

# Sulfur copolymer for the direct synthesis of ligand-free CdS nanoparticles

## Supporting Information

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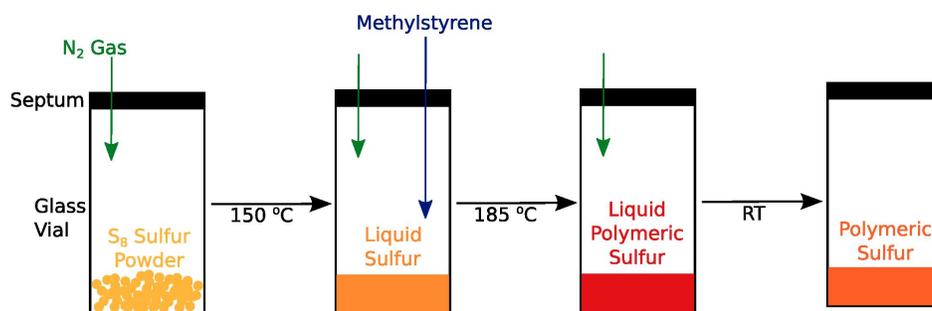
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## 1. Polymeric sulfur synthesis

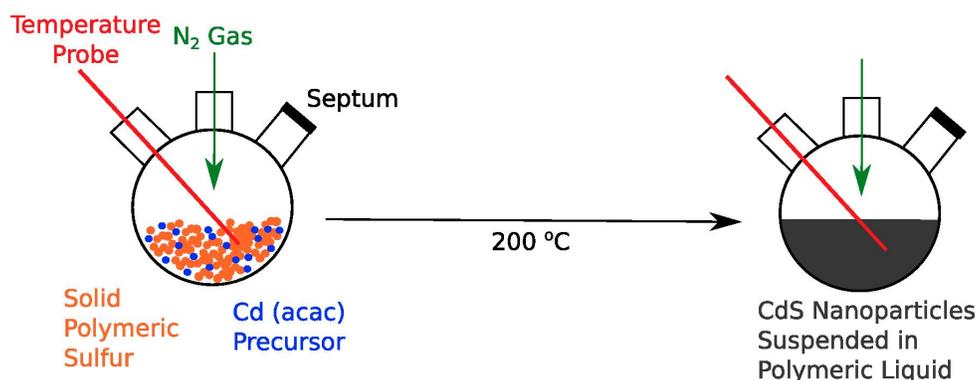
All chemicals were purchased from Sigma Aldrich and used as received. The procedure for synthesizing the methylstyrene based sulfur copolymer is outlined in Figure S1. Specifically, elemental sulfur (4 g, 124.8 mmol, S<sub>8</sub>, 99.5%), was placed in a 20 mL glass vial with a stir bar. The glass vial was capped with a septum and suspended in an oil bath. A needle connected to a Schlenk line was inserted through the septum to provide a nitrogen atmosphere for the synthesis. The mixture was then heated to 150 °C with stirring, and once all of the sulfur reached the liquid state,  $\alpha$ -methylstyrene (330  $\mu$ L, 2.5 mmol, 99%) was injected into the solution through the septum. After injection, the solution was heated to 185 °C for 10 min. At this stage, the liquid polymer underwent a color change as the polymerization process occurred. The polymer was then cooled to room temperature (RT), producing a solid material.



**Figure S1:** Experimental setup and procedure for the synthesis of polymeric sulfur.

## 2. CdS nanoparticle synthesis using polymeric sulfur

The procedure for synthesizing the CZTS nanoparticles using the methylstyrene based sulfur copolymer is outlined in Figure S2. Specifically, sulfur copolymer (4.0 g, 116 mmol) was combined with cadmium acetylacetonate (Cd(acac), 900 mg, 2.9 mmol 99.9%), in a three neck flask. The flask was subjected to several vacuum and nitrogen pump purge cycles. The flask was then filled with nitrogen and heated to 200 °C for 30 min with stirring after which the reaction mixture was cooled to RT, producing a black powder.

