SUPPLEMENTARY INFORMATION

Stabilization of plasmon resonance in Cu$_{2-x}$S semiconductor nanoparticles

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Experimental details

The solvents used include 1-dodecanthiol (≥98%) and oleic acid (technical grade, 90%), which were purchased from Sigma-Aldrich, as well as hexane (ACS grade, 95%) and acetone (ACS grade, 99.9%), which where purchased from Pharmco-Aaper. All solvents were used as received. Reactants used were elemental sulfur (powder, 99.98%), copper(II) acetylacetonate (Cu(II)(acac)$_2$, ≥99.99% metals basis), and iron(III) acetylacetonate (Fe(III)(acac)$_2$, 99.9%) from Sigma-Aldrich.

Synthesis of monoclinic and tetragonal chalcocite nanoparticles

The syntheses follow previously reported procedures.[1]

Surface treatment using ammonium tetrathiomolybdate

This procedure was adapted from that of Kovalenko et al.[2] In an N$_2$-filled dry box, an equal volume of ammonium tetrathiomolybdate solution (5 mM in DMSO was typically used, but a range from 2 to 50 mM was explored) was added to a suspension of particles in toluene (2 mg/mL, 3.0 mL). The solution was stirred from 24-48 hours. The control samples were isolated by centrifugation. The treated particles were isolated by electrodeposition, as follows.[3] Aluminum rods (1/4 in diameter) were placed approximately 1.5 in apart and 450 V potential was applied for 10 minutes. Deposited particles were washed off of the anode with hexane and sonication.

Oxidation and reduction of nanoparticles

Copper sulfide nanoparticles were suspended in dichloromethane or toluene. Either tetrakis(acetonitrile)-copper(I) tetrafluoroborate solution (0.020 M in methanol) or iodine solution (0.020 M in methanol) were added, drop-wise, to the cuvette and transmission visible/near-IR absorption spectra were immediately collected.

Powder X-ray diffraction (PXRD)

PXRD samples were prepared by casting an aliquot of nanoparticles suspended in hexane onto glass slides and then covering each slide in Parafilm. PXRD experiments were carried out using a PANalytical X'Pert Pro X-ray diffractometer using Cu Kα radiation (λ=1.54 Å). The detector was a 13 channel X'celerator with a Ni filter. The accelerating voltage and current were 45 kV and 40 mA. The irradiated length was 10 mm and an automated diffraction slit was employed. Scans were collected from 6 to 70° 2θ. Ten repetitions were summed. The samples were then analyzed using the program PANalytical X'Pert HighScore Plus (Version 2.2e), which allowed comparisons with the ICDD powder X-ray diffraction pattern database (PDF Release 2).

Visible/NIR spectroscopy (visible/near-IR)

Spectra were collected using a Perkin-Elmer Lambda 950 spectrometer featuring an integrating sphere with PMT and InGaAs detectors.

For diffuse reflectance of solid samples, spectra were collected in the range 2450 nm to 300 nm at 525.55 nm/min. Detector response settings were 0.40 s. The InGaAs detector gain was 12 with a servo-controlled slit width. The PMT detector used autogain and a 1.5 nm slit width. Solid samples were sandwiched between NIR transparent quartz plates (Spectrocell, Oreland, PA) and analyzed at the reflectance port of the integrating sphere. Prior to sample measurement, a background was collected using one glass plate in front of a Spectralon reference. When samples were analysed over time, they were stored between the NIR quartz plates.

For absorption spectra of liquid samples, samples were suspended in a NIR-transparent 1 cm cuvette (Spectrocell, Oreland, PA). Spectra were collected in the range 1500 nm to 300 nm at 405 nm/min. Detector response settings were 0.40 s. The InGaAs detector gain was 12 with a servo-controlled slit width. The PMT detector used autogain and a 1.5 nm slit width.

Transmission electron microscopy (TEM)

TEM samples were prepared by solvent-casting samples onto Ni-supported TEM grids with lacey carbon coating (Electron Microscopy Sciences). The microscope employed was either a JEOL 2010F or FEI Titan3 G2 with a field emission source at 200 kV in the Materials Characterization Laboratory at the Pennsylvania State University. For EDS measurements, samples were held in place using a Cu spacer and clip.

