Heterostructures of Cu$_{2-x}$S/Cu$_{2-x}$Te plasmonic semiconductors: Disappearing and reappearing LSPR with anion exchange

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Experimental information

Chemicals
The reagents used for the synthesis and transformation of roxbyite nanoparticles include copper nitrate dihydrate (Cu(NO₃)₂·3H₂O, 99.95%), trioctylphosphine oxide (≥90%), trioctylphosphine (≥85%), oleylamine (technical grade, 70%), 1-octadecene (technical grade, 90%), tert-dodecyl mercaptan (mixture of isomers, 98.5%), and 1-dodecanethiol (≥98%). All solvents used for precipitation and washing of nanoparticles, including isopropyl alcohol (IPA), toluene, hexane, and acetone, were of analytical grade. Unless specified, all reagents were purchased from Sigma-Aldrich and used as received.

General Safety Concerns
The synthetic methods in this report are done under air-free conditions at elevated temperatures using high-boiling-point solvents. As such, care should be taken to ensure proper monitoring and handling. For example, burns have been reported from exposure to high-temperature oleylamine. The safety data sheets for all chemicals used in the reactions should be reviewed, and proper personal protective equipment should be used. These reactions have the potential to evolve toxic gases and as such should be handled in a properly functioning fume hood.

Aliquots were collected of high temperature liquids. Care should be used to avoid burns.

Standard Reaction Vessel Setup
Each of the following procedures utilizes either a standard Schlenk line setup or an Ar gas manifold. Each three-necked, round-bottom flask was equipped with a magnetic stir bar, a reflux condenser with a glass adaptor connected either to the Schlenk line or to a bubbler, a type-K thermocouple through a silicone septum, and second septum with a needle to connect to the Ar gas. The temperature was controlled by heating mantles on magnetic stir plates.

Synthesis of copper sulphide nanorods
Cu₁₃S nanorods were synthesized using an adaptation of previously published procedures¹,² as previously described.³,⁴

Tellurium-exchange procedure
The Te-exchange procedure was modelled on that published by Saruyama et al.⁵ and detailed previously.⁴ Here, the exchange procedure was carried out at 200, 230, and 260 °C and aliquots were taken at various times. A metal cannula was inserted through the silicone septum on the reaction flask and into an Ar-purged, septum-capped vial. The Ar flow on the reaction set up was temporarily stopped and a syringe was used to pull vacuum on the septum-capped vial. Approximately 5 mL of reaction liquid was collected in each aliquot. Particles were microcentrifuged at 16000 rpm for 1 min, spread across several 1.5 mL microcentrifuge tubes. Particles were was by resuspending in toluene (0.5 mL) and adding isopropyl alcohol (0.5 mL) then precipitated by centrifugation.

Characterization

Visible/NIR Absorption spectroscopy (Vis/NIR)
Spectra were collected using a Perkin-Elmer Lambda 950 spectrometer featuring an integrating sphere with PMT and InGaAs detectors. Solid samples were drop-cast from ethanol, sandwiched between NIR transparent quartz plates (Spectrocell, Oreland, PA) and analyzed at the reflectance port of the integrating sphere. Spectra were collected in the range 2200 nm to 300 nm in 1 nm increments. Detector response settings were 0.40 s. The InGaAs detector gain was 15 with a servo-controlled slit width. The PMT detector used autogain and a 1.5 nm slit width. Prior to sample measurement, a background was collected using sandwiched glass plates in front of a Spectralon reference. Breaks in data at ~1700 nm are due to removal of solvent peaks.

Powder X-Ray Diffraction (PXRD).
After nanoparticles were cleaned and resuspended in hexane, they were cast onto glass slides and allowed to dry, then covered with Parafilm to avoid exposure to solid nanoparticles. The PXRD data were collected using a PANalytical X'Pert Pro X-ray diffractometer with Cu Ka radiation. The samples were scanned with 10 repetitions at a current of 40 mA and voltage of 45 kV. Using the PANalytical HighScore Plus software, the ten scans were summed and compared peaks with patterns from the ICDD database to determine the structure of the nanoparticles. Crystal structure and powder diffraction simulations were performed using CrystalMaker and CrystalDiffract from CrystalMaker Software Ltd., Oxford, England.

