Supporting Information

Plasmon-Enhanced Chemical Conversion using Copper Selenide Nanoparticles

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Table of Contents:
General Methods and Materials ..................................................................................................................3
Synthesis of OAm-Capped Cu_{2-x}Se NPs ..............................................................................................3
Ligand Exchange of Cu_{2-x}Se NPs with 10 kDa PVP .............................................................................3
High Resolution Transmission Electron Microscopy (HRTEM) ..............................................................4
Powder X-ray Diffraction (PXRD) ............................................................................................................4
Figure S1. Representative PXRD pattern of Cu_{2-x}Se NPs referenced to PDF # 00-006-0680. ..............................................................................................................................5
Method for Inductively Coupled Plasma Optical Emission Spectrometry Analysis 5
Addition of Raman Analytes to Cu_{2-x}Se NPs ........................................................................................5
Raman Spectroscopy Analysis ..................................................................................................................6
Estimating SERS Enhancement Factor for Cu_{2-x}Se NPs .....................................................................6
1. Measuring I_{NRS} and Quantifying N_{NRS} .........................................................................................7
2. Quantifying N_{SERS} ............................................................................................................................7
a. Calculating Cu_{2-x}Se NP Concentrations .........................................................................................7
Figure S2. Molar extinction spectrum of the OAm-capped Cu_{2-x}Se NPs dispersed in CHCl_3. The insets correspond to their extinction profiles. .......................................................................................8
b. Estimating the Theoretical Surface Coverage of BT ..........................................................................8
Figure S3. Lateral view of a representative BT bound to a copper atom and the measured S-para H distance at a tilt angle of 30°.

Figure S4. Shifts of LSPR maximum for OAm-capped Cu_{2-x}Se NPs as a function of increasing BT concentration in CHCl_3 ranging from 1µM to 0.1 M.

Table S1. Relative SERS Intensities of 1002 cm\(^{-1}\) mode of BT of various concentrations for the quantification of an enhancement factor for Cu_{2-x}Se NPs.

Time Resolved SERS Spectra of NBT Dimerization on OAm- and PVP-capped Cu_{2-x}Se NPs.

Figure S5. Time resolved SER spectra of NBT in the presence of (A) OAm-capped and (B) PVP-capped Cu_{2-x}Se NPs.

Figure S6. Time resolved SER spectra of NBT in the absence of Cu_{2-x}Se NPs. After 5 minutes of irradiation, DMAB has not formed.

References
General Methods and Materials
Copper(I) chloride (CuCl, > 99.995%), selenium powder (Se, > 99.5%), octadecene (ODE, 90% technical grade), oleylamine (OAm, 70% technical grade), chloroform (> 99%), polyvinylpyrrolidone (PVP, average molecular weight 10,000), benzenethiol (BT, ≥ 98%), 4-nitrobenzenethiol (NBT, 80% technical grade) were purchased from Sigma Aldrich (St. Louis, MO). Absolute ethanol (EtOH) was purchased from Thermo Fisher Scientific (Pittsburgh, PA). All chemicals were used as received with no additional purification unless otherwise noted. Prior to use, all glassware and Teflon stir bars were washed in aqua regia and rinsed with copious amounts of water prior to oven drying. Caution: aqua regia is highly toxic and corrosive, and should only be used with proper personal protective equipment and training. Aqua regia should be handled inside a fume hood only.

Synthesis of OAm-Capped Cu$_{2-x}$Se NPs
Cu$_{2-x}$Se NPs were synthesized using a previously described hot injection method. The synthetic procedure was completed using standard air-free techniques and is described in detail below. The selenium-octadecene-oleylamine mixture was created by dissolving 80 mg Se in 1 mL of ODE and 2 mL of OAm. The solution was heated in a round bottom flask for 12 hrs under argon gas at 195 °C. In a 3-neck round bottom flask, 200 mg CuCl was added with 5 mL OAm and 5 mL of ODE. The Cu-ODE-OAm mixture was heated to 140 °C under vacuum for 30 min then heated to 285 °C under Ar. Then, the Se mixture was injected into the Cu mixture. The precursors reacted for 10 min at ~285 °C to form Cu$_{2-x}$Se NPs. The NPs were cooled to room temperature by removing the heating mantle.

