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Determination of a Localized Surface Plasmon Resonance Mode of Cu$_7$S$_4$ Nanodisks by Plasmon Coupling

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Plasmon properties such as peak position, extinction cross-section, and local electric field intensity, are strongly dependent on excited, localized surface plasmon resonance (LSPR) modes. In non-spherical copper chalcogenide nanoparticles, assignment of the LSPR peaks to the corresponding oscillation modes has been controversial and requires experimental verification. We determined the in-plane LSPR mode of roxbyite Cu$_7$S$_4$ nanodisks from the plasmon coupling effect of nanodisks in solution. Compared with individual Cu$_7$S$_4$ nanodisks, self-assembled Cu$_7$S$_4$ nanodisk arrays in chloroform exhibited a blue-shifted LSPR peak with weaker optical density. This strongly suggests that the singular LSPR peak in the near-infrared region mainly originates from the in-plane oscillation mode. In addition, we demonstrate that the same LSPR peak can be readily tuned by controlling the number of disks in the array.

Introduction

Localized surface plasmon resonance (LSPR) is a collective oscillation of free carriers in resonance with incident light. At the LSPR frequency, the absorption cross-section, scattering cross-section, and local electric field intensity are significantly enhanced. The LSPR of metal nanoparticles (NPs) can be finely tuned through manipulation of composition, size, and shape, as well as the refractive index of the surrounding medium. As a result of the unique optical and electrical properties of LSPR, plasmonic NPs have stimulated a wide range of applications including photothermal therapy, surface-enhanced Raman scattering, metal-enhanced fluorescence, and photocatalysis. LSPR emerges not only in metals but also in semiconductors that have appreciable carrier density. Because they have a much lower carrier density (~10$^{19}$ cm$^{-3}$) relative to metals (~10$^{23}$ cm$^{-3}$), semiconductors exhibit LSPR responses in the near-infrared (NIR) and mid-infrared (MIR) regions. This is understood from the relation:

$$\omega_p = \sqrt{\frac{N}{m_e^*}}$$

where $\omega_p$ is the bulk plasma frequency, $N$ is the density of free carriers, $e$ is the electron charge, and $m_e^*$ is the hole effective mass. The advantages of LSPR in $p$-type semiconductors (Cu$_2$S, Cu$_2$Se) are controllable responses via carrier density, oxidative generation, and reductive filling of copper vacancies. In metal NPs, once the size, shape, or the refractive index of the surrounding medium is fixed, the LSPR response is locked and cannot be dynamically tuned. Another advantage over metallic NPs is the existence of various Cu$_2$S, Cu$_2$Se NP crystal structures. For example, in Cu$_2$S NPs, the degree of copper deficiency ($x$) varies in a wide range between 0 and 1, from the Cu-abundant Cu$_{2+}$S phase (chalcopyrite) to the Cu-poor CuS phase (coulvite). Cu$_2$S NPs with different crystal structures exhibit unique LSPR responses. Djerleite Cu$_{96}$S nanodisks have two distinct LSPR peaks in the NIR and MIR regions, while covellite Cu$_{4}$S nanodisks have only one peak in the NIR region. Carrier density and crystal structure control of Cu$_2$S, Cu$_2$Se NPs are good ways to investigate LSPR responses beyond metals. Because of the unique LSPR properties, Cu$_2$S, Cu$_2$Se NPs have potential applications in bio-imaging, photothermal therapy, and NIR optical switching.

Assignment of an LSPR peak to a corresponding oscillation mode is important for a better understanding of LSPR and its applications. However, this has been a challenge for copper chalcogenide NPs. The LSPR response of non-spherical gold and silver nanorods can be reproduced with numerical simulations such as the discrete dipole approximation or finite difference time domains. In contrast, numerical simulations cannot be applied to copper chalcogenides. For example, Feldmann et al. reported that the Drude model could not describe the LSPR responses well in Cu$_{x}$X (X=S, Se, Te) NPs, because the free holes in the Cu$_{x}$X valence band cannot be viewed as full free carriers, and the effects of hole localization need to be taken into consideration. In addition, the empirical dielectric function determined from thin films cannot be directly used to analyze the LSPR responses.

