High-Quality Dual-Plasmonic Au@Cu_{2−x}Se Nanocrescents with Precise Cu_{2−x}Se Domain Size Control and Tunable Optical Properties in the Second Near-Infrared Biowindow

Beibei Shan,† Yawen Zhao,‡ Yiwen Li,§ Haitao Wang,† Rui Chen,*§ and Ming Li*†‡

†School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China
‡China Academy of Engineering Physics, Mianyang 621900, China
§Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China

Supporting Information

ABSTRACT: Dual-plasmonic Au–Cu_{2−x}E (x > 0, E = S, Se, Te) hybrids present multifunctionalities for broad applications in photovoltaics, photocatalysis, and biomedicine. However, despite the increasing interest in these dual-plasmonic Au–Cu_{2−x}E hybrids, precise control over the morphology and size of their substituents is crucial but greatly challenging. Herein, a selenium-mediated two-step synthetic approach is developed to prepare the Au@Cu_{2−x}Se nanocrescents with precise control over their size and tunable plasmonic properties through varying the concentration of the SeO_2 precursor. The complete encapsulation of the Au domain within the Cu_{2−x}Se layer in the nanocrescent in an asymmetric manner enables the strong coupling between their substituents, significantly enhancing their optical properties supported by both experimental results and theoretical modeling. The increasing Cu_{2−x}Se domain size enables the tuning of carrier densities and thereby molar extinction coefficients corresponding to the respective visible and near-infrared (NIR) plasmon bands of the Au@Cu_{2−x}Se nanocrescents. Electron transfer from the Au to Cu_{2−x}Se domains is unambiguously determined in the Au@Cu_{2−x}Se nanocrescents by transient absorption (TA) and extinction spectral measurements. The Cu_{2−x}Se-dependent bleaching amplitude and carrier dynamics of both visible and NIR plasmon TA signals are observed, along with variations of the carrier–phonon and phonon–phonon relaxation processes. This work not only presents a facile synthetic approach of high-quality dual-plasmonic Au@Cu_{2−x}Se nanocrescents and a fundamental understanding of the coupling mechanism in the Au–Cu_{2−x}Se hybrid system, but also provides a paradigm for the study on the interplay in a dual-plasmonic metal–semiconductor system.

INTRODUCTION

Plasmonic materials find a plethora of applications ranging from photovoltaics and light-driven catalysis to biomedicine such as biosensing, bioimaging, and cancer theranostics.1–4 Noble metals and nonstoichiometric copper chalcogenides (Cu_{2−x}E, x > 0, E = S, Se, Te) are among the most studied plasmonic materials and have been extensively exploited as building blocks of multifunctional materials for those plasmon-based applications.5–9 Au and Ag are the most commonly used plasmonic noble metals, whose surface plasmon resonances (SPRs) mainly arise from the collective oscillation of their free conduction electrons driven by the electromagnetic field of incident light.5,10 The large intrinsic free carrier (electron) density (∼10^{23} cm^{-3}) in noble metals makes their SPR bands in the visible (400–700 nm) and first near-infrared (NIR-I, 700–900 nm) regions,11 the plasmonic response of these noble metals strongly depends on their composition, particle size, and geometric shape, and the dielectric function of the surrounding environments.2,12–14 Although tailoring the anisotropic shape (i.e., nanorods, nanocages, hollow spheres, and core–shell) allows for tuning the SPR band of noble metal nanostructures into the second NIR biowindow (NIR-II, 1000–1350 nm) favorable for in vivo biomedical applications, both large particle size of >100 nm and high power density exceeding the maximum laser permissible exposure (0.33 W/cm^2 for 808 nm laser, 1.0 W/cm^2 for 1064 nm laser) restrict their in vivo bioapplications.15–17 Nonstoichiometric copper chalcogenides are a novel class of p-type semiconducting materials with characteristic SPR bands in the NIR spectral region especially in the NIR-II transparent biowindow. Unlike noble metals, their plasmons are supported by the positively charged holes as a result of the Cu vacancy, with a carrier density of 10^{19}–10^{21} cm^{-3} relatively lower than noble metals.18,19 The SPR band of Cu_{2−x}E can be effectively