X-ray photoelectron spectroscopy (XPS)

XPS was carried out using the Kratos Axis Ultra instrument at the Materials Characterization Laboratory at the Pennsylvania State University. Samples were affixed to a Si wafer using 3M double-sized tape. Monochromatic Al Kα X-rays and a hybrid analyzer mode were employed. The X-ray gun was run at 14 keV and 20 mA anode current, giving power of 280 W. Analysis chamber

pressures were in the low 10-8 torr range. Charge neutralization was used and optimized on the S 2p peak. Survey scans employed a pass energy of 80 eV, a step size of 0.5 eV, and dwell time of 150 ms. High resolution scans employed a pass energy of 20 eV a step size of 0.1 eV, and dwell times varying from 600 ms to 2000 ms.

Additional data

Effect of increasing concentration of $(NH_4)_2MoS_4$

EDS maps (Fig. S1) show that as the concentration of $(NH_4)_2MoS_4$ used to treat tetragonal chalcocite nanoparticles increases from 5.0 mM—the concentration at which crystallinity and optical properties are little altered—to 20. mM and 54. mM there is an increase in the amount of an amorphous Mo-rich substance. At 54. mM, there appears to be complete conversion. The measured formula is $Cu_{5.0}MoS_{3.6}$ by EDS, although other data (XPS in Fig. S2 and visible/near-IR spectra in Fig. S3) suggests formation of Cu_2MoS_4. Excess Cu may be a result of use of Cu clip and spacer during EDS measurements.
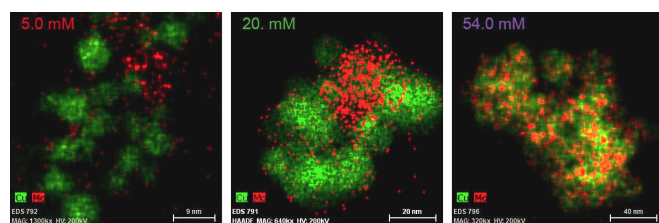
Fig S1. EDS maps of Cu and Mo of tetragonal chalcocite nanoparticles reacted with increasing concentrations of $(NH_4)_2MoS_4$: 5.0 mM (left), 20. mM (middle), and 54. mM (right).
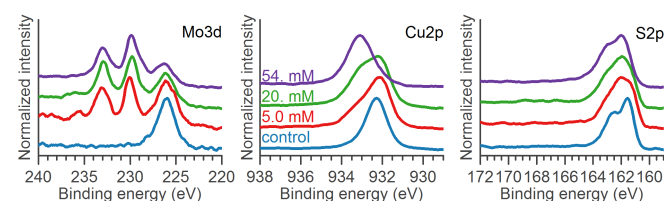
Fig S2. XPS of the Mo3d/S 2s, Cu 2p, and S 2p regions of tetragonal chalcocite nanoparticles reacted with increasing concentrations of $(NH_4)_2MoS_4$, as labelled.
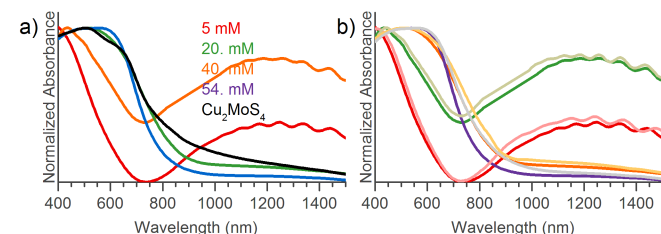

Fig S3. a) Visible/near-IR absorption spectra of tetragonal $Cu_{2-x}S$ nanoparticles treated with varying concentrations of $(NH_4)_2MoS_4$: 5.0 mM (red), 20. mM (green), 40. mM (orange), and 54. mM (purple) compared to an independently prepared sample of Cu_2MoS_4 (black).[4] b) Comparison of visible/near-IR absorption spectra of tetragonal $Cu_{2-x}S$ nanoparticles treated with varying concentrations of $(NH_4)_2MoS_4$ immediately after treatment (dark colors) and after 13 days in air (light colors).

Further characterization of passivated particles using low concentrations of $(NH_4)_2MoS_4$

Table S1. Particle diameters measured by TEM.

Sample	Average diameter (nm)	Number of measurements
Control	9.2±3.4	279
DMSO/toluene-treated	8.6±2.2	401
$(NH_4)_2MoS_4$-treated in DMSO/toluene	8.6±2.1	313
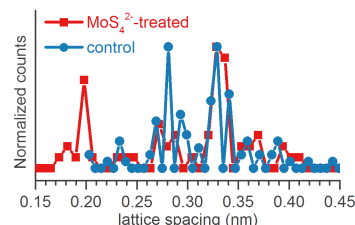
Fig S4. Histogram of the lattice spacings observed in high-resolution TEM images of tetragonal chalcocite nanoparticles with (red) and without (blue) $(NH_4)_2MoS_4$-exposure.

References

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