Localized Surface Plasmon Resonances of Anisotropic Semiconductor Nanocrystals

Su-Wen Hsu, Kathy On, and Andrea R. Tao*

Supporting Information

Methods

Chemicals:
1-dodecanethiol ($C_{12}H_{25}SH$, 98%, Labcaster), copper nitrate ($Cu(NO_3)_2$. $2.5H_2O$, Fisher), ethanol (CH_3OH, Goldshield chemical), chloroform ($CHCl_3$, Fisher), carbon tetrachloride (CCl_4, 99%, Sigma-Aldrich)

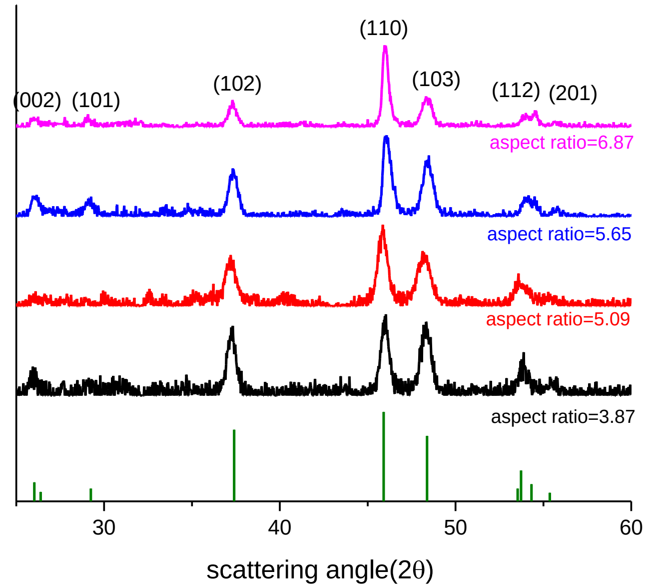
Synthesis of Cu-alkanethiolate precursor:
A 2.0 M solution of 1-dodecanethiol in ethanol was prepared by mixing 4.83 mL of 1-dodecanethiol (20 mM) with 10 mL ethanol in a glass vial. An aqueous 1.0 M copper nitrate solution was prepared by dissolving 1.16 g copper nitrate (5 mM) in 5 mL DI water in a glass vial. The dodecanethiol solution was added to the copper nitrate solution by vigorous stirring until the solution became colorless and a yellow-white suspension formed. The yellow-white suspension was collected by centrifugation, washed two times with DI-water and ethanol (volume ratio of 1:2) to remove the excess reagents, and then dried in a vacuum desiccator overnight to remove residual solvent and to obtain a yellow-white powder.

Synthesis of $Cu_{2-x}S$ nanoparticles and nanodisks:
The precursor was placed in a glass vial and heated in an oil bath at a temperature between 200°C to 220°C. The precursor turned into a dark-brown liquid which was then cooled to room temperature, dispersed in chloroform, and centrifuged at 7500 rpm for 7.5 min. to remove any by-products. This purification process was repeated three times. The purified product was dried under vacuum to obtain a brown powder for characterization.

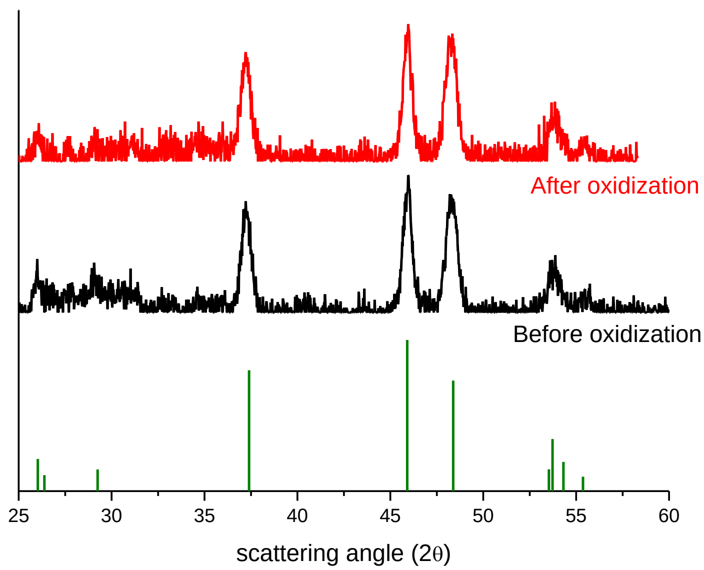
Oxidation of $Cu_{2-x}S$:
The purified and dried $Cu_{2-x}S$ powder was placed into an uncovered glass vial and heated in an oven at 80°C.