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tuned by varying the degree of the Cu vacancy. Moreover, the plasmonic properties of Cu$_{2-x}$E can be postsynthetically modulated by chemically doping or electrochemically charging and discharging, a unique feature different from the classical metal plasmonics. Considerable efforts have been made to develop noble metal–semiconductor hybrids that combine the respective merits of their constituents to synergistically enhance their performances in surface-enhanced spectroscopies, biosensing, bioimaging, and cancer photothermal therapy. The interest in such dual-plasmonic hybrids is mainly driven by the electronic interactions that modulate the energy transfer and local plasmonic field. The combination of two entirely different types of plasmonic materials such as noble metals and semiconductors could also yield new unexpected phenomena due to the interaction of two intrinsically dissimilar plasmonic building blocks. Previous studies showed that the plasmonic coupling caused the red-shift of the Au-associated plasmon band and the blue-shift of the Cu$_{2-x}$Se-associated plasmon band in the Au@Cu$_{2-x}$Se core–shell structures with respect to the plasmon bands of Au nanoparticles (AuNPs) and Cu$_{2-x}$Se nanoparticles only. Because of the synergistic interactions, the optical properties of the Au–Cu$_{2-x}$Se hybrids are not simply the sum of those of the Au and Cu$_{2-x}$Se constituents. The influence of the refractive index, plasmonic coupling, charge redistribution, and others could intertwine together to account for the unique plasmonic properties in such a dual-plasmonic Au–Cu$_{2-x}$Se system. A systematic study for the in-depth understanding of the interplay of the Au and the Cu$_{2-x}$E domains in the Au–Cu$_{2-x}$E hybrids becomes greatly crucial but is still lacking.

Here, we developed a selenium-mediated two-step synthetic approach to prepare the dual-plasmonic Au@Cu$_{2-x}$Se nanocrescents with tunable Cu$_{2-x}$Se domain size and NIR surface-enhanced Raman spectroscopy (SERS), photoacoustic imaging, and X-ray computed tomography in a single system for diagnostics, along with photothermal therapy and photodynamic therapy for cancer therapy. However, despite intensive efforts, few reports are dedicated to elucidate the interplay between the free electron- and free hole-based plasmons in the Au and Cu$_{2-x}$Se domains of the Au–Cu$_{2-x}$E hybrids, respectively. Previous studies showed that the plasmonic coupling caused the red-shift of the Au-associated plasmon band and the blue-shift of the Cu$_{2-x}$Se-associated plasmon band in the Au@Cu$_{2-x}$Se core–shell structures with respect to the plasmon bands of Au nanoparticles (AuNPs) and Cu$_{2-x}$Se nanoparticles only. Because of the synergistic interactions, the optical properties of the Au–Cu$_{2-x}$Se hybrids are not simply the sum of those of the Au and Cu$_{2-x}$Se constituents. The influence of the refractive index, plasmonic coupling, charge redistribution, and others could intertwine together to account for the unique plasmonic properties in such a dual-plasmonic Au–Cu$_{2-x}$Se system. A systematic study for the in-depth understanding of the interplay of the Au and the Cu$_{2-x}$E domains in the Au–Cu$_{2-x}$E hybrids becomes greatly crucial but is still lacking.

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plasmonic properties. The Cu$_{2-x}$Se domain size of the nanocrescents was precisely controlled by varying the concentration of the SeO$_2$ precursor. The increasing Cu$_{2-x}$Se domain size is able to modulate the interactions between the Au and Cu$_{2-x}$Se domains in the Au@Cu$_{2-x}$Se nanocrescents and their optical properties accordingly. Unlike previous studies on the Au–Cu$_{2-x}$Se dimers where the interfacial contact area is partial, the complete encapsulation of the Au domain within the Cu$_{2-x}$Se in the present nanocrescent structures enables an intimate contact over a larger surface area without native Au surface exposure and thus excludes the unnecessary interference from the external environment. The asymmetric geometry of the nanocrescents yields the asymmetric electric field distribution along the Au–Cu$_{2-x}$Se interface and the nanocrescent surface, which is responsible for the unique plasmonic properties. We employed the theoretical modeling and transient absorption (TA) measurements to understand the evolution of plasmonic properties of the Au@Cu$_{2-x}$Se nanocrescents with the Cu$_{2-x}$Se domain size and elucidate the physics of the interplay between their Au and Cu$_{2-x}$Se domains. Results show that the electron transfer from the Au domain to the Cu$_{2-x}$Se domain accounts for their strong coupling interactions, modulating the carrier–phonon scattering and phonon–phonon relaxation processes. Our findings unambiguously reveal the underlying physics of the strong coupling of the Au domain with the Cu$_{2-x}$Se domain in the hybrids, and provide a guidance for designing dual-plasmonic metal–semiconductor nanostructures with optimal NIR optical performances.