Several experimental approaches could be used to assign LSPR peaks of Cu$_2$S nanodisks to corresponding oscillation modes. With an increasing aspect ratio AR (diameter/thickness), the in-plane LSPR peak of silver nanodisks is expected to be red-shifted, while the out-of-plane peak is expected to be blue-shifted. In contrast, in-plane LSPR peak shift for Cu$_2$S nanodisks with increasing AR is not observed, while the in-plane LSPR peak for Cu$_{96}$S nanodisks is blue-shifted with increasing AR because of the increased...
carrier density. Finally, the in-plane LSPR peak of the CuS nanodisk is red-shifted with increasing AR. Thus, assignment of LSPR peaks is not possible by simply increasing the ARs of the Cu$_2$S$_x$ nanodisks. Interaction between excited LSPR modes in solution (plasmon coupling) can be used to assign a Cu$_2$S nanodisk LSPR peak to the corresponding oscillation mode. This is because when the NPs are assembled with small gaps between the disks, plasmon coupling between excited LSPR modes induces significant LSPR changes such as peak position, extinction cross section, and local electric field intensity. Thus, it is possible to determine the excited LSPR mode from the plasmon coupling. For example, compared with single Cu$_2$S nanodisks, the in-plane plasmon coupling of face-to-face assembled Cu$_2$S nanodisks is expected to induce a blue shift of the LSPR peak and a decrease in optical density. Conversely, the out-of-plane plasmon coupling of face-to-face assembled Cu$_2$S nanodisks is expected to induce a red shift of the LSPR peak and an increase in optical density. By way of this difference, one can assign the observed LSPR peak to the corresponding oscillation mode experimentally.

Here, we synthesized high-quality roxbyite Cu$_2$S$_x$ nanodisks as described previously, and assigned the LSPR peak in the NIR region to the corresponding oscillation mode. To induce plasmon coupling, column-like Cu$_2$S$_x$ nanodisk arrays are fabricated via ligand replacement of oleylamine (OAm) with 1-dodecanethiol (1-DT). The formation of Cu$_2$S$_x$ nanodisk arrays in CHCl$_3$ is investigated through real-time dynamic light scattering (DLS) and $^1$H-NMR. From LSPR spectral shifts during nanodisk array formation, we conclude that the singular LSPR peak in the NIR region resulted mainly from the in-plane plasmon coupling of face-to-face assembled Cu$_2$S$_x$ nanodisks. Scanning electron microscopy (SEM) images, TEM images, and high-resolution transmission electron microscopy (HRTEM) images of oxidized Cu$_2$S$_x$ nanodisks were acquired on a JEM-1011 (JEOL) at an accelerating voltage of 100 kV. All the air-sensitive samples were dried in a glove box. Ultraviolet-visible (UV-vis)-NIR absorption spectra were acquired with an IRPrestige-21 (Shimadzu). Photoluminescence analysis was performed with a Fluorolog-3 Model:TITT6 (NanoLog). Cu$_2$S$_x$ nanodisks were excited at 400 nm, and the 1-cm quartz cuvette was tightly sealed to prevent oxidation. X-ray diffraction (XRD) patterns of oxidized Cu$_2$S$_x$ nanodisks were acquired on a X'Pert Pro MPD (PANalytical) with CuKα radiation ($\lambda$=1.542 Å) at 45 kV and 40 mA. DLS measurements to monitor the size variation of the Cu$_2$S$_x$ nanodisk arrays in CHCl$_3$ were performed with an ELS-ZA2 (Otsuka Electronics). To determine the surface-capping agent of the Cu$_2$S$_x$ nanodisks, $^1$H-NMR was acquired with a 200-MHz Varian Gemini 200 NMR spectrometer.