Transmission Electron Microscopy (TEM).
Samples were prepared by placing a drop of nanoparticles suspended in toluene on a Ni-supported ultra-thin carbon-coated TEM grid (Electron Microscopy Sciences). Low-resolution TEM images of the particles were obtained using a Delong Instruments LVEM25 Low-Voltage TEM at Franklin & Marshall College. The LVEM25 was operated under 25 kV with the Zyla 5.5 Scientific CMOS camera with appropriate alignments and enhancements. ImageJ software was used to analyse the TEM images.

HAADF STEM/EDS mapping.
Samples were prepared by placing a drop of nanoparticles suspended in hexane or toluene on a Ni-supported ultra-thin carbon-coated TEM grid (Electron Microscopy Sciences). The microscope employed was an FEI Talos F200X with a SuperX EDS at 200 kV in the Materials Characterization Laboratory at the Pennsylvania State University. ImageJ software was used to analyse the HR-TEM images. Bruker ESPIRIT 2 software was used to interpret the STEM-EDS element map data.

Cyclic voltammetry (CV).
CV was carried out using a CH Instruments CHI604C Electrochemical Analyzer. Pt wire mesh (Alfa Aesar, 99.9%) was the counter electrode. A silver wire quasi-reference electrode was used (Alfa Aesar, 99.9985%) and ferrocene (50 nM, Alfa Aesar, 99%)/ferrocenium (ferrocenium hexafluorophosphate, 50 nM, Sigma Aldrich) was used for calibration. The measured ferrocene/ferrocenium standard reduction potential (E_{Fc/Fc+}) was subtracted from the applied potentials for plots. Nanoparticle solutions were cast onto 2 mm diameter Pt working electrodes. Electrodes were immersed using a custom H-cell with two 50 mL compartments was used. Acetonitrile (Sigma-Aldrich, HPLC-grade further dried by passage through a JC Meyer Solvent System) was stored over molecular sieves (3 Å, Sigma Aldrich). Tetrabutylammonium hexafluorophosphate (TBAF_6, 0.1 M, Sigma Aldrich, >99%) was used as a supporting electrolyte.

Additional data
Discussion of the origin of the broad NIR optical feature
To address the crucial point that the broad NIR absorption feature seen Figures 2 and 3 before anion exchange for Cu_{2-x}S nanorods and after initial shell formation to form Cu_{2-x}S/Cu_{2-x}Te structures is truly a plasmon band, we considered the alternative explanations that this feature may be due to a charge transfer process such as metal-to-ligand (M→L) charge transfer or intervalence charge transfer. Upon review of the literature, intercalation charge transfer has been observed in copper-containing molecular complexes in this same NIR region.6

Several characteristics distinguish optical features due to charge transfer from plasmons, a scattering process that occurs due to oscillation free carriers in metals or highly doped semiconductors rather than excitation between different energy levels. Two key features that distinguish charge transfer from plasmon scattering that have been reported for non-stoichiometric copper chalcogenide nanoparticles in the literature and confirmed in our laboratory (as presented below) are 1) large changes in the peak position in response to size or shape of the nanoparticle that are not explained by quantum confinement and 2) tuning of the peak position by alteration of the free charge carrier concentration through oxidation. Furthermore, behaviors induced by the strong electric fields produced at the surface of plasmonic particles such as surface enhanced Raman spectroscopy have been demonstrated.7,8