## RESULTS AND DISCUSSION

Dual-plasmonic Au@Cu$_{2-x}$Se nanocrescents were synthesized by a selenium-mediated two-step process: (i) the direct synthesis of Au@Se nanocrescents and (ii) the subsequent conversion into the Au@Cu$_{2-x}$Se nanocrescents (Figure 1A). First, the hexadecaethyltrimethylammonium chloride (CTAC)-stabilized AuNPs were coated with an amorphous Se layer through the reduction of SeO$_2$ by the ascorbic acid (Vitamin C, Vc) reducing agent, forming the Au@Se nanocrescent structure. The resulting Au@Se nanocrescents then were reacted with Cu$^{2+}$ in an aqueous solution of CTAC and Vc, yielding the Au@Cu$_{2-x}$Se nanocrescent structure.

### Figure 2.
Morphology, size, and compositional distributions of AuNPs, Au@Se nanocrescents, and Au@Cu$_{2-x}$Se nanocrescents. (A) TEM images and size distribution (inset) of (i) AuNPs, (ii) Au@Se nanocrescents, and (iii) Au@Cu$_{2-x}$Se nanocrescents. The size of Au@Se nanocrescents and Au@Cu$_{2-x}$Se nanocrescents is the total size in the largest dimension of the nanoparticles containing the Au and Se or Cu$_{2-x}$Se domains. (B) HRTEM image of a representative Au@Cu$_{2-x}$Se nanocrescent. 1.0 mM SeO$_2$ was used for the synthesis of the Au@Cu$_{2-x}$Se nanocrescents. (C) HAADF-STEM and the corresponding EDX elemental mapping of the Au@Cu$_{2-x}$Se nanocrescent. 2.0 mM SeO$_2$ was used for the synthesis of the Au@Cu$_{2-x}$Se nanocrescents. (D) A schematic model illustrating the three-dimensional structure of the Au@Cu$_{2-x}$Se nanocrescent.
produce the Cu-de reducing agent, and then reacted with the elemental Se to higher refractive index ($\sim 2.70$ at 524 nm after the Se layer coating, which is ascribed to the characteristic SPR peak of the AuNPs red-shifts from 524 to that ($n > 2.70$ at 524–608 nm) of Se than $n < 1$ for Cu$_{2−x}$Se crystals. A blue-shift by 30 nm of Cu$_{2−x}$Se nanocrescents, also reflected by the spectral variation of their extinction spectra (Figure 1B(ii)). The characteristic SPR peak of the AuNPs red-shifts from 524 to 608 nm after the Se layer coating, which is ascribed to the higher refractive index ($n = 2.6$ for Cu$_{2−x}$Se; $n < 1$ for Au at >500 nm), charge redistribution, and plasmonic coupling effects may be responsible for the red-shift of the Au-associated SPR band and the blue-shift of the Cu$_{2−x}$Se-associated SPR band in Au@Cu$_{2−x}$Se nanocrystals with respect to the SPR bands of AuNPs and Cu$_{2−x}$Se nanocrystals (NCs), respectively. The powder XRD result confirms the amorphous form of the Se layer on the AuNP surface (Figure 1C). In the Au@Cu$_{2−x}$Se nanocrystals, characteristic 2θ peaks at 26.7°, 44.6°, 52.9°, and 64.9° all can be indexed to the cubic berzelianite structure of Cu$_{2−x}$Se (JCPDS no. 06-0680 of cubic berzelianite Cu$_{2−x}$Se), while the 2θ peaks at 38.1° and 77.5° are attributed to the cubic Au structure (JCPDS no. 01-1172 of cubic Au). We also synthesized Cu$_{2−x}$Se nanocrystals (33.8 ± 1.9 nm) in the absence of AuNPs, showing the same cubic berzelianite structure as the Au@Cu$_{2−x}$Se nanocrystals (Figures 1C and S3). Thus, the XRD patterns confirm the successful synthesis of highly crystalline Au@Cu$_{2−x}$Se nanocrystals.