The Cu$_{2-x}$Se NP product was purified via centrifugation. First, the as-synthesized NPs were transferred to glass centrifuge tubes containing 10 mL of EtOH and centrifuged in an Eppendorf 5804R centrifuge with a swing bucket rotor (A-44-4) (Eppendorf, Inc.) at a force of 2850 rcf at 20 °C for 5 min. The resulting supernatant was removed and the pellet was resuspended in a small amount of CHCl$_3$ for additional centrifugation in another 10 mL of EtOH. This washing procedure was repeated once. All purified NPs were then characterized by high resolution transmission electron microscopy (HRTEM), ultraviolet-visible-near infrared (UV-vis-NIR) extinction spectroscopy, powder X-ray diffraction (PXRD), and Raman spectroscopy.

Ligand Exchange of Cu$_{2-x}$Se NPs with 10 kDa PVP
Purified OAm-capped Cu$_{2-x}$Se NPs were dispersed in 4mL CHCl$_3$. 6 mL of 8 mM of 10 kDa PVP solution in CHCl$_3$ was added into the dispersed NP solution and the mixture solution was left stirring overnight at room temperature. After incubation, the Cu$_{2-x}$Se NP product was purified via centrifugation. First, the as-synthesized NPs were distributed to Eppendorf tubes in aliquots of 0.5 mL. 1 mL hexanes were added into the Eppendorf tubes and centrifuged in an Eppendorf 5424 centrifuge with a fixed angle rotor (F-45-30-11) (Eppendorf, Inc.) at a force of 15,000 rpm at 20 °C for 10 min. The resulting supernatant was removed and the pellet was resuspended in a small amount of CHCl$_3$ for additional centrifugation in another 1 mL of hexanes. This washing procedure was repeated once. All purified NPs were then characterized by HRTEM, UV-vis-NIR extinction spectroscopy, and Raman spectroscopy.
High Resolution Transmission Electron Microscopy (HRTEM)

Cu$_{2-x}$Se NPs were prepared for electron microscopy by drop casting an aliquot of purified NP solution (diluted 1:10 or 1:100 with CHCl$_3$) onto carbon film-coated copper transmission electron microscopy (TEM) grids (Ted Pella, Inc.) for routine bright field imaging analysis. TEM characterization was performed on a Hitachi H9500 Environmental TEM with an accelerating voltage of 300 kV (NanoScale Fabrication and Characterization Facility, Petersen Institute of NanoScience and Engineering, Pittsburgh, PA). The size distributions of the NPs were determined from TEM images of at least 200 NPs from various areas of the grid using ImageJ 1.47d (National Institutes of Health, USA).

Powder X-ray Diffraction (PXRD)

Purified Cu$_{2-x}$Se NPs were characterized by PXRD using a Bruker AXS D8 Discover XRD (NanoScale Fabrication and Characterization Facility, Petersen Institute of NanoScience and Engineering, Pittsburgh, PA) at 40 kV, 40 mA for Cu Kα (λ = 1.5406 Å) X-ray source with a scan speed of 0.7 s/step from 10.00 - 90.00° with a step size of 0.02°. Samples were prepared by drop casting an aliquot of purified NP solution (diluted 1:10 or 1:100 with toluene) on a glass microscope slide (Fisher Scientific). All spectra were baseline corrected with respect to the spectrum of the amorphous glass background.

The lattice parameter (a) of the antifluorite structure was determined using the PXRD peak at 27°, which corresponds to the cubic (111). Using the Bragg equation described below:

$$ a = \frac{\lambda \sqrt{h^2+k^2+l^2}}{2 \sin(\theta)} $$

(1)

where λ is the X-ray source, h=k=l=1, the lattice parameter was calculated to be 0.57 nm, and this value was used to estimate the volume of the unit cell for the quantification of NP concentration (vide infra).
Figure S1. Representative PXRD pattern of Cu$_{2-x}$Se NPs referenced to PDF # 00-006-0680.

