Supporting Information for:

Synthesis of FeS_2-CoS_2 core-frame and core-shell hybrid nanocubes

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Methods

General

All glassware was oven dried prior to use. Standard Schlenk line techniques were used in an inert Ar atmosphere for all reactions. A J-KEM Scientific Model 210 temperature controller was used with a heating mantle for reaction temperature control. All reagents and solvents were used as received unless otherwise noted.

Materials

Anhydrous iron(II) chloride beads ($FeCl_2$, 99.99%), anhydrous cobalt(II) chloride ($CoCl_2$, 98%), hexadecylamine (HDA, 90%), oleylamine (OAm, 70%), and elemental sulfur were purchased from Sigma-Aldrich.

Characterization

TEM images and quantitative EDS measurements were acquired using a FEI Tecnai Osiris S/TEM operating at 200 kV with ChemiSTEM for EDS detection. Particle sizing measurements were taken in ImageJ. STEM-EDS tomography was performed on a Tecnai Osiris operating at 200kV with probe current on the order 0.5 nA. The sample was baked under high vacuum at 145 °C and then loaded onto a Fischione model 2020 tomography holder. STEM-EDS maps were collected from -65° to 65° at 2° intervals using Bruker Esprit 1.9 with acquisition times of 70 seconds, pixel dwell time of 70 ms and a pixel size of 0.6 nm. The individual maps for each element were rendered in grayscale and assembled into a tilt series. The tilt series for each element was then aligned and reconstructed using the SIRT method in Inspect 3D. The individual reconstructed volumes were then rendered and colorized using Amira 6.2. X-ray diffraction analysis was performed on a Rigaku SmartLab® X-ray diffractometer equipped with a CuKa radiation source and a D/teX Ultra 250 detector, operating at 40 kV and 44 mA. XRD samples were prepared by drop casting a concentrated solution of NPs onto a glass holder. SEM images were acquired with a Zeiss Merlin SEM working at 3.31 kV with the Inlens detector. The working distance at 5.7 mm

Synthesis of FeS_2 nanocube stock solution

The FeS_2 seed particles used in the present study were prepared using a modified method from Macpherson and Stoldt.[11] Anhydrous $FeCl_2$ beads (2.0 mmol, 253.5 mg), elemental sulfur (12.0 mmol, 384.8 mg), and hexadecylamine (40g) were added to a 250mL three-neck round bottom flask, and reacted at 250°C for 3h under and inert argon atmosphere with magnetic stirring at 350 rpm (1 x 5/16" stir bar). The reaction solution was allowed to cool to room temperature resulting in the freezing of the solution due to the hexadecylamine. Additional $FeCl_2$ (4.0 mmol, 507.0 mg), sulfur (8.4 mmol, 269.4 mg), and oleylamine (60 mL) were added through one of the necks of the flask with argon flowing over the frozen solution. The flask was resealed and heated to 200°C for 9h, stirring at 1000 rpm. Once again, the reaction flask was allowed to cool to room temperature and additional $FeCl_2$ (4.0 mmol, 507.0 mg) and sulfur (8.4 mmol, 269.4 mg) were added to the frozen reaction solution, resealed, and reacted at 200°C for 9h under Ar. The resulting solution was allowed to cool below 80°C after which ~40mL of $CHCl_3$ was injected to prevent freezing. The solution was then centrifuged (2000 rpm, 2min) followed by decanting of the supernatant. The precipitated nanocrystals were then cleaned using two cycles of resuspension in $CHCl_3$ followed by centrifugation (2000 rpm, 5 min), and the resulting nanocrystal product stored in $CHCl_3$.