The TEM image clearly confirms the coating of the Se layer on the spherical AuNPs, forming the Au@Se nanoparticle structure (Figure 2A). In the nanocrescent structure, the AuNP domain appearing in much darker contrast was completely encapsulated by a lighter Cu$_{2−x}$Se layer because of the different atomic numbers. The conversion of the amorphous Se into crystalline Cu$_{2−x}$Se preserves the initial nanocrescent morphology but causes a slight (~2 nm) increase
Nanocrescents Synthesized with Various SeO2 Concentrations

The HRTEM image of a representative Au@Cu2-Se nanocrescent in Figure 2B unveils the complete encapsulation of the AuNP by a Cu2+ layer of high crystallinity. The lattice fringes with the interplanar spacings of 0.333 and 0.203 nm correspond to the (111) and (200) planes of the Cu2-Se and Au domains, respectively. This is consistent with the XRD results. Both HRTEM and HAADF-STEM images clearly show that the as-prepared Au@Cu2-Se nanocrescents made with the SeO2 concentrations of 0.083, 0.33, 1.00, 1.33, and 2.00 mM, respectively (Figure S4). It is worth pointing out that Cu2-Se nanocrescents made with the SeO2 concentrations of 0.083, 0.33, 1.00, 1.33, and 2.00 mM (Figure 3). It can be clearly seen that all samples have a crescent structure where the AuNP is completely encapsulated by a Cu2-Se layer in an asymmetric manner. Furthermore, the STEM-EDX mapping shows a clear distribution of Cu and Se on the one side of the Au domain even with more addition of the SeO2 precursor, forming the crescent structure. The replacement of the CTAC stabilizer with other stabilizers such as poly(vinylpyrrolidone) and poly(diallyldimethylammonium chloride) produced symmetrical core–shell or isolated nanostructures rather than the crescent-like structure. It is suggested that the shielding effect of CTAC on the deposition of Se atoms is responsible for the formation of Au@Cu2-Se nanocrescents.31 The color of the suspension of the Au@Se nanocrescents gradually evolves from red to dark green with the SeO2 concentration increasing up to 2.00 mM, while the Au@Cu2-Se nanocrescents appear violet to dark green accordingly (Figure S4). The UV–vis–NIR extinction spectra show a gradual red-shift of the SPR band of the Au@Se nanocrescents with the increasing Se domain size (due to the increasing SeO2 concentration), while the extinction intensity undergoes first a steep decrease and then a gradual increase with the increasing Se domain size. The rationale is the relatively large refractive index of Se and the lack of the electronic interactions between the Au and the amorphous Se. There exist two SPR bands corresponding to the Au and Cu2-Se domains for all Au@Cu2-Se nanocrescents; the SPR band corresponding to the Cu2-Se domain is located in the NIR-II region of ca. 990–1050 nm, and the SPR band corresponding to the Au domain is in the visible region of 560–585 nm, red-shifting with respect to that of the AuNPs. The intensity of the NIR SPR band is proportional to the total size of the Cu2-Se domain. We also noted the red-shift of the interband transition-induced absorption onset around 300–500 nm of Cu2-Se in Au@Cu2-Se nanocrescents with the increasing Cu2-Se domain size, probably resulting from the quantum size effects (Figure 3C(ii)). Thus, we confirm that the size of the Au@Cu2-Se nanocrescents can be effectively controlled by the initial concentration of the SeO2 precursor, tuning their plasmonic properties accordingly. The corresponding plasmonic properties of all Au@Cu2-Se nanocrescents along with those of AuNPs and Cu2-Se NCs were listed in Table 1.

We analyzed the elemental composition of all as-synthesized Au@Cu2-Se nanocrescents by ICP-OES, and then derived their “x” values and the molar ratios of the Cu2-Se to Au atom accordingly (N(Cu2-Se):N(Au), equivalent to the Se to Au atomic ratio) (Table 1). It can be seen that the N(Cu2-Se):N(Au) value increases from 0.18 to 3.77 with the increasing SeO2 concentration from 0.083 to 2.00 mM. Results show similar x value of ~0.2 for all Au@Cu2-Se nanocrescents, consistent with the literature.21,42 Furthermore, we determined the molar extinction coefficients (ε(λ)) corresponding to the respective SPR bands of the Au and Cu2-Se domains according to the Lambert–Beer law:43

$$A(\lambda) = \epsilon(\lambda) \cdot l \cdot c$$

where A(λ), l, and c are the optical density at the SPR wavelength (λ), the length of the solution the incident light passes through (1 cm for the standard cuvette), and the concentration of the Au and Cu2-Se domains (mol/L), respectively. The atomic concentrations of Au, Cu, and Se determined by ICP-OES were converted to the particulate concentration of the Au and Cu2-Se domains, whose details were shown in the Supporting Information.43 A dramatic decrease of the molar extinction coefficient of the Au domain-associated SPR band (ε(Au)) is observed after being encapsulated with the Cu2-Se, followed by a monotonic and

