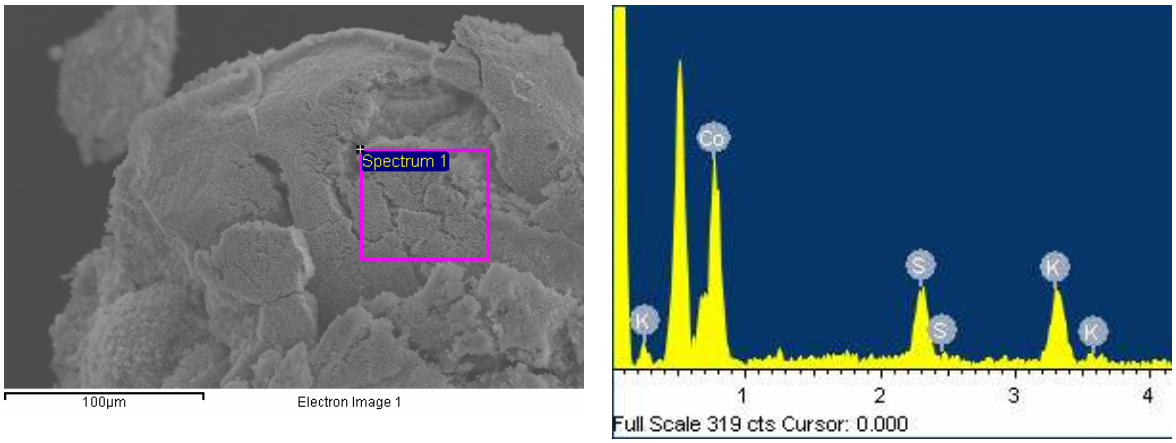


Figure S5: a) TGA of the KCo_6S_{21} gel showing a gradual weight loss (heating rate 5ºC/min, Ar flow 30 ml/min). b) PXRD of the residue after TGA. The high back ground is from X-ray fluorescence of Co. c) SEM/EDS after TGA shows the presence of excess Co over K and S. This indicates loss of sulfur and reaction of the aerogel with traces of oxygen or chemically bound oxygen of solvent traces.

Table S6: Porosity data for KCo_6S_{21}.

sample	S_{BET} (m^2g^{-1})	Silica equivalence surface area[§] (m^2g^{-1})	V_p[‖] (cm^3g^{-1})	V_{N2}[¶] (cm^3g^{-1})	% microporosity[#]
KCo_6S_{21}	483	810	1.08	0.16	14.8

§ Per mol of gel is converted into per mol of SiO_2 using respective formula weights. ‖ Adsorption total pore volume is measured at a relative pressure (P/P_0) of 0.97. ¶ Limiting micropore volume is obtained in the relative pressure region of 5×10^{-6} to 2×10^{-2}. # Percentage microporosity is obtained by using the equation $(V_{N2}/V_p) \times 100$.