**Results and discussion**

**Morphologies and optical properties of Cu$_2$S$_x$ nanodisks.**

High-quality Cu$_2$S$_x$ nanodisks were synthesized using DBTU as the sulfur source. Figure 1a and b shows SEM and TEM images, respectively of the Cu$_2$S$_x$ nanodisks. Because of their uniform size (diameter: 14±1.0 nm, thickness: 4.5±0.5 nm) and shape, the nanodisks stack in a layer-by-layer fashion on the Si substrate. The obtained Cu$_2$S$_x$ nanodisks were found to have a triclinic roxbyite structure from an XRD measurement (Fig. S1). Figure 1c shows a strong LSPR absorption peak for the Cu$_2$S$_x$ nanodisks, which derives from collective free-hole oscillations generated by excess copper vacancies in the valence band. OAm forms a complex with copper ions, which may generate the copper vacancies in the NPs during nucleation and growth. Alivisatos et al. reported the synthesis of stoichiometric Cu$_2$S NPs without OAm, and the non-oxidized Cu$_2$S NPs exhibited no LSPR absorption band. Therefore, OAm-induced vacancies led to the LSPR absorption in our nanodisks. Previous studies have shown that freshly synthesized Cu$_2$S NPs were easily oxidized and reduced. Oxidative agents including oxygen, iodine, and the Ce(IV) complex can induce the creation of copper vacancies in the Cu$_2$S lattice, leading to an increase in carrier density. In UV-vis-NIR spectra, oxidation causes a blue shift in the LSPR peak.
increases the absorption intensity, narrows the line width, and increases the onset of absorption. Conversely, reductive agents including DIBAH\textsuperscript{10}, thiols,\textsuperscript{21} and Cu(I) salts\textsuperscript{22} induce the filling of copper vacancies in the Cu\textsubscript{2}S\textsubscript{4} lattice, leading to a decrease in carrier density. The reduction causes a red shift in the LSPR peak, decreases the absorption intensity, broadens the line width, and decreases the onset of the absorption band. The oxidation of Cu\textsubscript{2}S\textsubscript{4} nanodisks by air, reduction by DIBAH, and re-oxidation by air is displayed in Figures S2 and S3. All the Cu\textsubscript{2}S\textsubscript{4} nanodisk spectral shifts and variations in optical density were consistent with previous reports.\textsuperscript{7,10}

![Graph showing UV-vis-NIR spectrum](Image)

**Fig. 1** (a) SEM and (b) TEM images of Cu\textsubscript{2}S\textsubscript{4} nanodisks. (c) UV-vis-NIR spectrum of Cu\textsubscript{2}S\textsubscript{4} nanodisks in toluene before oxidation.

**Formation of Cu\textsubscript{2}S\textsubscript{4} nanodisk arrays.**

Face-to-face contacts, with narrow inter-disk spaces in the arrays, enable plasmon coupling between the Cu\textsubscript{2}S\textsubscript{4} nanodisks. From the UV-vis-NIR spectral shift caused by array formation, we can assign the Cu\textsubscript{2}S\textsubscript{4} nanodisk LSPR peak in the NIR region to the corresponding oscillation mode. Previously, Tao et al. reported that 1-DT-capped Cu\textsubscript{2}S\textsubscript{4} nanodisks formed Langmuir-Blodgett films of nanodisk arrays.\textsuperscript{19} Hence, we developed a convenient and versatile method for forming one-dimensional nanodisk arrays in solution. The Cu\textsubscript{2}S\textsubscript{4} nanodisk arrays were fabricated via ligand exchange of OAm-Cu\textsubscript{2}S\textsubscript{4} nanodisks (5.1 nmol) by sonication with 1-DT (80 µmol) in CHCl\textsubscript{3} (5 mL) under N\textsubscript{2}. TEM and SEM images of the arrays are in Figure S4. Strong intermolecular interaction among linear 1-DT molecules leads to the formation of the Cu\textsubscript{2}S\textsubscript{4} nanodisk arrays. In addition, the TEM images in Figure 2b reveal that the inter-particle distance (~2.2 nm) is shorter than twice the molecular length of 1-DT (2×1.6 nm), indicating that inter-penetration among linear 1-DT molecules on the nanodisks induces strong hydrophobic interactions. The latter enables face-to-face self-assembly of growing Cu\textsubscript{2}S\textsubscript{4} nanodisks arrays with time. In contrast, the non-linear cis-conformation of OAm leads to a strong steric repulsion that prevents face-to-face self-assembly of the nanodisks. Thus, OAm capped nanodisks are dispersed in CHCl\textsubscript{3} and no arrays are observed.

![Graph showing time evolution of DLS spectra](Image)

**Fig. 2** (a) Time evolution of DLS spectra recorded after addition of 1-DT (80 µmol) to oxidized Cu\textsubscript{2}S\textsubscript{4} nanodisks in CHCl\textsubscript{3} (5 mL) (final 1-DT conc. = 16.2 mM), and then sonication under N\textsubscript{2} for 30 min. (b) TEM images of Cu\textsubscript{2}S\textsubscript{4} nanodisks and nanodisk arrays for growth time at 20 min and 3.5 h.
Assignment of LSPR mode in NIR region.

