Colloidal Synthesis and Photocatalytic Properties of 
Cu$_3$NbS$_4$ and Cu$_3$NbSe$_4$ Sulvanite Nanocrystals

Supporting Information

Chen-Yu Chang$^a$, Roberto Prado-Rivera$^a$, Mimi Liu$^a$, Cheng-Yu Lai$^{a,*}$, & Daniela R. Radu$^a$*

$^a$Department of Mechanical and Materials Engineering, Florida International University, Miami, FL 33174, USA

chechang@fiu.edu (C.-Y.C.); rprad009@fiu.edu (R.P.-R.); mliu@fiu.edu (M.L.); clai@fiu.edu (C.-Y.L.) * Correspondence: dradu@fiu.edu, clai@fiu.edu

Computational details. All calculations were performed using density functional theory (DFT) with the projected-augmented wave (PAW) method as implemented within the Vienna $ab$ initio Software Package (VASP). The Perdew-Burke-Ernzerhof revised for solids (PBEsol) exchange-correlation functional was used throughout and a Hubbard parameter of $U=5.2$ eV was placed on the $d$-orbital of Cu, which has been shown to provide values in agreement with experimental results, using the method proposed by Dudarev et al. The electronic kinetic-cutoff energy was set to 500 eV. Geometric optimization was done on bulk unit cells by obtaining the total energies over a range of fixed-volume calculations while allowing the lattice parameter to vary and fitting to the Birch-Murnaghan equation-of-state. Relaxation was done for an electronic convergence criterion of $1 \times 10^{-8}$ and until the Hellman-Feynman forces were below 1 meV/Å using a 4×4×4 Γ-centered k-point mesh. The lattice parameters were determined by this fitting method to be 5.445 Å and 5.616 Å for Cu$_3$NbS$_4$ and Cu$_3$NbSe$_4$, respectively. The optical properties were calculated using a 6×6×6 Γ-centered k-point mesh and a Gaussian smearing width of 0.2 eV.

Dielectric Function and Absorption Spectra

To study the optical properties of a material from DFT, the complex dielectric function must first be determined. From the complex dielectric function, several optical properties may be derived. The complex dielectric function $\varepsilon_{\alpha\beta}(\omega) = \varepsilon_{\alpha\beta}^{(1)} + i\varepsilon_{\alpha\beta}^{(2)}$ was calculated within the independent particle approximation (IPA) in which the imaginary part is determined by summing over the empty states,
\[ \varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\varepsilon_{c,k} - \varepsilon_{v,k} - \omega) \times \langle u_{c,k+e_\alpha q}|u_{v,k}\rangle \langle u_{v,k}|u_{c,k+e_\alpha q}\rangle \] (Eq. 1)

where \( \Omega \) is the volume of the primitive cell, \( q \) is the Bloch vector of the incident wave, \( w_k \) are the \( k \)-point weights, \( u \) is the polarization of the incident wave, \( e_\alpha \) Cartesian unit vectors, and \( c \) and \( v \) denote the conduction and valence bands, respectively. The real part is determined by using the Kramers-Kronig transformation,

\[ \varepsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_{\alpha\beta}^{(2)}(\omega')\omega'}{\omega^2 - \omega'^2 + i\eta} d\omega' \] (Eq. 2)

Where \( P \) denotes the principle value. Further information on these equations can be found in the paper by M. Gajdoš et al.\textsuperscript{11}. The dielectric functions for each compound are shown in Figure S1.

From the complex dielectric function, the absorption coefficient is determined from the following relation,

\[ \alpha(\omega) = \frac{4\pi}{\lambda} \sqrt{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1} \] (Eq. 3)

where \( \lambda \) is the wavelength, and \( \varepsilon_1, \varepsilon_2 \) are the real and complex parts of the dielectric function, respectively.