Responsiveness to particle shape or size
The free carrier movement in LSPR is restricted by the particle size and shape, thus the resonance wavelength can be altered by changing the shape or size of the particle; this is not a general behavior of charge-transfer processes. Spheres and rods of Cu_{2-x}S, Cu_{2-x}Se, and Cu_{2-x}Te show distinct shifts and intensities of the ~1200 nm NIR feature based on their shapes.9 In our laboratory, we have confirmed this behaviour by comparing the spectra of Cu_{2-x}S rods and spheres before and after anion exchange to create Cu_{2-x}S/Cu_{2-x}Te nanoheterostructures (Fig. S1a). Spheres were obtained by transformation of the original rods by heating at 185 °C in dodecanethiol (Fig. S1a). Qualitatively, the shift in the LSPR
between Cu$_{2-x}$S rods and spheres is consistent with that observed by Kriegel et. al, with a larger, red-shifted NIR peak for spheres versus rods as well as a red-shift in the apparent band-gap onset. Copper chalcogenide nanoparticles with various shapes and sizes have been compared, and the NIR absorption feature is consistently responsive to these variables.$^{10-12}$ Furthermore, the Drude model has been used extensively to model the NIR feature of copper chalcogenides. The Drude model relates the LSPR wavelength and peak breadth to the free carrier concentration and the dielectric constants of the material and its surroundings. It has been applied directly to model the behavior of Cu$_{2-x}$S nanoparticles of different diameters.$^{13}$ It was modified to describe the ensembles of inhomogeneous particles commonly resulting from nanoparticle synthesis, using Cu$_{1.85}$Se as a model system.$^{14}$ It has been applied to spheres and adapted to platelets of pure Cu$_{2-x}$S$^{15}$ and the ZnS-Cu$_{2-x}$S heterostructures resulting from cation exchange.$^{16}$

**Fig. S1.** a) Visible/NIR optical absorption of nanorods and spheres before and after Te-anion exchange. b) TEM demonstrating the spherical shape of the Cu$_{2-x}$S particles.

**Responsiveness to free carrier concentration**

The second feature that makes plasmonic absorption distinct from absorption due to a charge-transfer process is the dependance on the free carrier concentration. In copper chalcogenides, sufficient levels of doping to observe the NIR optical feature are typically caused by removal of Cu$^+$, creating vacancies and free holes in the valence band, referred to as the Moss-Burstein effect.$^{17}$ Several different oxidants and reductants have been demonstrated to tune the hole concentration and subtly shift the NIR absorption feature.$^9,18-20$ We demonstrate this effect in our laboratory using Cu$_{2-x}$S nanospheres, where addition of increasing amounts of I$_2$ solution in THF systematically shift the NIR absorption feature (Fig. S2). This is consistent with our publication reporting that the broad NIR absorption feature is responsive to change in the phase and oxidation with I$_2$.$^3$ Furthermore, electrochemical doping without removal of Cu$^+$ also induces the NIR optical absorption feature.$^{21}$ The Drude model has been used to match the NIR peak position and breadth of particles with different levels of Cu$^+$-vacancy doping due to exposure to I$_2$.$^3$ For Cu$_{2-x}$Se nanocrystals, the Drude model has been used relate charge carrier density, the NIR absorption feature, and $T_1$ values for $^{77}$Se NMR.$^{22}$

**Fig. S2.** Visible/NIR optical absorption of spheres with increasing amounts of oxidation with I$_2$, increasing the hole concentration.
Discussion of control experiment

Ligands alter the dielectric constant at the surface,$^{11,25}$ but surface chemistry can play an even more complex role in the LSPR of copper chalcogenides. TOP can alter copper chalcogenide phase (and therefore Cu$^+$-vacancies and free carrier concentrations). While Lesnyak et al.$^{26}$ observed that hexagonal Cu$_{2+x}$Se became more copper-deficient with TOP exposure, Steimle et al.$^{27}$ observed that removal of S from the surface transformed digenite Cu$_{2-x}$S into stoichiometric tetragonal Cu$_2$S. A control experiment (Fig. S2) showed that the LSPR peak blue shifts when Cu$_{2-x}$S nanorods are subject to anion exchange conditions in the absence of Te. This confirms that the anion exchange reaction is essential to the observed LSPR quenching and suggests that somehow the initial core/shell formation is responsible for quenching. Further experimentation focused on distinguishing the subtle differences in the heterostructures of the particles with and without LSPR using TEM-EDS imaging (Figs. 3, S3-S7).