Because of the 2.2-nm inter-particle distance in the Cu$_2$S$_4$ nanodisk arrays, a strong near-field coupling is expected. By comparing the LSPR properties between the isolated Cu$_2$S$_4$ nanodisks and the arrays, we can determine the LSPR mode in the NIR region. Figure 4a plots the time evolution of UV-vis-NIR spectra after the addition of 1-DT. The LSPR peak is gradually blue-shifted, while the optical density gradually decreases. This spectral change is attributed to the formation of nanodisk arrays. As discussed above, the reduction of nanodisks by 1-DT decreases the hole density, leading to a red-shifted LSPR peak and a weak optical density. In general, the LSPR peak and the extinction intensity of plasmonic NPs are sensitive to the refractive index of the surrounding medium and the type of molecules capping the NPs. These two effects are excluded here, however, because the Cu$_2$S$_4$ nanodisks and arrays are both dispersed in CHCl$_3$, and both OAm and 1-DT have essentially the same refractive indexes (1.46, 1.45, respectively).

Length control of Cu$_2$S$_4$ nanodisk arrays.

To demonstrate the tunability of in-plane plasmon coupling in Cu$_2$S$_4$ nanodisk arrays, the dependence of the LSPR peak shift on 1-DT concentration was investigated. Figure 5a plots the DLS spectra of the Cu$_2$S$_4$ nanodisk arrays formed by the addition of different concentrations of 1-DT.

Low concentrations of 1-DT (# 2, 10 µmol) cause the formation of short nanodisk arrays (15–85 nm); there are also a large number of free Cu$_2$S$_4$ nanodisks (Fig. 5b). This indicates that the OAm is not completely replaced by the 1-DT. An increase in 1-DT concentration (# 3, 80 µmol) results in longer arrays (18–130 nm), with a smaller number of free nanodisks. For an excess of 1-DT (# 4, 420 µmol), the array distribution is narrower (20–100 nm). The average length of the nanodisk arrays increases to 16 nm with increasing 1-DT concentration. When the amount of 1-DT was sufficient for complete replacement of the OAm, the LSPR shift leveled off. We estimate that 6.3 µmol of 1-DT is necessary to completely...
passivate the hexagonal \{100\} facets of the Cu$_2$S$_4$ nanodisks and saturate the growth of the arrays (see ESI and Fig. S6). This fact can be understood in terms of the equilibrium between the adsorption of OAm and 1-DT on the nanodisk surface. Figure 5 plots the UV-vis-NIR absorption spectra of the corresponding samples. As discussed above, in-plane plasmon coupling causes the adsorption of OAm and 1-DT on the nanodisk surface. Figure 5 plots the UV-vis-NIR absorption spectra of the corresponding samples. As discussed above, in-plane plasmon coupling causes the LSPR blue shift, which is determined by the number of disks in the arrays.

Conclusions

In summary, we synthesized high-quality, OAm capped Cu$_2$S$_4$ nanodisks that have a single strong LSPR peak in the NIR region. Cu$_2$S$_4$ nanodisk arrays were fabricated via ligand exchange and their formation mechanism was investigated. By comparing the LSPR properties of isolated nanodisks with the nanodisk arrays, the singular LSPR peak of roxbyite Cu$_2$S$_4$ was assigned, for the first time, to the in-plane oscillation mode. In addition, LSPR spectra of Cu$_2$S$_4$ nanodisks can be controlled by the amount of 1-DT because of the variable length of the nanodisk arrays. Our versatile method could provide a way to determine the LSPR oscillation mode of copper-based binary, ternary, and quaternary semiconductors with different crystal structures.

Acknowledgements

This work was supported by the Artificial Photosynthesis Project (ARPCChem) of the New Energy and Industrial Technology Development Organization (NEDO) of Japan and JSPS KAKENHI (No. 25390017) (M.S.). We thank Dr. Nakata and Prof. Morii (Institute of Advanced Energy, Kyoto University) for the $^1$H-NMR measurement. We thank Dr. Sakakibara and Prof. Tsuji (ICR, Kyoto University) for the DLS measurement.

Notes and references