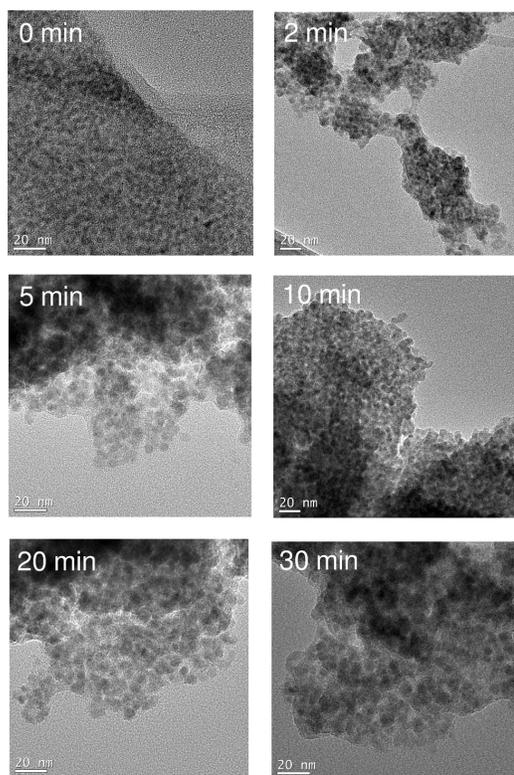


**Figure S2:** Experimental setup and procedure for synthesizing metal-sulfide nanoparticles using polymeric sulfur.

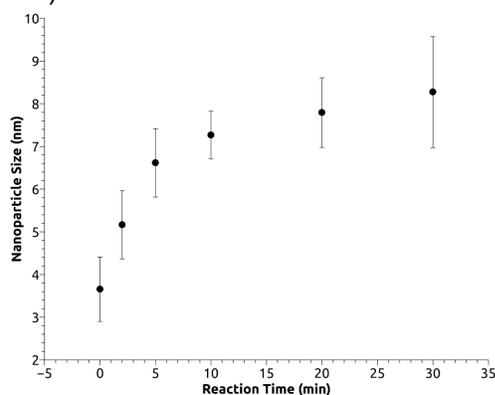
### 3. Nanoparticle Size and Growth

Aliquots of the reaction solution were collected at 0, 2, 5, 10, 20 and 30 minutes. The aliquots were collected by removing several milligrams of solution, which was then immediately dissolved in 10 ml of chloroform and sonicated. Figure S3a shows respective TEM images for each aliquot and Figure S3b shows the nanoparticle size measured using the TEM images. Figure S4 shows the UV-Vis spectra for each aliquot. For these samples, the sulfur copolymer was not removed due to the small amount of material present in each aliquot. The sulfur copolymer and the CdS nanoparticles both exhibit absorbance peaks within the 350-500 nm region, so the spectra represent a convolution of signals from both materials. However, the UV-Vis spectra shown in Figure S4 show a trend towards higher wavelength absorbance over time, which is consistent with the growth pattern of the nanoparticles.

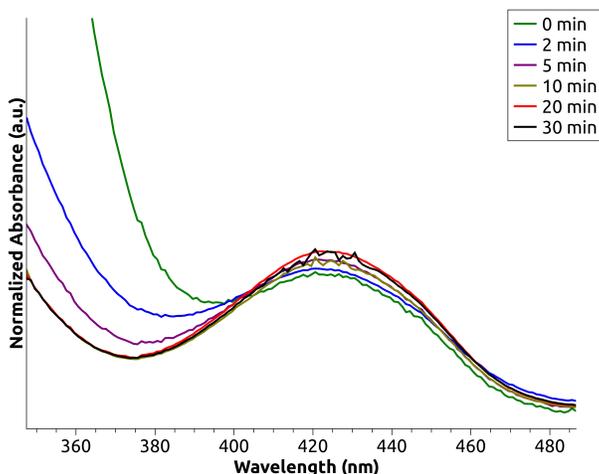
a)



b)



**Figure S3:** a) TEM images depicting nanoparticle growth within the liquid sulfur copolymer. b) Nanoparticle growth profile; the size of the nanoparticles was measured using TEM images.