Synthesis of FeS_2/CoS_2 core-frame hybrid nanocubes

In order to synthesized FeS_2/CoS_2 core-frame hybrid nanocubes, a portion of the FeS_2 nanocube stock solution was vacuumed dried to remove the $CHCl_3$ solvent. Afterwards, the dried FeS_2 powder (0.5 mmol, 60 mg), anhydrous $CoCl_2$ powder (0.5 mmol, 65 mg), elemental sulfur (1.25 mmol, 40 mg), hexadecylamine (5g), and oleylamine (7.5mL) were added to a 50 mL three-neck round bottom flask with a magnetic stir bar and heated for 4h at 200°C. The reaction mixture was then allowed to cool to below 80°C after which ~20 mL of $CHCl_3$ was added to prevent freezing. The solution was then centrifuged (2000 rpm, 2min) followed by decanting of the supernatant. The precipitated nanocrystals were then cleaned using two cycles

of resuspension in $CHCl_3$ followed by centrifugation (2000 rpm, 5 min), and the resulting nanocrystal product stored in $CHCl_3$.

Synthesis of CoS_2

In a 25 mL 3-neck round-bottom flask, $CoCl_2$ (0.5 mmol) and 10 mL of OAm were placed under vacuum for 1 h at 60°C. The temperature was increased to 170°C under an inert N_2 atmosphere. In a separate vial, elemental sulfur was dissolved in 5 mL of OAm and placed under vacuum at room temperature for 45 min followed by backfilling with N2 for 15 min. The S precursor/OAm solution was then injected into the reaction flask and heated to 220°C for 2 h under N_2. The reaction solution was then cooled in air to room temperature, and ~ 40 mL of chloroform was added, followed by centrifugation 5-10 min at 8000 rpm. Particles were further purified by two cycles of suspension with chloroform followed by ethanol (total ~20 mL) then centrifugation for 5 min at 4400 rpm. The particles were stored in chloroform.

Electrode Fabrication

Electrode substrates were prepared by binding copper wire to FTO with conductive silver epoxy and allowed to dry. The copper wire was encased in a glass tube in order to isolate it from the electrolyte solution during measurements. The FTO with attached glass encased copper wire was then covered with epoxy (Loctite ® 1C), completely isolating the copper wire, and exposing only a square area measuring 1cm^2 of FTO (picture of electrode included in supporting info). The epoxy was allowed to dry in an oven at 120°C for at least 4hr.

A suspension was made based on a method adapted from Jasion et al.,[22] where 25mg of nanocrystals, 2.5 mg of activated carbon (Vulcan XC-72R, Fuel Cell Store), 100uL of Nafion suspension (D521, 5 wt% alcohol based, Fuel Cell Store), and 500uL of $CHCl_3$ were combined. The suspension was then sonicated for 15 minutes and then 50uL were dropcast on the prepared FTO electrode described previously and allowed to dry at least 30 min before testing.

A platinum electrode was also fabricated in order to compare to the nanocrystal electrodes. In short, a Pt film was electrodeposited onto a 1cm^2 area of a Au/Si wafer from a 0.01M K_2PtCl_6 solution in 0.1M HCl at for 30 min at -0.25V.

Electrochemical measurements

All electrochemical characterizations were performed in a three-electrode configuration and recorded using a Gamry Series G300 with PHE200 software package. Electrodes were evaluated individually submerging in a 0.5 M H_2SO_4(aq) electrolyte with a Ag/AgCl reference electrode in saturated KCl and platinum mesh counter electrode. Linear sweep voltammetry was performed from -0.1 to -0.5 V at a scan rate of 25 mV s^{-1} and 1 mV voltage step.