Fig. S3. TEM data documenting that particle sizes are not changing during anion exchange at 230 °C. Triocetylphosphine can etch copper sulphide in the presence of small amounts of oxygen,$^{23,24}$ so it is important to ensure that overall particle size changes are not altering LSPR.

Fig. S4. Visible/NIR optical absorption of Cu$_{2-x}$S nanorods subject to anion exchange conditions in the absence of Te. The observed blue shift of the LSPR absorption indicates oxidation by the triocetylphosphine (TOP)-containing reaction mixture. This confirms that reaction with triocetylphosphine by surface ligand exchange or phase change is not responsible for LSPR quenching.
Fig. S5. TEM/EDS maps for Cu$_{2}$-xS nanorods before anion exchange.

Fig. S6. TEM/EDS maps for Cu$_{2}$-xS/Cu$_{2}$-xTe nanorods from anion exchange at 230 °C for 5 min. Four different areas are shown.
Fig. S7 TEM/EDS maps for Cu$_2$S/Cu$_2$Te nanorods from anion exchange at 230 °C for 20 min. Three different areas are shown.

Fig. S8. TEM/EDS maps for Cu$_2$S/Cu$_2$Te nanorods from anion exchange at 230 °C for 35 min. Four different areas are shown.
Fig. S9. TEM/EDS maps for Cu$_{2}$S/Cu$_{2}$Te nanorods from anion exchange at 230 °C for 65 min. Three different areas are shown.

Fig. S10. Visible/NIR absorption spectra of samples from Figure 4 on the same day as anion exchange and after 24 hours in dilute toluene suspension in air. Dilute samples left in toluene overnight showed oxidation-induced LSPR, as would be expected for a stoichiometric phase such as a-chalcocite.$^{28,29}$
Discussion of lower temperature experiments
The initial quenching of LSPR occurs as quickly as we can measure at 200 and 230 °C (Figs. 2a and 3a), so we attempted lower temperature (170 °C) anion exchange to monitor the incremental quenching of LSPR over time and confirm the role of the crystal structure in the switch to a non-plasmonic state. At 5, 10, and 20 min of reaction the particles were still plasmonic, but by 30 min the LSPR was no longer visible (Fig. S10a). PXRD of the 5 and 10 min samples (Fig. S10b,c) were nearly identical, but for 20 min and 30 min there was a continual shift in the diffraction peaks to lower 2θ, consistent with formation of more copper-rich phases. The correlation between PXRD peak position and LSPR is notable. The identical PXRD for the 5 and 10 min samples gave rise to nearly identical LSPR. The significantly shifted LSPR at 20 min arose from a significant shift in PXRD with respect to the 5 and 10 min samples. The switch from plasmonic to non-plasmonic behaviour between 20 and 30 min is associated with further shifts in the PXRD without alteration of the S/Te mole ratios (Fig. S10d), confirming that the solid-state transformation to more a copper-rich center is the key difference in LSPR behaviour.

Fig. S11. Cyclic voltammetry further supports the claim that transformation to a stoichiometric copper sulphide phase occurs at the early stages of anion exchange. The valence band edge shifts to a higher energy for the non-plasmonic sample, as would be expected if Cu⁺ vacancies were filled and no reduction of the valence band is observed for the non-plasmonic sample due to the small concentration of free holes to be filled.¹⁰

Fig. S12. Visible/NIR absorption spectra (a), PXRD (b,c), and EDS data (c) for a series of samples that underwent anion exchange at 170 °C for 5, 10, 20, or 30 min. Breaks in data at ~1700 nm are due to removal of solvent peaks.
References