Sample characterization:
To prepare samples for TEM, the $Cu_{2-x}S$ powder obtained from synthesis was dispersed in chloroform and drop-casted onto a 200 mesh carbon-film coated Cu grid, then dried overnight to remove all traces of chloroform. UV-Vis-NIR spectroscopy (Shimadzu UV-3600) was used to characterize the surface plasmon resonance peaks of the $Cu_{2-x}S$ products. For LSPR measurements, the powder product was dispersed in carbon tetrachloride and NIR transmission was obtained in the range of 800 nm to 3200 nm.

XRD Characterization



XRD spectra for powder samples of $Cu_{2-x}S$ nanodisks that possess different aspect-ratios. As aspect ratio-increases, the relative intensity of the diffraction peak corresponding to the (110) plane increases.



XRD spectra for powder samples of the nanodisks before and after thermal oxidation. After oxidation, a small decrease is observed in the relative intensity of the peak corresponding to the (110) crystal plane.

Calculation of free carrier density for a nanodisk

We used the scattering theory for an oblate spheroid with semiaxes $a < b = c$. Polarizability can be expressed as:

$$\alpha_j = 3\varepsilon_0 V \frac{\varepsilon_j - \varepsilon_m}{3\varepsilon_m + 3L_j(\varepsilon_j - \varepsilon_m)} \quad (1)$$

Where $j = 1,2 \; or \; 3$, V is spheroid volume, ε_0 is free space permittivity, and L_j is a shape-dependent constant which calculate by the ratio of axes of spheroid. For the disk-like spheroid with an aspect ratio (diameter –to-height) of 5, $L_1 = 0.588$ for the electric field perpendicular to the basal plane and $L_2 = L_3 = 0.206$ for the in-plane electric field. For the resonance, the denomination term in equation (1) must be zero:

$$3\varepsilon_m + 3L_j(\varepsilon_{r,j} - \varepsilon_m) = 0$$

$$\varepsilon_{r,j} = -\frac{(1-L_j)}{L_j}\varepsilon_m \quad (2)$$

where $\varepsilon_{r,j}$ is real part of ε_j. ε_r can be expressed according to Drude theory

$$\varepsilon_r = 1 - \frac{\omega_p{}^2}{\omega^2 + \gamma^2} \quad (3)$$

where ω is the incident radiation frequency, γ is the loss associated collision frequency term, and ω_p is the bulk plasma frequency. The collision frequency γ can be calculated from the extinction spectrum according to:

$$\gamma = c\frac{\lambda_{1/2}}{\lambda_{max}{}^2} \quad (4)$$

where c is speed of light, $\lambda_{1/2}$ is the full width wavelength at half-maximum (FWHM) of the absorption peak, and λ_{max} is the absorption maximum wavelength.

To calculate the free carrier density of a copper sulfide nanodisk, we used the relationship between bulk plasma frequency (ω_p) and carrier density (N_h). The relationship can be expression as:

$$\omega_p = \sqrt{\frac{N_h e^2}{\varepsilon_0 m_h}} \quad (5)$$

where m_h is the hole effective mass, approximated as $0.8m_0$ (where m_0 is electron mass), and e is electron charge.

Using the information from the Fig. 1, we can calculated the free carrier density for in-plane and out-of-plane polarization:

a. **Out-of-plane:**

$$\lambda_{max} \approx 1800nm \; , \omega_{sp} = 0.69 \; eV, \lambda_{1/2} \approx 1100nm$$

$$\gamma = c\frac{\lambda_{1/2}}{\lambda_{max}{}^2} = 0.42 \; eV$$

Using $L_1 = 0.588$ and equation (2):

$$\varepsilon_{r,1} = -1.57$$

Using equation (3):

$$\omega_p = \sqrt{(1 - \varepsilon_{r,1})(\omega_{sp}{}^2 + \gamma^2)} = 1.29 \; eV = 1.96 \times 10^{15} \; s^{-1}$$

Using equation (5):

$$N_h = \frac{{\omega_p}^2 \varepsilon_0 m_h}{e^2} = 9.69 \times 10^{20}\ cm^{-3}$$

