

Supporting Information

Open Framework Metal Chalcogenides as Efficient Photocatalysts for Reduction of CO₂ into Renewable Hydrocarbon Fuel

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Experimental section

-Chemicals and instrumentation

All of the reagents used were obtained from commercial supplies without further purification. Germanium (= Ge, -100 mesh, 99,999%, Alfa Aesar), germanium (IV) oxide (= GeO₂, 99.999%, Acros Organics), sulfur powder (= S, -100 mesh, 99.5%, Alfa Aesar), Zn(NO₃)₂·6H₂O (98% extrapure, Acros Organics), *N*-(2-aminoethyl)-morpholine (= AEM, C₆H₁₄N₂O, 98+%, Alfa Aesar).

Powder X-ray diffraction (PXRD) experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$). The data collection was performed with a step size of 0.02° and counting time of 2 or 5 or 10 seconds per step. The simulated powder XRD pattern was obtained from the single-crystal data. The thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500 apparatus in the temperature range of 30 °C to 900 °C under N₂ flow at a heating rate of 5 °C/min. Elemental Analysis (EA) was carried out with a Perkin-Elmer 2400 CHNS Elemental Analyzer (Atlantic Microlab, Inc.). Metal contents were measured by Agilent inductively coupled plasma

mass spectrometer (ICP-MS) 7500cx with the autosampler (chemistry, UCR). Solid-state diffuse reflectance spectra were recorded on an Shimadzu UV-3101PC spectrophotometer, its absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function. Scanning electron microscopy (SEM) images were taken on Philips FEI XL30 field emission scanning electron microscope (FESEM) equipped with PGT-IMIX PTS energy dispersive spectroscopy (EDS) detector, or on Nova NanoSEM450 (Schottky field emission scanning electron microscope).

- Synthesis of AEM@GeZnS material

0.090 mg (1.23 mmol) of Ge (or GeO₂, 0.120 g, 1.14 mmol), 0.090 mg (0.30 mmol) of Zn(NO₃)₂·6H₂O, 0.220 g (6.88 mmol) of sulfur, and 2.5 mL of *N*-(2-aminoethyl)morpholine (AEM) were mixed in a 23 mL Teflon-lined stainless autoclave and stirred for ca. 30 min. The vessel was then sealed and heated at 190 °C for 12 days. After cooling to room temperature, 0.108 g of AEM@GeZnS crystals was obtained as large light-yellow rhombic-dodecahedral crystals.¹

-Ion-exchange experiments

Freshly prepared compound AEM@GeZnS was soaked in aqueous (or acetonitrile) of variable metal salts, after selected time, the crystals were taken out of solution and washed with respective solvents to remove residual complex on the surface. The concentrations of encapsulated cationic species were measured by energy-dispersive-X-ray (EDS), inductively coupled plasma (ICP) mass spectrometer and powder XRD.

-Preparation of Au@GeZnS

The crystals of AEM@GeZnS (50 mg) were immersed in a 10 mL acetonitrile solution of AuCl₃ (0.02 M) and the mixture was shaken for several seconds and undisturbed for 12 hrs. The color of the soaked crystals gradually turned dark from light-yellow. The crystals were immersed in CH₃CN-H₂O solution (vol:vol, 1:1) for 12 hrs during which fresh CH₃CN-H₂O was replenished three times. The presence of incorporated Au was confirmed by EDX, ICP and optical spectra.

-Preparation of Pd@GeZn

Immersing 50 mg AEM@GeZnS material in the 20 mL Pd(NH₃)₄(NO₃)₂-H₂O solution (0.01 M, diluted from 10% wt%), which was kept at r.t. for 24 hrs. The color of the soaked crystals gradually turned black from light-yellow. Then the black crystals of Pd@GeZnS were taken out of solution and washed with water to remove residual species on the surface. The presence of incorporated Pd was confirmed by EDX, ICP and optical spectra.

-Preparation of AEM@GeZnS film on FTO electrode

Typical preparation of film of AEM@GeZnS on FTO electrode: 25.0mg of ground AEM@GeZnS powder was dispersed in 50mL isopropanol with the presence of 5.0 mg of Mg(NO₃)₂·6H₂O. The sealed mixture suspension was continuously stirred for 2 days, and then was ultrasonically vibrated for one hour before electrophoretic deposition. The clean and sleek platinum plate electrode was used as anode, and the fluorine-doped tin-oxide (FTO) conductive glass as cathode. Constant working voltage was set up to 50V. The whole electro-deposition process lasted for 30 minutes. The obtained FTO electrode decorated with ISC- 10s film on its surface was finally washed with ethanol to remove residual isopropanol and Mg(NO₃)₂ salt left in suspension.