The calculated absorption coefficients are shown in Figure S2. The most notable feature of the absorption coefficients is the presence of two prominent peaks followed by a shoulder for both compounds, which can be ascribed to direct optical transitions between the valence band and the conduction band, namely between the Cu \( d \)-states and chalcogen \( p \)-states. These peaks can be seen as well from the imaginary part of the dielectric function between 3 and 6 eV. For Cu\textsubscript{3}NbS\textsubscript{4}, the peaks are located at 236 nm (5.2 eV), 289 nm (4.3 eV), and 345 nm (3.6 eV). For Cu\textsubscript{3}NbSe\textsubscript{4}, the peaks are located at 259 nm (4.8 eV), 301 nm (4.1 eV), and 388 nm (3.2 eV). The maximum value of the absorption is \( 8.7 \times 10^5 \) and \( 8.9 \times 10^5 \) cm\(^{-1} \) for Cu\textsubscript{3}NbS\textsubscript{4} and Cu\textsubscript{3}NbSe\textsubscript{4}, respectively. The calculated absorption coefficient shown in Figure S2 can be relatively compared to the measured UV-vis absorbance spectra shown in Figure 1(e) as the absorbance \( A \) is directly proportional to the absorption coefficient, i.e., \( \alpha = A \times \ln(10)/d \), where \( d \) is the path length. The presence of the two peaks and shoulder in the absorption coefficient appears as two broad, flat peaks plus a shoulder in the UV-vis absorbance spectra, showing that the calculated and experimental spectra agree relatively well.
Figure S1. Calculated real $\varepsilon_1$ (a) and imaginary $\varepsilon_2$ (b) dielectric functions within IPA for Cu$_3$NbS$_4$ (blue) and Cu$_3$NbSe$_4$ (red).

Figure S2. Calculated absorption coefficient for Cu$_3$NbS$_4$ (blue) and Cu$_3$NbSe$_4$ (red).

**Exciton Bohr Radius**

At the nanoscale, the effects of quantum confinement can become prevalent for semiconducting materials that have very small particle sizes. Notable effects of quantum confinement include discretization of the energy levels and an increase in the size of the band gap. The characteristic size at which such effects may happen is the exciton Bohr radius. To understand whether quantum confinement effects are present for the sulvanite compounds, the exciton (electron-hole pair) Bohr radius was calculated. The exciton radius can be approximated using the following equation,

$$a = \frac{a_0 m_0 \varepsilon}{\mu} \quad \text{(Eq. 5)}$$
where $a_0$ is the hydrogen Bohr radius (0.053 nm), $m_0$ is the electron mass, $\varepsilon$ is the static dielectric constant, and $\mu$ is the reduced effective mass of the exciton. The reduced effective mass was calculated from the effective masses of the electron and hole,

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$  \hspace{1cm} (Eq. 6)

where the subscripts $e$ and $h$ denote the electron and hole, respectively. The static dielectric constant was determined within IPA from the complex dielectric function for $\omega=0$. The resulting dielectric constants were found to be 7.49 and 8.66 for Cu$_3$NbS$_4$ and Cu$_3$NbSe$_4$, respectively. The relation between the electronic band structure and the effective masses is given by the following equation,

$$\frac{1}{m_{i,j}^*} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j}$$  \hspace{1cm} (Eq. 7)

where $i$ and $j$ run over the three Cartesian coordinates in reciprocal space, and $E_n$ is the energy eigenvalue of the $n$-th band. This expression is evaluated using a finite-difference stencil method along with high symmetry points on the band structure.\(^\text{12}\)

Table S1. Calculated values along R-X for the electron effective mass $m_e^*$, hole effective mass $m_h^*$, reduced effective mass $\mu$, static dielectric constant $\varepsilon$, and exciton Bohr radius $a$. The effective masses are in terms of the electron mass $m_0$.

|       | $m_e^*$ | $m_h^*$ | $\mu$ | $\varepsilon$ | $a$ (nm) |
|-------|---------|---------|-------|---------------|---------|
| Cu$_3$NbS$_4$ | 1.313   | 0.531   | 0.378 | 7.49          | 1.050   |
| Cu$_3$NbSe$_4$ | 1.285   | 0.451   | 0.334 | 8.66          | 1.375   |