Method for Inductively Coupled Plasma Optical Emission Spectrometry Analysis
ICP-OES analysis was performed using an argon flow with an Optima spectrometer (Perkin Elmer, Inc.). An aqua regia solution was prepared with a 3:1 ratio of hydrochloric acid (Sigma Aldrich, > 99.999% trace metal basis): nitric acid (Sigma Aldrich, > 99.999% trace metal basis) and diluted with water for a 5% v/v aqua regia matrix. Unknown Se and Cu concentrations were determined by comparison to a 7-point standard curve with a range of 0.10 - 10 ppm Cu and Se (0.10, 0.50, 1.0, 2.5, 5.0, 7.5, and 10 ppm of each metal prepared by volume) using a selenium standard for ICP (Fluka, TraceCERT 1000 ± 2 mg/L Se in HNO3) and Cu standard for ICP (Fluka, TraceCERT 1000 ± 2 mg/L Cu in HNO3), diluted in a 5% aqua regia matrix. All standards and unknown samples were measured 6 times and averaged. A 7-minute flush time with 5% aqua regia matrix was used between all runs, and a blank was analyzed before each unknown sample to confirm removal of all residual metals from the instrument.

Addition of Raman Analytes to Cu$_{2-x}$Se NPs
To prepare the BT solutions of various concentrations listed in Figure 2A of the main text, 250 µL of OAm-capped Cu$_{2-x}$Se NPs dispersed in CHCl$_3$ with an estimated optical density of ~1.5 at LSPR$_{max}$ was added into a 1.5 mL Eppendorf tube, followed by a 200 mM BT solution of volumes ranging from 154 to 769 µL in CHCl$_3$ into the Eppendorf tubes to reach a final solution volume of 1.5 mL to ensure that the NP concentrations and the final volume of each sample aliquot were constant. The solution was thoroughly mixed by incubation on the thermomixer (Eppendorf R Thermomixer) for at least one hour. In order to maintain NP dispersity in solution, it is important to note that all mixtures containing Cu$_{2-x}$Se NPs and Raman analytes were not purified after the addition of analytes. The
mixture solutions were then characterized by UV-vis-NIR extinction spectroscopy and Raman spectroscopy.

To prepare the NBT solutions for the plasmonically driven dimerization reactions represented in Figure 3 of the main text and Figure S5, 250 µL Cu$_{2-x}$Se NPs (either OAm- or PVP-capped) dispersed in CHCl$_3$ with an estimated optical density of ~1.5 at LSPR$_{\text{max}}$ was added into a 1.5 mL Eppendorf tube, followed by a 300 mM NBT solution of volumes ranging from 154 to 769 µL in CHCl$_3$ into the Eppendorf tubes to reach a final solution volume of 1.5 mL to ensure that the NP concentrations and the final volume of each sample aliquot were constant. The solution was thoroughly mixed by incubation on the thermomixer (Eppendorf R Thermomixer) for at least one hour. In order to maintain NP dispersity in solution, it is important to note that all mixtures containing Cu$_{2-x}$Se NPs and Raman analytes were not purified after the addition of analytes. The mixture solutions were then characterized by UV-vis-NIR extinction spectroscopy and Raman spectroscopy.

Raman Spectroscopy Analysis
The SERS instrument is a modified version of a previously published set-up. Briefly, 6W of <250 fs pulses, centered at 1035 nm, from a fiber amplifier (Clark MXR, Impulse), are sent through a spectral filter to generate picosecond pulses. In the spectral filter, the beam is directed through a transmission grating and focused onto a slit. The beam is then focused onto the sample. The spectral resolution is 17.8 cm$^{-1}$ as measured by the 786 cm$^{-1}$ peak in toluene and the pulse duration is 2.8 ps, as measured by the optical Kerr effect in toluene. After the sample, the spontaneous Raman signal is sent through a 1064 nm Razor Edge Raman filter and focused into a spectrograph (Princeton Instruments, Acton SP2300) containing a 300 gr/mm grating blazed at 1 µm. The Raman signal is collected with a 1024 pixel, liquid N$_2$ cooled InGaAs array (Princeton Instruments, Pylon-IR 1.7). The spectra were collected as 3 frames with 20 s acquisitions. The frames were averaged together and the spectra were scaled with respect to acquisition time and laser power. For all SERS EF measurements, the flux was 560 W/cm$^2$, which corresponds to 40 MW/cm$^2$ peak power. For all plasmonically driven dimerization reactions, the flux was 350 W/cm$^2$, which corresponds to 5.4 MW/cm$^2$ peak power.