- Photoelectrochemical measurements

Photoelectrochemical studies on the films of ISC-10s samples on FTO substrate were performed on a Solartron SI 1287 electrochemical interface analysis instrument operated with CorrWare program in a standard three-electrode configuration with a FTO electrode modified with AEM@GeZnS samples as the photoanode (an effective area is $\sim 2.0 \text{ cm}^2$), a Pt foil as the counter electrode and a Ag/AgCl electrode as the reference electrode (see Scheme S1). Mixed solution of Na_2SO_3 (0.35M) and Na_2S (0.25M) was used as electrolyte. A 150 W Xenon lamp (Spectra Physics) coupled with an AM 1.5G filter (Newport) was utilized as the simulated sunlight source and to remove light of wavelength below 420nm. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 10⁻¹ to 10⁵ Hz with an AC voltage amplitude of 10 mA at a DC bias of 0V vs. Ag/AgCl.

- Photoreduction of CO₂

Photocatalytic reduction of CO_2 in the presence of H_2O was carried out in a lab bench reactor (volume, $\sim 400 \text{ mL}$) with a quartz window on the top of the reactor. The light source was a 300 W Xe lamp. The photocatalytic reaction was performed in a gas (vapor)-solid upper region of the reactor. Liquid water with a volume of 4 mL was pre-charged in the bottom of the reactor. It should be noted that the catalyst was not immersed into the liquid water. Instead, the catalyst was surrounded by H_2O vapor and CO_2 . The pressure of CO_2 was typically regulated to 1 atm. The photocatalytic reaction was typically performed for 6 h. The amounts of CH_4 formed were analyzed by gas chromatography. We adopted a flame ionization detector (FID) for quantifying the amounts of CH_4 formed from CO_2 to ensure high sensitivities. Argon was used as the carrier gas. We performed the same experiment (including both reaction and detection) for at least 3 times for each catalyst, and the relative error was $< 5\%$.

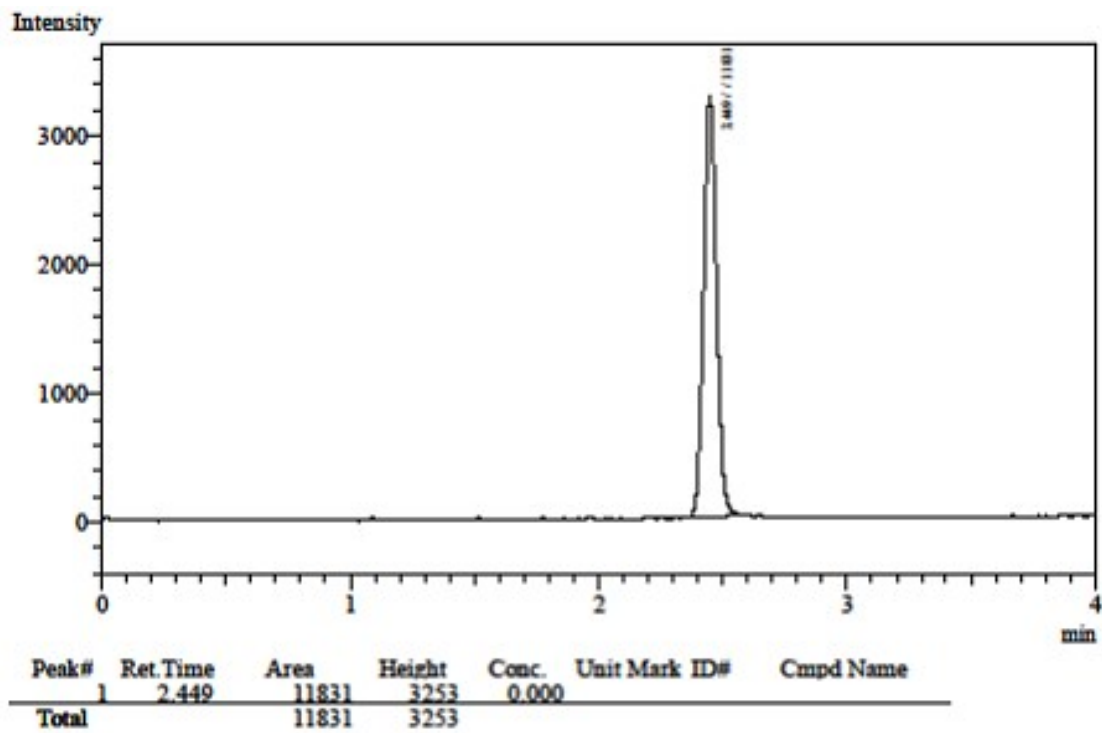


Figure 1. CH₄ peaks measure by FID GC.