<table>
<thead>
<tr>
<th>sample</th>
<th>[SeO2] (mM)</th>
<th>N(Cu2-Se):N(Au)</th>
<th>x value</th>
<th>λmax(Au) (nm)</th>
<th>ε(Au) (×10³)</th>
<th>N, (cm⁻³)</th>
<th>λmax(Cu2-Se) (nm)</th>
<th>ε(Cu₂-₃Se) (×10³)</th>
<th>N, (cm⁻³)</th>
</tr>
</thead>
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<tr>
<td>AuNPs</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
<td>524</td>
<td>8.57 × 10³</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Au@Cu2-Se-1</td>
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<td>0.20</td>
<td>560</td>
<td>2.18 × 10³</td>
<td>1011</td>
<td>8.47 × 10⁷</td>
<td>4.45 × 10¹</td>
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</tr>
<tr>
<td>Au@Cu2-Se-2</td>
<td>0.33</td>
<td>0.71</td>
<td>0.19</td>
<td>571</td>
<td>3.25 × 10³</td>
<td>1002</td>
<td>9.25 × 10⁸</td>
<td>4.37 × 10¹</td>
<td>NA</td>
</tr>
<tr>
<td>Au@Cu2-Se-3</td>
<td>1.00</td>
<td>1.90</td>
<td>0.19</td>
<td>578</td>
<td>3.00 × 10³</td>
<td>996</td>
<td>2.37 × 10⁹</td>
<td>4.30 × 10¹</td>
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<tr>
<td>Au@Cu2-Se-4</td>
<td>1.33</td>
<td>2.42</td>
<td>0.20</td>
<td>579</td>
<td>3.46 × 10³</td>
<td>1025</td>
<td>4.12 × 10⁹</td>
<td>4.05 × 10¹</td>
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<td>Au@Cu2-Se-5</td>
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<td>3.77</td>
<td>0.19</td>
<td>585</td>
<td>3.66 × 10³</td>
<td>1052</td>
<td>6.99 × 10⁹</td>
<td>3.83 × 10¹</td>
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</tr>
<tr>
<td>Cu2-Se NCs</td>
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<td>0.20</td>
<td>NA</td>
<td>NA</td>
<td>1053</td>
<td>1.97 × 10⁹</td>
<td>4.05 × 10¹</td>
<td>NA</td>
</tr>
</tbody>
</table>

aThe N(Cu2-Se):N(Au) ratio is the atomic ratio of the Cu2-Se to Au atoms in the Au@Cu2-Se nanocrescents estimated by ICP-OES. The x value was estimated by ICP-OES. bThe molar extinction coefficients (ε(Au) and ε(Cu₂⁻₃Se)) correspond to the SPR wavelengths λmax(Au) and λmax(Cu₂⁻₃Se) associated with the Au and Cu₂⁻₃Se domains, respectively. NA: Not Available. The molar extinction coefficients (ε(Au) and ε(Cu₂⁻₃Se)) correspond to the SPR wavelengths λmax(Au) and λmax(Cu₂⁻₃Se) associated with the Au and Cu₂⁻₃Se domains, respectively.
their maximal electric field was observed in the Au@Cu$_{2-x}$Se nanocrescents; the maximal electric field corresponding to the visible or NIR SPR band appears at the left side of the Cu$_{2-x}$Se domain, quite different from those of AuNPs and Cu$_{2-x}$Se NCs (Figure 4A,B). A close examination reveals that the electric field is much stronger at the right side of the Au domain of the nanocrescent than that at its left side. On the basis of the average size statistically estimated from the TEM images for all Au@Cu$_{2-x}$Se nanocrescents, we further examined the effect of the Cu$_{2-x}$Se domain size on the electric field (Figures 4C,D, S5, and S6). Both visible and NIR SPR bands gradually red-shift and concomitantly increase in the intensity with the increasing Cu$_{2-x}$Se domain size (Figure 4C). We can clearly see that the maximal electric field intensity at the visible SPR wavelength decreases from the AuNPs to nanocrescents, and then gradually increases with the increasing Cu$_{2-x}$Se domain size; in contrast, all Au@Cu$_{2-x}$Se nanocrescents exhibit the maximal electric field intensity at the NIR SPR wavelength much higher than Cu$_{2-x}$Se NCs alone, indicating the coupling effect that enhances the NIR electric field in the Au@Cu$_{2-x}$Se nanocrescents (Figure 4D).