Estimating SERS Enhancement Factor for Cu$_{2-x}$Se NPs
The SERS enhancement factor (EF) for Cu$_{2-x}$Se NPs was determined by the following equation:

$$EF = \frac{I_{\text{NRS}}}{I_{\text{NRS}}} \cdot \frac{N_{\text{SERS}}}{N_{\text{NRS}}}$$

where $I_{\text{SERS}}$ and $I_{\text{NRS}}$ are the Raman intensities of a specific mode for the SERS and normal Raman spectroscopy (NRS) measurements, respectively, while $N_{\text{SERS}}$ and $N_{\text{NRS}}$ correspond to number of BT molecules adsorbed on the plasmonic substrate and in solution, respectively, for the probed volume. Details on how we obtain each component that makes up the SERS EF estimation are explained below.
1. **Measuring $I_{\text{NRS}}$ and Quantifying $N_{\text{NRS}}$**

In Figure 2A of the main text, the grey dotted spectrum represents a normal Raman spectrum of a 200 mM BT solution in CHCl$_3$. We can fit each Raman peak to a Gaussian to extrapolate the peak amplitude which is equivalent to $I_{\text{NRS}}$ for each mode. From the known concentration of the solution, we can calculate $N_{\text{NRS}}$ after measuring the focal volume of the laser. The spot radius of the laser beam at the focus was determined by measuring the power before and after a 50 µm diameter pinhole at the sample position and placing the values in the following equation:

$$\text{spot radius} = 2 \sqrt{-\frac{2(\frac{d}{2})^2}{\ln\left(1 - \frac{p_a}{p_b}\right)}}$$  \hspace{1cm} (3)

where $d$ is the diameter of the pinhole, $p_b$ is the power before the pinhole, and $p_a$ is the power after the pinhole. For these experiments, the focal volume was $1.80 \times 10^{-5}$ mL. By multiplying the focal volume by the concentration of the BT solution and converting moles to molecules using Avogadro’s number, $N_{\text{NRS}}$ is $2.18 \times 10^{15}$ molecules. Obtaining these values give us the ability to express $N_{\text{NRS}}/I_{\text{NRS}}$ as $8.04 \times 10^{15}$.

2. **Quantifying $N_{\text{SERS}}$**

$N_{\text{SERS}}$ was calculated by first determining the concentration of NPs in the focal volume ($1.80 \times 10^{-5}$ mL).

a. **Calculating Cu$_{2-x}$Se NP Concentrations**

Cu$_{2-x}$Se NP concentrations were determined using the UV-vis-NIR spectrum of the NPs before BT addition in CHCl$_3$. Spectra were taken using a Cary 5000 UV-vis-NIR (Agilent, Inc.). UV-vis-NIR measurements were collected of NP suspensions diluted in CHCl$_3$ using 1.0 cm quartz cuvettes (Hellma, Inc.). Three trials of six serial dilutions of the concentrated NP stock were prepared. These particles were air dried, digested in 5% aqua regia and then further diluted for analysis. The extinction spectra were measured from 800-1500 nm, the concentrations of NPs were measured by ICP-OES (*vide supra*), and the average diameters of the NPs were determined using HRTEM micrographs. The total number of unit cells per particle was estimated by dividing the volume of the NP sphere by the volume of the cubic antifluorite lattice of Cu$_2$Se. The volume of the antifluorite unit cell was determined by PXRD (*vide supra*). The total number of Se atoms was then estimated per particle by multiplying the number of unit cells per particle by 4, which is the number of Se atoms present in an antifluorite unit cell. The slope of the linear regression can be used to estimate NP concentration in a specific optical density measured.
Figure S2. Molar extinction spectrum of the OAm-capped Cu$_{2-x}$Se NPs dispersed in CHCl$_3$. The insets correspond to their extinction profiles.