**Figure S4:** UV-Vis spectra illustrating nanoparticle growth.

#### 4. Removing Sulfur Copolymer from Nanocomposite

The nanocomposite powder (200 mg) was dissolved in chloroform (20 mL) and ultrasonicated for 1 h. Chloroform (20 mL) was added to the solution, which was then separated into two 20 mL centrifuge tubes and centrifuged at 10k rpm for 15 min. The sulfur copolymer was then decanted from the settled nanoparticles. The nanoparticles were dispersed in chloroform and sonicated for 15 min, followed by another centrifugation step. This process was repeated until all of the orange colored sulfur copolymer was removed (4-5 repeats). The final CdS nanoparticles were placed under high vacuum to remove all of the residual solvent (12.9 mg, 75% yield).

#### 5. TEM characterization

For TEM characterization, the nanoparticles were dispersed in chloroform to facilitate drop casting onto a substrate. Specifically, the nanoparticles (20 mg) were diluted in chloroform (20 mL) and this solution was ultrasonicated for 1 h. 3-4 drops of this solution was further diluted in chloroform (10 mL) and was subsequently sonicated for 15 min. This final solution was then dropped onto an ultrathin carbon film substrate with holey carbon support films on a 400 mesh copper TEM grid (Ted Pella, Inc.). This TEM grid was placed in a vial and held under vacuum overnight, to remove any residual solvent from the sample. The nanoparticles were imaged on an FEI Tecnai G2 F-20 TEM with a 200 kV accelerating voltage, a spot size of 3 and an EDAX detector.

#### 6. XRD characterization

The nanoparticles were diluted in chloroform (20 mg/mL) and were drop cast onto 1 cm<sup>2</sup> Mo coated soda lime glass substrates in 7  $\mu$ L increments. Prior to the drop casting step, the substrates were cleaned by sonicating in detergent, deionized water, acetone and isopropyl alcohol, each for 10 min. Finally, the substrates were then placed in an air plasma cleaner for 10 min prior to drop casting. The data were collected using 7000 data points at a scan rate of 1 data point per second with a Bruker F8 Focus diffractometer with a Cu-K $\alpha$  X-ray source and an incident wavelength of 1.54059  $\text{\AA}$ .

## 7. Proton NMR Spectroscopy

Each spectrum was collected using 99.8% deuterated chloroform as a solvent. The  $^1\text{H}$  NMR data were collected using a Bruker AV300 system operating at a frequency of 300.13 MHz with a Bruker BBI probe.

## 8. Standard Ligated CdS Nanoparticle Synthesis

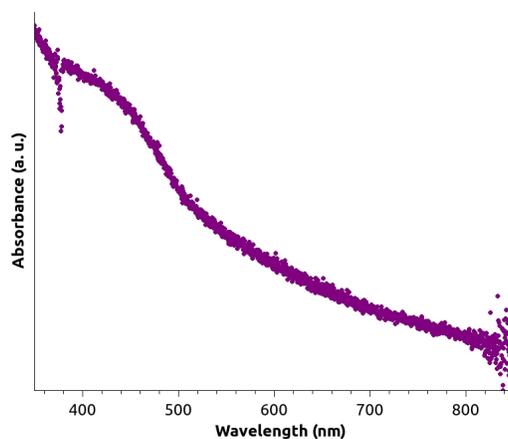
Cadmium oxide (CdO, 99.5%), oleic acid (90%), octadecylamine (ODA, 95%), and elemental sulfur ( $\text{S}_8$ , 99.5%), and 1-octadecene (ODE, 95%, GC) were purchased from Sigma-Aldrich. All chemicals and reagents were used as received. Briefly, CdS nanocrystals were synthesized according to a modified version of the CdO/amine synthesis of Yu and Peng [W. W. Yu and X. G. Peng, *Angew. Chem., Int. Ed.*, 2002, **41**, 2368]. In a typical reaction, CdO (0.077 g, 600  $\mu\text{mol}$ ) was heated with oleic acid (1.696 g, 6 mmol) in ODE (2 g, 7.92 mmol) in a  $\text{N}_2$  purged three neck flask to 200  $^\circ\text{C}$  until the solution turned clear, indicating the formation of Cd-Oleate. The solution was then allowed to cool to room temperature and ODA (0.75 g, 2.78 mmol) was added before increasing the temperature to 280  $^\circ\text{C}$ , and a solution of  $\text{S}_8$  (0.0096 g, 300  $\mu\text{mol}$ ) in ODE (0.5 g, 1.98 mmol) was swiftly injected into the reaction mixture and the nanocrystals were grown at 260  $^\circ\text{C}$  for 10 min before removing from heat and allowing to cool to room temperature. The CdS nanocrystals were then extracted in hexanes and washed with methanol three times before being dried by rotary evaporation. The dry CdS was then washed three times with acetone to remove any remaining impurities, followed by drying under vacuum. Samples were stored in the dark in a glovebox with an  $\text{N}_2$  atmosphere.