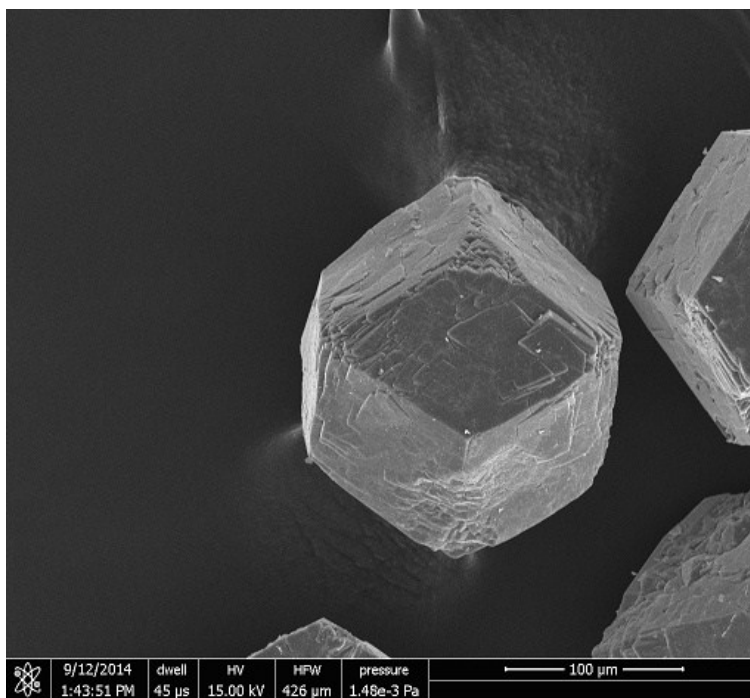


Figure 2. SEM image of Au@GeZnS.

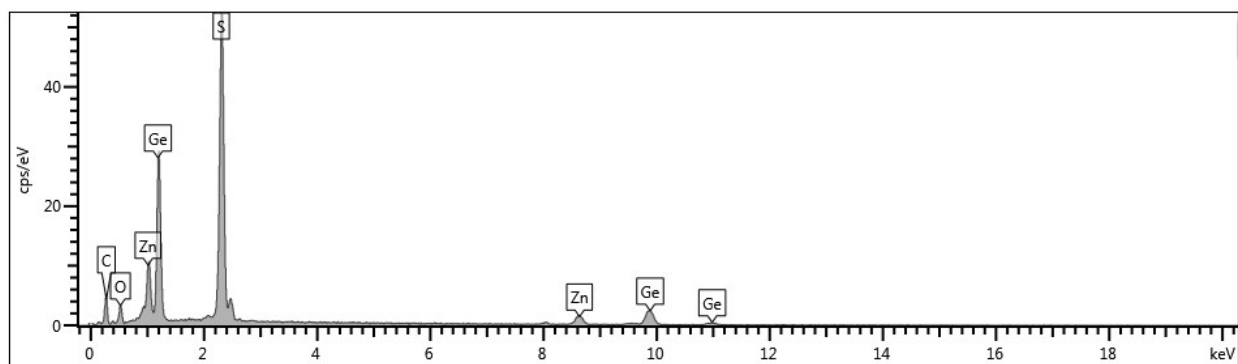


Figure 3. EDS of AEM@GeZnS.

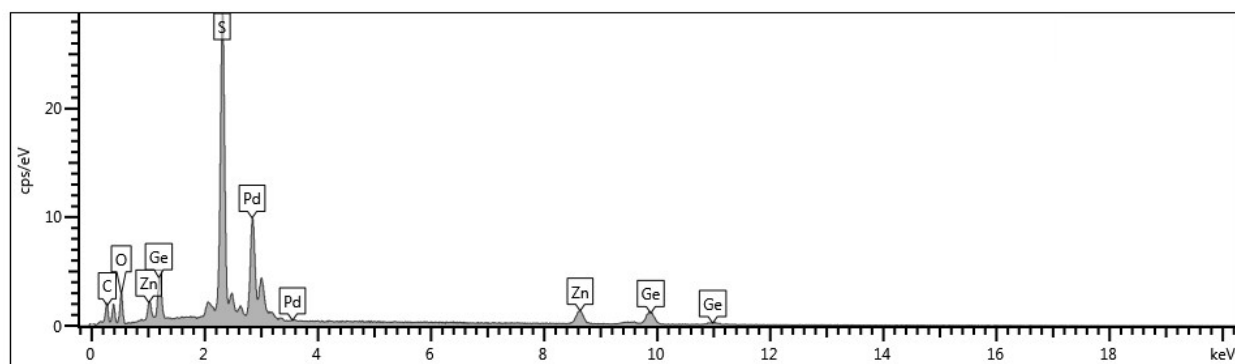


Figure 4. EDS of Pd@GeZnS.