At the symmetry point $R$, there is a three-band degeneracy with corresponding hole effective masses; for the current calculation, the lowest hole effective mass was chosen. In terms of the electron mass $m_0$, the electron effective mass at $X$ was found to be $1.313m_0$ for Cu$_3$NbS$_4$ and $1.285m_0$ for Cu$_3$NbSe$_4$. At $R$ the hole effective mass was $0.531m_0$ and $0.451m_0$ for Cu$_3$NbS$_4$ and Cu$_3$NbSe$_4$, respectively. From these results, the reduced effective mass of the systems is $0.378m_0$ (S) and $0.334m_0$ (Se) and produces an exciton Bohr radius of 1.050 nm (S) and 1.375 nm (Se). The above information is summarized in Table S1. Depending on the value of the exciton Bohr radius, the effects of quantum confinement can be categorized in two ways: strong confinement, in which the radius of the nanocrystal is smaller than effective masses, and weak confinement, in which the radius is larger than the effective masses. Given that the average measured particle sizes of 34 nm and 19 nm for Cu$_3$NbS$_4$ and Cu$_3$NbSe$_4$ (Figure S3), respectively, are much larger than the calculated exciton Bohr radii, both types of nanocrystals exhibit weak quantum confinement. A similar calculation by Mantella et. al.\(^\text{13}\) concluded that Cu$_3$VS$_4$ nanocrystals also are under weak quantum confinement, a result that can be expected due to the chemical and structural similarity between the sulvanite nanocrystals.
Size distribution of the nanoparticles

Figure S3. Low-magnification TEM and particle size distribution of Cu$_3$NbS$_4$ and Cu$_3$NbSe$_4$.

Table S2. Dimensions of Sulvanite Cuboids

| Unit (nm)      | Long side     | Short side    |
|----------------|---------------|---------------|
| Cu$_3$NbS$_4$  | 39.00 ±10.30  | 29.27 ± 10.06 |
| Cu$_3$NbSe$_4$ | 22.25 ± 6.70  | 15.33 ± 4.94  |
Intermediate compounds and control experiment for mechanism study

Figure S4. HR-TEM of the time-dependent study product obtained at 5 and 30 minutes.

Figure S5. (a) XRD pattern (b) Raman spectrum-in agreement with literature-published spectra for NbSe₂ (c) TEM of the synthesized NbSe₂ nanosheet.
The Effect of Size and Strain on XRD diffraction pattern of Cu$_3$NbSe$_4$

The diffraction pattern obtained from standard powder X-ray diffraction is heavily dependent on the underlying structure of the material being analyzed. Oftentimes, peaks in the diffraction pattern are seen to undergo broadening and/or shift in position compared to an otherwise ideal sharp peak. Peak broadening and shifting can be ascribed to crystallite size and internal strain present in the sample, which are often seen in nanocrystals due to size confinement. To better understand the shift and broadening in the obtained XRD patterns, analysis of the peak profiles was done as follows.

The most popular method for analyzing the relationship between the crystallite size and peak broadening is through the Scherrer equation

$$ D = \frac{K \lambda}{\beta \cos \theta} $$

(Eq. 8)

where $D$, $K$, $\lambda$, $\beta$, and $\theta$ are the average crystallize size, the Scherrer constant (usually taken as 0.9), the wavelength of the XRD used, the peak width, and the Bragg angle, respectively. Under this method, $\beta$ is the corrected broadening of the measured pattern after subtracting instrumental broadening

$$ \beta^2 = \beta^2_{\text{measured}} - \beta^2_{\text{instrument}} $$

(Eq. 9)

It is standard to take $\beta$ as the full width at half-maximum (FWHM) of the peak profile, typically approximated as a Gaussian or Lorentzian function. From the Scherrer equation, $1/\beta$ versus $\cos(\theta)$ is plotted and a linear fit applied. The slope of the linear fit corresponds to $K \lambda/D$, which can readily be solved to obtain the average crystallite size.