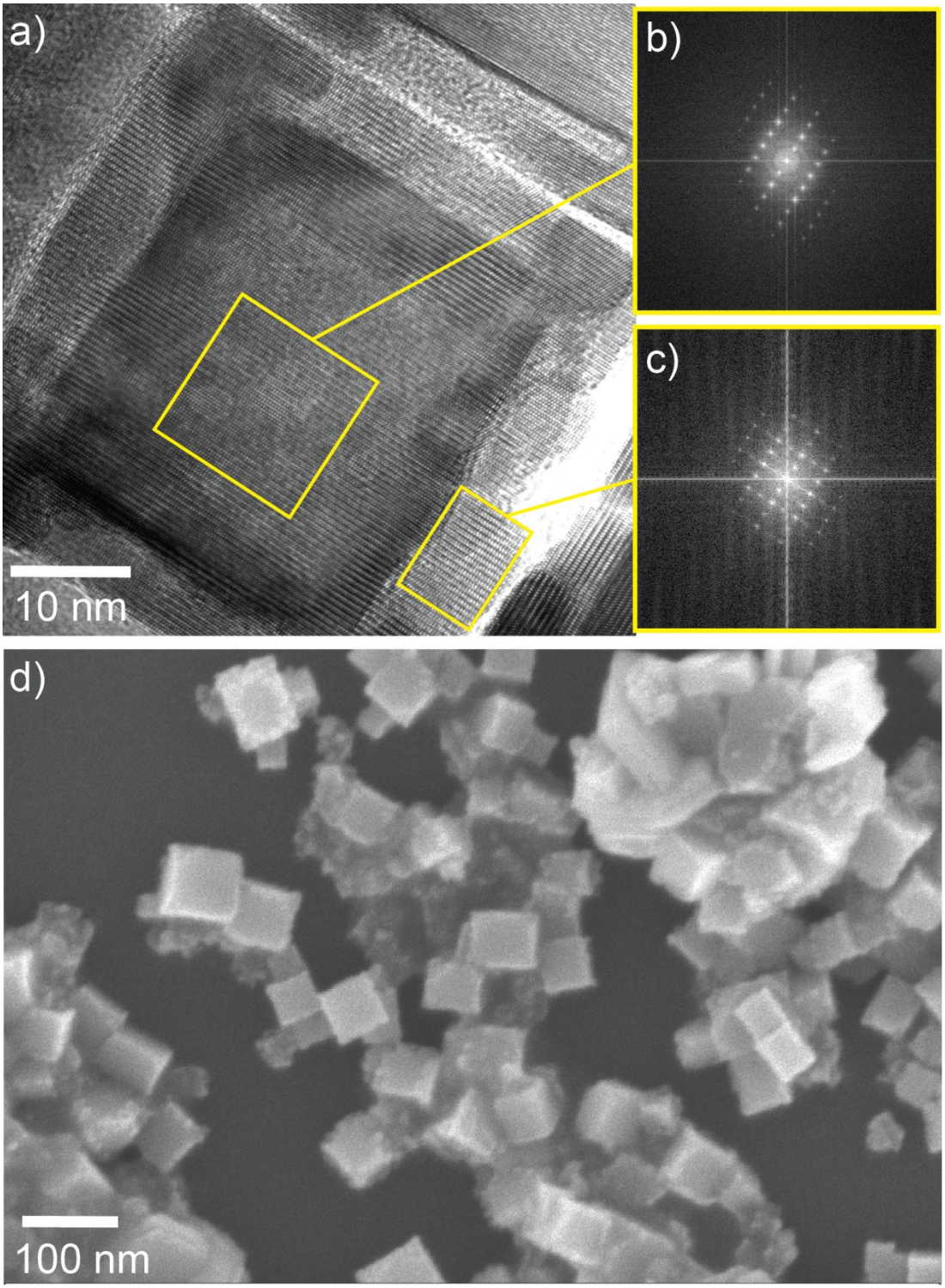

Figure S1. a) A high resolution TEM image of a hybrid nanocrystal with b) including FFT analysis of lattice fringing pattern from FeS_2 core nanocube and c) including FFT analysis of lattice fringing from CoS_2 frame demonstrating epitaxial growth, as well as d) a SEM image depicting the core-frame hybrid nanocubes.