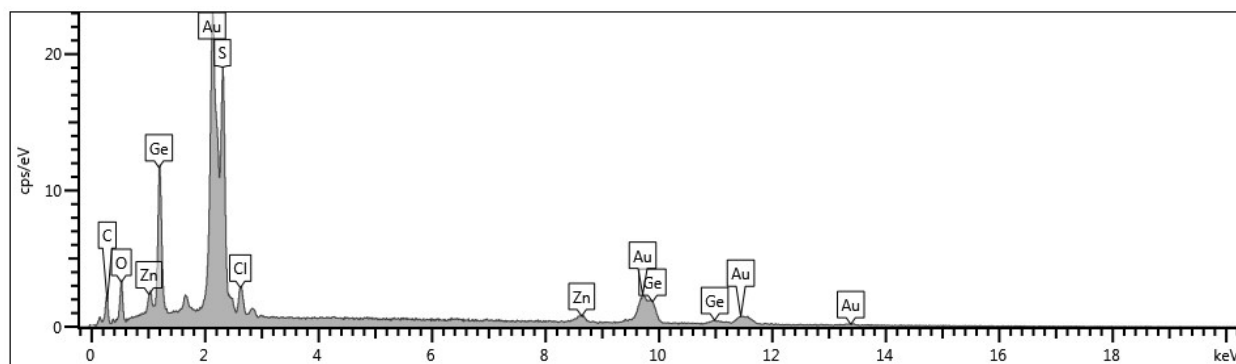


Figure 5. EDS of Au@GeZnS.

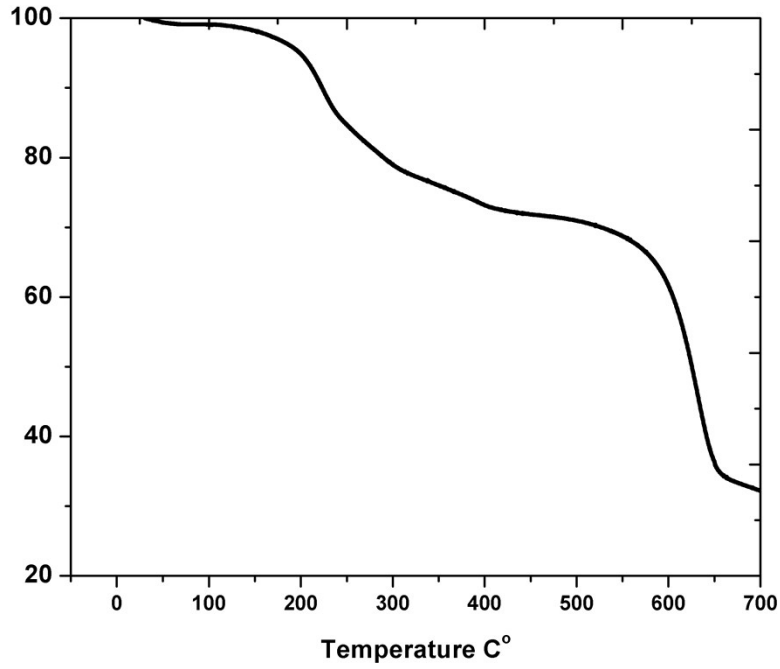


Figure 6. TGA data of AEM@GeZnS.

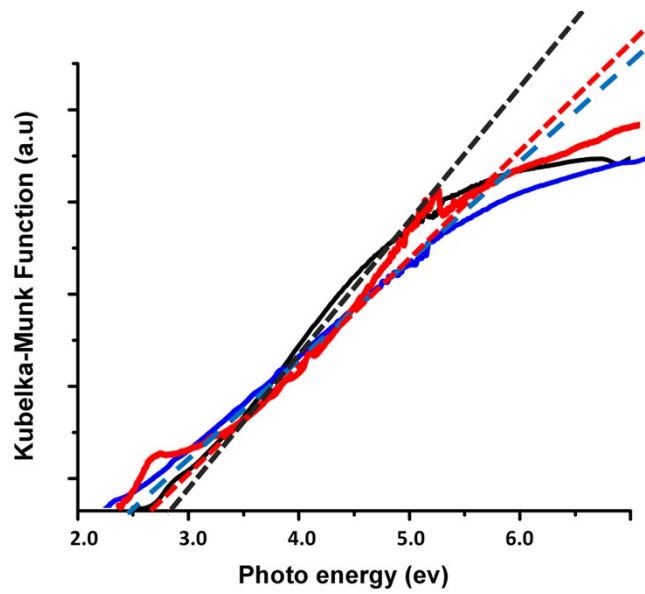


Figure 7. Normalized solid-state diffuse reflectance AEM@GeZnS (black), Pd@GeZnS (red) and Au@GeZnS (blue).

References:

1. Lin, Q.; Bu, X.; Mao, C.; Zhao, X.; Sasan, K.; Feng, P.,. *Journal of the American Chemical Society* **2015**, *137* (19), 6184-6187.