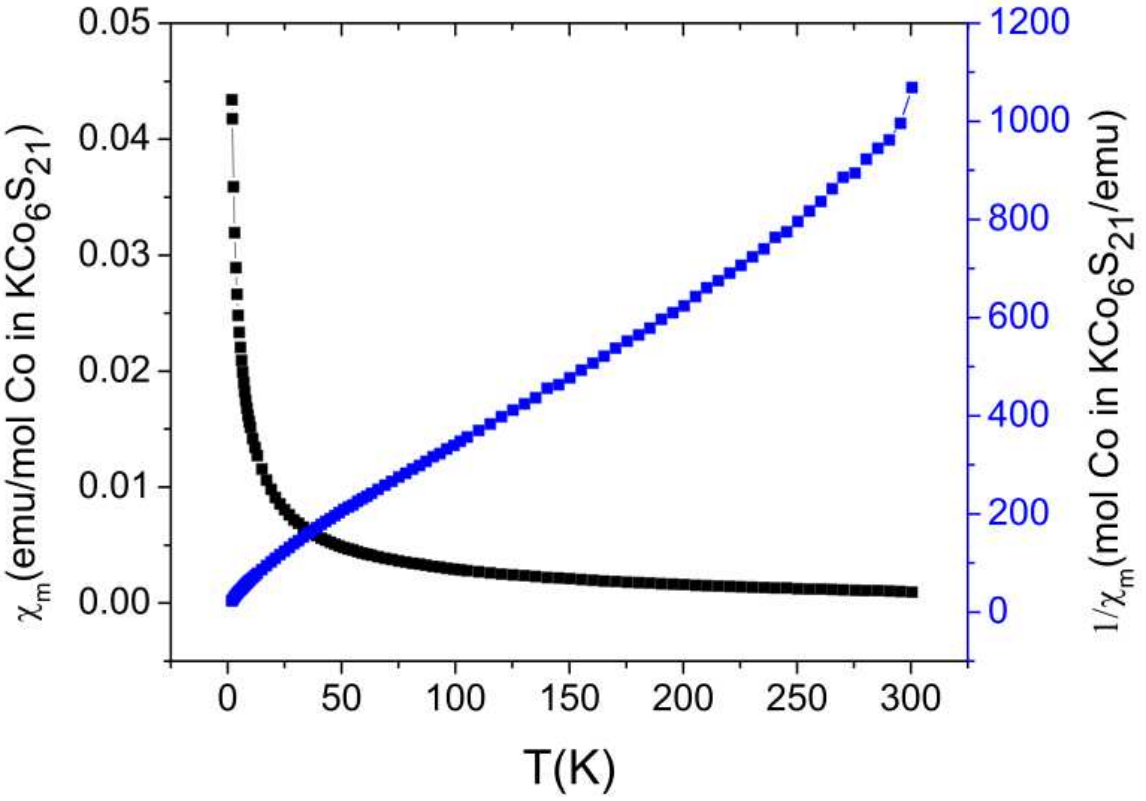


Figure S7: A Curie-Weiss plot of the magnetization from 2-300 K at constant field revealed the paramagnetic nature of the KCo_6S_{21} aerogel. The data for the polysulfide gel follow the Curie-Weiss law in the 50K-250K range from which μ_{eff} of 1.58 μ_B (T_c ca. 27 K) was obtained per mol of Co within the aerogel. This value is close to one unpaired electron only effective magnetic moment of 1.73 μ_B suggesting low spin octahedral or square pyramidal Co^{2+} species.

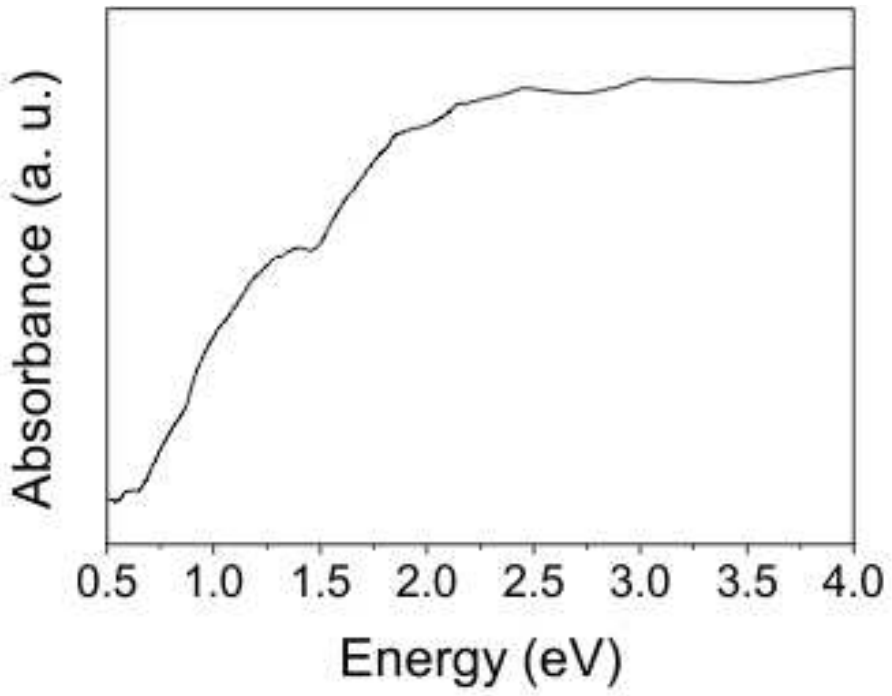


Figure S8: Characterization and properties of the KCo_6S_{21} gel. Solid-state UV-vis optical absorption spectrum (converted from reflectance) gave a bandgap of ca. 0.7–1 eV.