## 9. Absorbance Spectroscopy (UV-Vis-NIR)

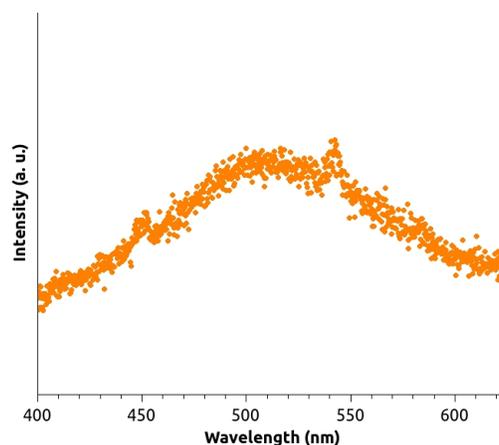
The nanoparticles were dissolved in chloroform and placed in a sealed quartz cuvette. An analogous cuvette filled with chloroform was used as a reference sample. Optical absorbance measurements were conducted using a Perkin Elmer Lambda 1050 UV-Vis-NIR spectrometer.

## 10. Photoluminescence Spectroscopy (PL)

The nanoparticles were dissolved in chloroform and placed in a sealed quartz cuvette. PL measurements were conducted using a Horiba FL3-21tau fluorescence spectrophotometer with an excitation wavelength of 330 nm.



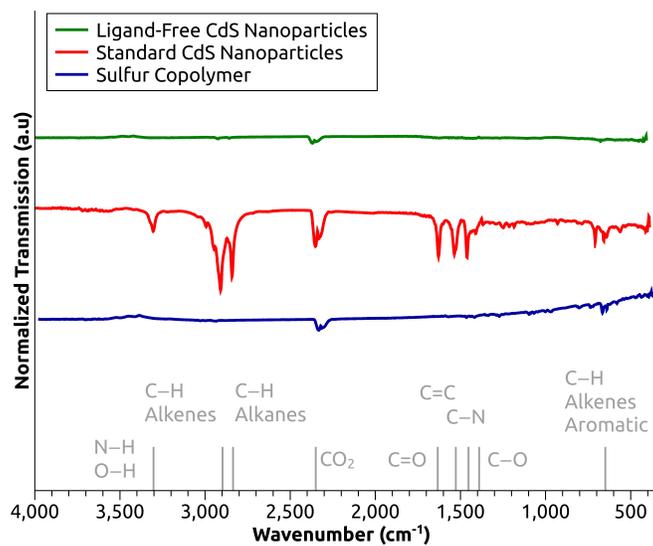
**Figure S3:** Solution UV-Vis-NIR spectrum for CdS nanoparticles. The discontinuity at  $\sim 380$  nm is due to a lamp change in the instrument and the discontinuity at  $\sim 850$  nm is due to a detector change.



**Figure S4:** Solution PL spectrum for CdS nanoparticles.

## 11. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was conducted using a Bruker Vector 33 instrument. Samples were prepared by mixing 200 mg of KBr with 1 mg of sample powder. The resulting mixture was pressed into a pellet and analyzed by averaging 32 cumulative scans. The FTIR data presented in Figure S5 was normalized using the spectrum from a blank KBr pellet.



**Figure S5:** FTIR spectra for the ligand-free CdS nanoparticles. Standard CdS nanoparticles capped with oleic acid and octadecylamine, and the sulfur copolymer are also included for comparison.