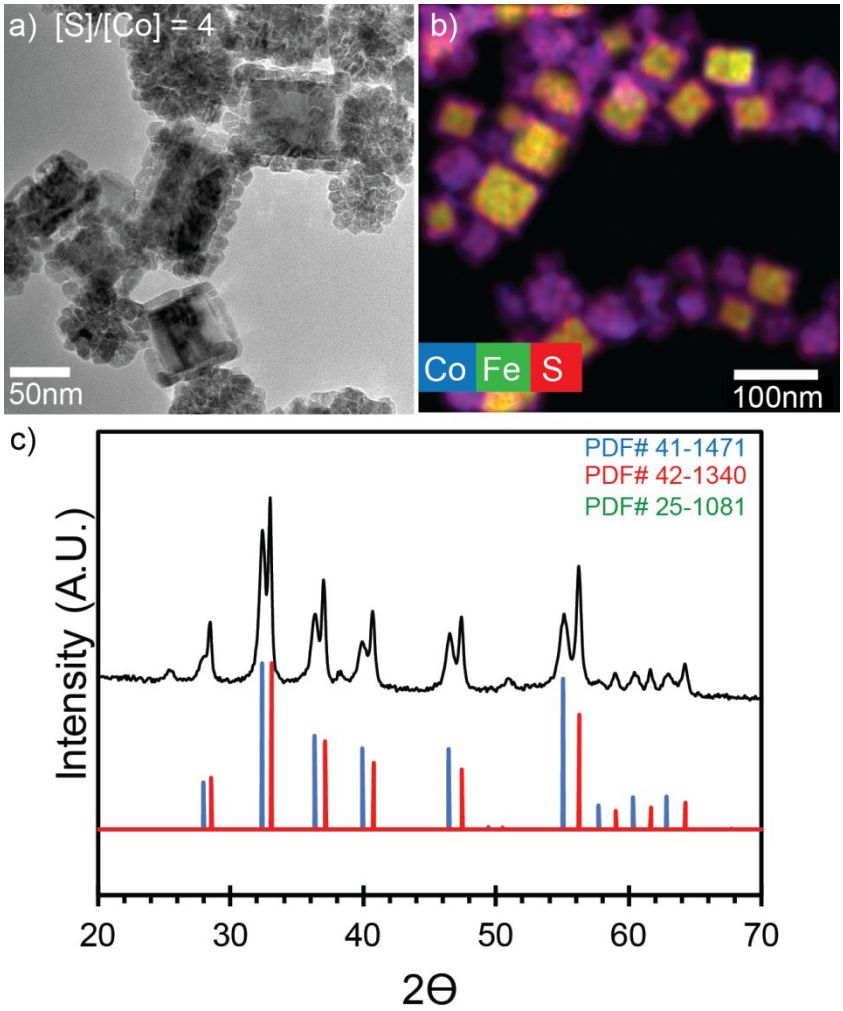

Figure S2. Characterization of resulting hybrid nanocrystal product when [S]/[Co] = 4. Greater surface coverage of FeS_2 nanocubes by CoS_2 is observed as well as heterogenous nucleation of CoS_2 and presence of a minor CoS (Jaipurite) impurity phase.