To calculate % copper deficiency:

$$V = \pi r^2 a = 2.07 \times 10^{-18}\ cm^3$$

The number of copper atoms in the nanodisk $= N_A \times V \times \frac{\rho_{Cu2S}}{Mw_{Cu2S}} \times 2 = 87778$

The number of vacancies in the nanodisk $= V \times N_h = 2006$

% deficiencies in the nanodisk $= \frac{number\ of\ deficiency\ in\ nanodisk}{number\ of\ copper\ in\ nanodisk} \times 100\% = 2.29\%$

b. <u>In-plane:</u>

$$\lambda_{max} \approx 3100nm,\ \omega_{sp} = 0.40\ eV, \lambda_{1/2} \approx 500nm$$

$$\gamma = c\frac{\lambda_{1/2}}{{\lambda_{max}}^2} = 1.56 \times 10^{13}\ s^{-1} = 0.06\ eV$$

Using $L_2 = 0.206$ and equation (2):

$$\varepsilon_{r,2} = -8.63$$

Using equation (3):

$$\omega_p = \sqrt{(1 - \varepsilon_{r,1})({\omega_{sp}}^2 + \gamma^2)} = 1.26\ eV = 1.91 \times 10^{15}\ s^{-1}$$

Using equation (5):

$$N_h = \frac{{\omega_p}^2 \varepsilon_0 m_h}{e^2} = 9.20 \times 10^{20}\ cm^{-3}$$

To calculate % copper deficiency:

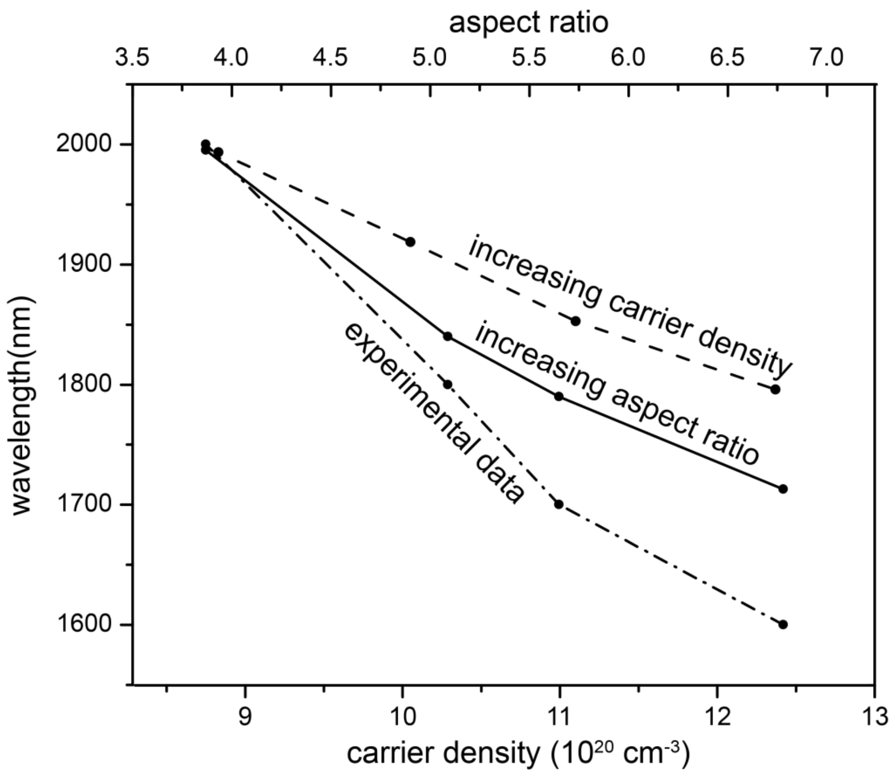
$$V = \pi r^2 a = 2.07 \times 10^{-18}\ cm^3$$

The number of copper atoms in the nanodisk $= N_A \times V \times \frac{\rho_{Cu2S}}{Mw_{Cu2S}} \times 2 = 87778$

The number of vacancies in the nanodisk $= V \times N_h = 1904$

% deficiency in the nanodisk $= \frac{number\ of\ deficiency\ in\ nanodisk}{number\ of\ copper\ in\ nanodisk} \times 100\% = 2.17\%$

Change in wavelength for the out-of-plane LSPR mode



The calculated change in LSPR wavelength for the out-of-plane mode for nanodisks with independently increasing aspect ratios (solid) and carrier densities (dashed), compared to the experimental data (dot-dash) obtained from the spectra in Figure 2a.