Following Scherrer’s equation, more sophisticated methods exist that account for other factors, most importantly internal strain. One such method is through the Williamson-Hall (WH) method, which assumes the broadening is composed of contributions from size and internal strain

$$ \beta_{hkl} = \beta_{\text{size}} + \beta_{\text{strain}} $$

(Eq. 10)

The $\beta_{\text{size}}$ is inferred from Scherrer’s equation while $\beta_{\text{strain}}$ can be determined in several ways, the simplest of which is the uniform deformation model (UDM) under which the strain $\varepsilon$ is assumed uniform such that

$$ \beta_{\text{strain}} = 4 \varepsilon \tan \theta $$

(Eq. 11)

Combining the two broadening terms, the following equation is obtained

$$ \beta_{hkl} \cos \theta = 4 \varepsilon \sin \theta + \frac{K \lambda}{D} $$

(Eq. 12)

Plotting $\beta \cos(\theta)$ versus $4 \sin(\theta)$, a linear fit can be made, and the slope gives the strain $\varepsilon$ and the y-intercept gives the average crystallite size.
Figure S7 shows the Williamson-Hall plot using UDM for the diffraction pattern of Cu$_3$NbSe$_4$. The XRD peaks were fitted to a Gaussian function and their FWHM determined. The calculated average crystallite size and strain were determined to be 15.51 nm and 10.88$\times$10$^{-4}$, respectively. The average crystallite size is in good agreement with the results listed in Table S1. Notably, the dimension of the short side of the Cu$_3$NbSe$_4$ cuboids are a close match (15.33 nm vs 15.51 nm) while not being far off from the 22.25 nm of the long side of the cuboid. Furthermore, the calculated strain is consistent with the cuboid morphology of the obtained sulvanite-type nanocrystals in which the dimensions of the nanocrystals are constrained along one dimension compared to a perfect cube. Overall, the combination of size confinement and intrinsic strain within the sample will cause a shift and small broadening of the XRD peaks with respect to the bulk reference.

**Niobium concentration gradient during the time dependent study**

Figure S6. Williamson-Hall plot of the diffraction pattern for Cu$_3$NbSe$_4$.

Figure S7. (a) The particle with Nb concentration gradient shown in the red circle in figure 4b. (b) An isolated particle with Nb concentration gradient.
**EDX elemental study for the completely formed nanocrystal**

Table S3. STEM-EDX element analysis result for Figure 4c

| Percentage (%) | Cu    | Nb    | Se    |
|----------------|-------|-------|-------|
|                | 38.63 | 11.92 | 49.45 |

**Supporting Information References**

1. Blochl, P. E., Projector augmented-wave method. *Phys Rev B Condens Matter* **1994**, *50* (24), 17953-17979.
2. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6* (1), 15-50.
3. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B* **1996**, *54* (16), 11169-11186.
4. Kresse, G.; Hafner, J., Ab initio molecular dynamics for liquid metals. *Phys Rev B Condens Matter* **1993**, *47* (1), 558-561.
5. Kresse, G.; Hafner, J., Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Rev Mod Phys* **1994**, *49* (20), 14251-14269.
6. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B* **1999**, *59* (3), 1758-1775.
7. Csonka, G. I.; Perdew, J. P.; Ruzsinszky, A.; Philipsen, P. H. T.; Lebegue, S.; Paier, J.; Vydrov, O. A.; Angyan, J. G., Assessing the performance of recent density functionals for bulk solids. *Phys Rev B* **2009**, *79* (15), 155107.
8. Kehoe, A. B.; Scanlon, D. O.; Watson, G. W., Modelling potential photovoltaic absorbers Cu3 MCh 4 (M= V, Nb, Ta; Ch= S, Se, Te) using density functional theory. *Journal of Physics: Condensed Matter* **2016**, *28* (17), 175801.
9. Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P., Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys Rev B* **1998**, *57* (3), 1505-1509.
10. Birch, F., Finite Elastic Strain of Cubic Crystals. *Physical Review* **1947**, *71* (11), 809-824.
11. Gajdoš, M.; Hummer, K.; Kresse, G.; Furthmüller, J.; Bechstedt, F., Linear optical properties in the projector-augmented wave methodology. *Phys Rev B* **2006**, *73* (4), 045112.
12. Fonari, A.; Sutton, C. *Effective Mass Calculator*, 2012.
13. Mantella, V.; Ninova, S.; Saris, S.; Loiduce, A.; Aschauer, U.; Buonsanti, R., Synthesis and Size-Dependent Optical Properties of Intermediate Band Gap Cu3VS4 Nanocrystals. *Chemistry of Materials* **2019**, *31* (2), 532-540.