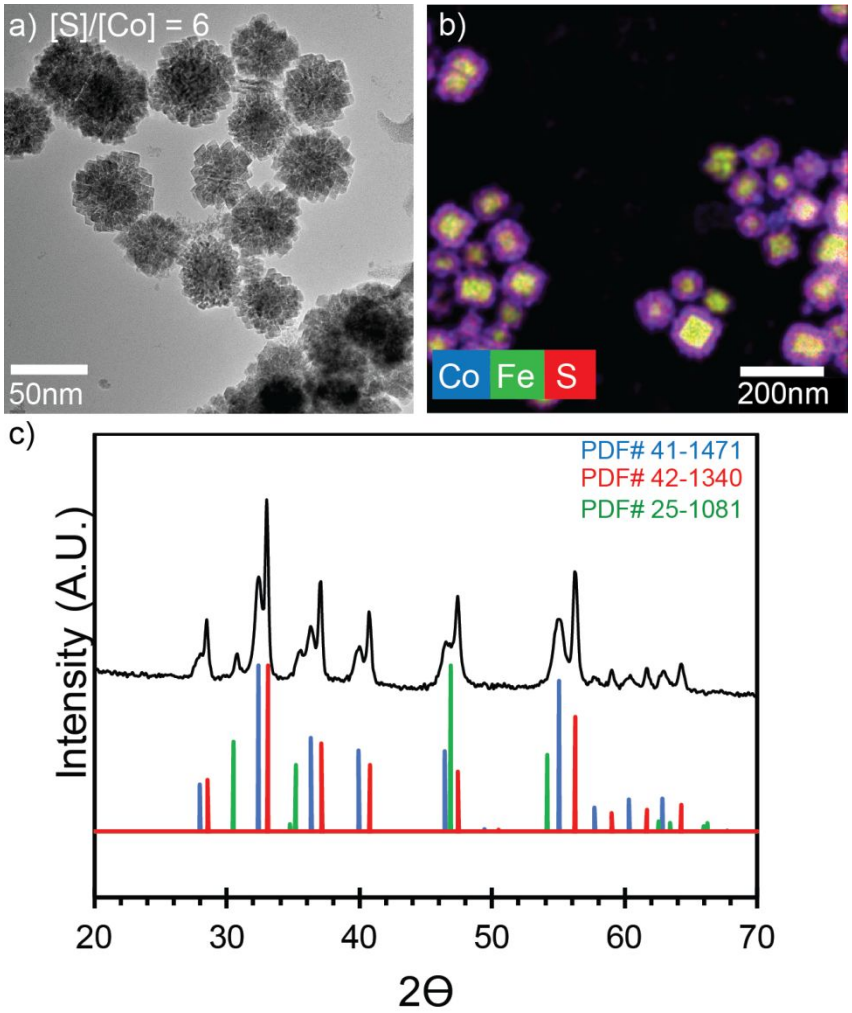

Figure S3. Characterization of resulting hybrid nanocrystal product when [S]/[Co] = 6. Complete coverage of FeS_2 nanocubes by CoS_2 is observed as well as heterogenous nucleation of CoS_2 and presence of a minor CoS (Jaipurite) impurity phase.

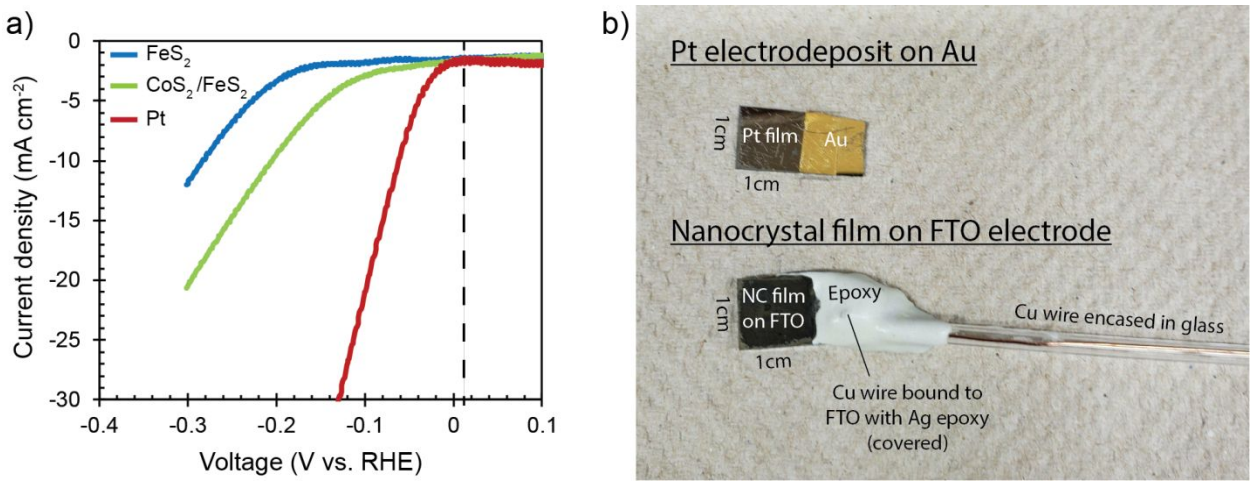

Figure S4. A) Electrochemical characterization of the catalytic activity of FeS_2 nanocubes (blue trace) and FeS_2/CoS_2 core-frame nanocubes (green trace), compared to Pt electrodeposited on Au coated silicon (red trace) toward HER. There is background current due to double layer capacitance. B) Fabricated electrodes for electrochemical analysis. Pt film was electrodeposited on Au. Nanocrystal films were deposited on FTO electrode with attached glass encased copper wire, sealed with epoxy.