Before the Raman excitation, we monitor the Cu$_{2-x}$Se NP optical density (O.D.) at the LSPR maximum using extinction measurement. At approximately 0.302 O.D., which corresponds to 6.72 x 10$^{13}$ particles/L based on the molar extinction coefficient (vide supra, Figure S2). By multiplying the focal volume by the particle concentration, the number of particles in the focal volume is 1.2 x 10$^6$. Next, we can estimate the surface area of a particle from the average particle diameter measured by TEM (Figure 1B, 15.8 ± 1.7 nm). Assuming the particles are spheres, the surface area of a single particle is 7.9 x 10$^{-4}$ µm$^2$.

b. Estimating the Theoretical Surface Coverage of BT

In addition to particle concentration, the other key component of determining $N_{\text{SERS}}$ is estimating the packing density of the analyte on the NP surface. Theoretical BT footprint was determined using a model system generated by the Avogadro molecular editor (v1.2.0), which was mainly used to aid in the measurement of atomic distances. Specifically, the geometry of BT was intentionally placed bound to a copper atom at a tilt angle of 30° consistent with reports by Osawa and coworkers for BT bound to a Au(111) surface. The BT-Cu interaction was geometrically optimized by relaxation with the universal force field (UFF) to an average force of 10$^{-4}$ kJ/mol/atom before bond lengths were measured and bond angle was intentionally changed.
The distance between sulfur and hydrogen in the para position of the benzene ring was measured to be 0.247 nm (Figure S3), where the measurement is from one atom center to the other. Therefore, the van der Waals sphere must also be considered, where the Van der Waals radius for hydrogen was estimated to be 1.09 Å. By summing the two values we obtain an overall molecular radius estimate of 0.356 nm and its corresponding footprint of 0.4 nm²/ligand.

From this footprint, a calculated maximum of 2,122 ligands could be added to the surface of a Cu$_{2-x}$Se NP. This density assumes that the analyte completely displaces the capping ligand on the surface of the NPs at a 1:1 equivalence.

From these packing density values and NP concentrations measured in Section 2a, we conservatively estimate $N_{SERS}$ to be $2.37 \times 10^9$ molecules. We note that this likely significantly overestimates the amount of BT on the nanoparticle surface, as the BT coverage reported on other metal chalcogenide systems are lower (0.73 nm²/ligand on CdSe NPs.) If the concentration of BT on the nanoparticle surface is lower than we have estimated (as it likely is), our enhancement factor will be higher than we have calculated. For example, if the ligand concentration is half of what we estimate, the SERS EF will be double what we have calculated based on that estimate.

c. Experimental BT Concentrations Necessary for Full Coverage
As noted previously, all BT-Cu$_{2-x}$Se NP mixtures were not purified after the addition of analytes in order to maintain NP dispersity in solution. To ensure the concentrations of BT used were sufficient to achieve full coverage on the surface of the NPs, the LSPR peak positions of Cu$_{2-x}$Se NPs before and after the addition of BT were analyzed using
UV-vis-NIR spectroscopy. As a function of increasing BT concentration, the LSPR of Cu$_{2-x}$Se NPs redshifted and plateaued (Figure S4). This observation resulted from the interaction between the thiol binding moiety present in both the Raman analytes and the NP surface, where the more electron donating thiolated head groups reduce the carrier densities in Cu$_{2-x}$Se NPs. Overall, these experiments indicate that an excess of 100x is sufficient to saturate the Cu$_{2-x}$Se NP surfaces with BT. This 100x excess of BT, then becomes our benchmark for BT concentrations used in Raman measurements.

Figure S4. Shifts of LSPR maximum for OAm-capped Cu$_{2-x}$Se NPs as a function of increasing BT concentration in CHCl$_3$ ranging from 1µM to 0.1 M.

