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Tuning the LSPR in copper chalcogenide nanoparticles by cation intercalation, cation exchange and metal growth

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Electronic Supplementary Material (ESI)



Fig. S1 HAADF-STEM image and EDX mappings of Ag, Se and Cu averaged with the corresponding HAADF-STEM image, of a Cu_{2-x}Se sample after addition of 25 % Ag(I).

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Fig. S2 UV/Vis/NIR absorption measurements plotted against energy (eV) to determine γ as the full width half maximum of the plasmon band. Spectra shown are of (A, B) Cu2-xSe NPs and (C, D) Cu1.1S NPs dissolved in toluene which are treated with different amounts of a (A, C) 0.04 M Cu(I) solution or (B, D) different amounts of a 0.16 M Ag(I) solution.



Fig. S3 UV/Vis/NIR absorption spectra of Cu_{2-x}Se-Au hybrids with Cu_{2-x}Se:Au ratios (A) 1:0.24 and (B) 1:0.56 that have been treated with different amounts of an 0.16 M Ag(I) solution. The spectra of the so treated particles after storing under air for 24 h hours (dotted lines) are also shown. * The sharp absorption peaks (around 1700 nm) are due to solvent absorption.



Fig. S4 TEM image of the pure, parent $Cu_{1.1}S$ covellite NPs.

Dependence of the extinction cross section on $\boldsymbol{\gamma}$

The LSPR frequency (ω_{LSPR}) of both self-doped systems can be described by the Drude model^{1, 2}:

$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{1+2\varepsilon_m} - \gamma^2} \tag{S1}$$

 γ is a damping factor that represents the linewidth of the plasmon resonance band and is associated with the frequency of carrier-carrier collisions in the bulk. \mathcal{E}_m is the dielectric constant of the surrounding medium. The bulk plasma frequency (ω_p) can then be derived in relation to the free carrier density (N_h):

$$\omega_p = \sqrt{\frac{N_h e^2}{\varepsilon_0 m_h}} \tag{S2}$$

with m_h being the effective mass of the hole, approximately $0.8 \cdot m_0$. m_0 being the electron mass.^{1, 2} As the LSPR position shifts only slightly, it can be seen that the carrier density, the effective mass of the hole, and the dielectric constant of the surrounding medium are relatively unaltered. For NPs that are small compared to wavelength of the incident light (λ >>2R, R being the NP radius) the extinction cross section (σ_{ext}) of the NPs is only built of the dipole absorption of the Mie equation. Hence the equation is reduced to:

$$\sigma_{\text{ext}}(\omega) = 12\pi \frac{\omega}{c} \varepsilon^{1.5} R^3 \frac{\varepsilon''(\omega)}{[\varepsilon'(\omega) + 2\varepsilon_m]^2 + \varepsilon''(\omega)^2}$$
(S3)

 $\mathcal{E}'(\omega)$ and $\mathcal{E}''(\omega)$ are the real and imaginary part of the dielectric function of the NP. Following equation (S3) the resonance will be at $\mathcal{E}'(\omega) \approx -2 \mathcal{E}_m$ if $\mathcal{E}''(\omega)$ is only weekly dependent on ω or is small.³ Hence the extinction of the plasmon band is mainly dependent on $\mathcal{E}''(\omega)$, that can be written as:⁴

$$\varepsilon''(\omega) = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)} \tag{S4}$$

For $\omega >> \gamma$ this can be approximated with:

$$\varepsilon''(\omega) \approx \frac{\omega_p^2 \gamma}{\omega^3}$$
 (S5)

From this it can be seen, that at a given plasma frequency the increase of the damping factor leads to an increase of $\mathcal{E}''(\omega)$ and according to equation (S2) to a decrease of σ_{ext} .

References

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