3. Extrapolating $I_{SERS}$

The total intensity ($I_{Total}$) at each BT concentration is measured by fitting each peak (Figure 2A) to a Gaussian to extrapolate the peak amplitude, which includes intensities coming from both bound ($I_{SERS}$) and excess ($I_{Excess}$) BT molecules (Table S1). After finding the $I_{Total}$ for each BT concentration, we can calculate the $I_{Total}/N_{SERS}$ ratio. As noted previously, in these experiments, at least 100x excess of BT was used and this excess must be considered by subtracting our estimated $N_{SERS}$ from $N_{Total}$ at the focal volume, where $N_{SERS}$ is constant for all concentrations.
| [BT] (mM) | $\frac{I_{\text{Total}}}{(I_{\text{SERS}} + I_{\text{Excess}})}$ | $\frac{I_{\text{Total}}}{N_{\text{SERS}}}$ | $\frac{N_{\text{Excess}}}{N_{\text{Total}} - N_{\text{SERS}}}$ |
|-----------|-----------------|-----------------|-----------------|
| 20.5      | 0.0279 ± 0.0041 | 1.17 ± 0.31 x 10^{-11} | 2.23 x 10^{14} |
| 41.1      | 0.0451 ± 0.0073 | 1.90 ± 0.17 x 10^{-11} | 4.47 x 10^{14} |
| 61.6      | 0.070 ± 0.0049  | 2.95 ± 0.21 x 10^{-11} | 6.71 x 10^{14} |
| 82.0      | 0.0921 ± 0.0056 | 3.88 ± 0.23 x 10^{-11} | 8.93 x 10^{14} |
| 102.5     | 0.110 ± 0.0063  | 4.63 ± 0.27 x 10^{-11} | 1.12 x 10^{15} |

4. Calculating SERS EF

In Figure 2B in the main text, we plot the $\frac{I_{\text{Total}}}{N_{\text{SERS}}}$ ratio against the $N_{\text{Excess}}$ at each concentration. If we fit these data to a linear regression, the y-intercept (an average of 2.41 ± 1.04 x 10^{-12}) represents the case where $N_{\text{excess}} = 0$, in other words, the intensity due only to the SERS active molecules. With this value in hand, we can bring together all the components acquired in the previous sections and obtain a SERS EF. By multiplying the y-intercept value by $N_{\text{NRS}}/I_{\text{NRS}}$, we obtain an enhancement factor of ~10^4.

Time Resolved SERS Spectra of NBT Dimerization on OAm- and PVP-capped Cu_{2-x}Se NPs

The representative difference spectra in Figure S5 for OAm- (Figure S5A) and PVP-(Figure S5B) capped Cu_{2-x}Se NP samples were obtained by subtracting the spectrum obtained upon initial exposure to the laser (0 min) from the spectrum obtained after 5 minutes of irradiation. The grey spectra in both Figure S5 panels represent the normal Raman spectrum of NBT. The NBT peaks are marked by black dashed lines and the DMAB product peak is denoted with a red dashed line. Solvent (CHCl_3) peaks are denoted by asterisks.
Figure S5. Time resolved SER spectra of NBT in the presence of (A) OAm-capped and (B) PVP-capped Cu$_{2-x}$Se NPs. Black dashed lines denote NBT and the red dashed line marks the growth of a DMAB peak in the spectrum obtained after 5 minutes of irradiation.

From these spectra, we can estimate a percent yield for this reaction on Cu$_{2-x}$Se NPs. First, we fit the 1344 and 1580 cm$^{-1}$ reactant peaks before and after irradiation to a Gaussian function to extrapolate the peak amplitude. We account for any changes in signal by comparing the amplitude changes between the nitro stretch (1344 cm$^{-1}$) and the C-C stretch (1580 cm$^{-1}$) from before and after irradiation. Then we can fit the N=N stretch (1458 cm$^{-1}$), which corresponds to the product peak to obtain its peak amplitude. By placing the peak amplitudes into Equation 4, we can obtain a percent yield for this reaction for OAm-capped and PVP-capped Cu$_{2-x}$Se NPs to be 25 ± 3% and 24 ± 4%, respectively.

$$\text{Percent Yield} = \frac{\text{Final Product Amplitude}}{\text{Final Reactant Amplitude}}$$  \hspace{1cm} (4)

Additionally, we performed a control experiment by irradiating a concentrated NBT solution in the absence of Cu$_{2-x}$Se NPs at the same power and duration as the samples containing Cu$_{2-x}$Se NPs. As can be seen in the difference spectrum in Figure S6, no DMAB peaks are present after 5 minutes of irradiation showing the necessity of the plasmonic Cu$_{2-x}$Se NPs for the dimerization of NBT.
Figure S6. Time resolved SER spectra of NBT in the absence of Cu$_{2-x}$Se NPs. After 5 minutes of irradiation, DMAB has not formed.

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