According to the Drude model, we calculated the free electron ($N_e$) and free hole ($N_h$) densities corresponding to the visible and NIR SPR bands of the nanocrescents, respectively. According to the Drude model, we calculated the free electron ($N_e$) and free hole ($N_h$) densities corresponding to the visible and NIR SPR bands of the nanocrescents, respectively.  

$$
\omega_{sp} = \sqrt{\frac{\omega_p^2}{\varepsilon_\infty + 2\varepsilon_m} - \gamma^2}
$$

where $\omega_{sp}$ and $\gamma$ are the frequency and full-width-at-half-maximum (fwhm) of the SPR bands, respectively; $\varepsilon_\infty$ and $\varepsilon_m$ are the high frequency dielectric constant and the solvent dielectric constant ($\varepsilon_m = n^2 = 1.33^2 = 1.77$ for water here), respectively; $\omega_p$ is the bulk plasma oscillation frequency related to the free electron or hole density. $\gamma$ can be determined by fitting the SPR band to a Gaussian function, and $\omega_{sp}$ can be treated as 7.0 for Cu$_{2-x}$Se at $x = 0.2$ according to the
Thus, we calculated the free carrier density ($N = N_e$ or $N_h$) by the following equation:

$$\alpha_p^2 = \frac{Nq_e^2}{\varepsilon_0 \hbar m^*}$$

where $m^*$ is the charge carrier effective mass ($m^* = m_0$ for a free electron, $m^* = 0.336m_0$ for a free hole, and $m_0$ is the mass of an electron), $q_e$ is the elementary charge ($1.6 \times 10^{-19}$ C), and $\varepsilon_0$ is the free space permittivity. From eq 3, the $N_e$ value in the Au domain was estimated to be in the range of $(1.50−1.68) \times 10^{22}$ cm$^{-3}$, and the $N_h$ value in the Cu$_{2-x}$Se domain is in the range of $(3.83−4.45) \times 10^{21}$ cm$^{-3}$; both $N_e$ and $N_h$ decrease with the increase of the Cu$_{2-x}$Se:Au molar ratio from 0.18 to 3.77 (Table 1). The $N_e$ value of all Au@Cu$_{2-x}$Se nanocrescents is slightly lower than $1.87 \times 10^{22}$ cm$^{-3}$ of the AuNPs, but their $N_h$ values are much higher than $4.05 \times 10^{21}$ cm$^{-3}$ of the Cu$_{2-x}$Se NCs except the nanocrescent of the Cu$_{2-x}$Se:Au molar ratio of 3.77. The present Au@Cu$_{2-x}$Se nanocrescents were made with the fixed Au domain size and the varied Cu$_{2-x}$Se domain size. The "x" value representing the degree of Cu deficiency in Cu$_{2-x}$Se nanoparticles is proportional to the free hole density; previous studies showed the insensitivity of the SPR wavelength of Cu$_{2-x}$Se nanoparticles to the particulate size. As shown in Table 1, all Au@Cu$_{2-x}$Se nanocrescents possess the similar "x" value of 0.2, which cannot explain the different free hole densities among these nanocrescents. We attribute the different hole densities to the interplay between the Au domain and the Cu$_{2-x}$Se domain due to the varied Cu$_{2-x}$Se domain size.

TA spectra have been widely used to study the carrier dynamics, and the carrier–phonon and phonon–phonon interactions in plasmonic noble metals, but few efforts have been devoted to examine the dynamics of charge carriers in the Au–Cu$_{2-x}$Se hybrid system. Here, we performed TA studies to gain insights into the carrier dynamics in the Au@Cu$_{2-x}$Se nanocrescents pumped with a 100 fs pulse laser at 380 and 800 nm, respectively (Figure 5). Because the threshold energy of
the interband transition in AuNPs is \( \sim 2.4 \) eV (\( \sim 520 \) nm), the pulse laser of 380 nm is able to trigger its interband transition from 5d-band to the hybridized 6sp-band, resulting in a transient increase in both hole density in the 5d-band and electron density in the 6sp-band.\(^{17}\) With the excitation of 380 nm-pulse laser, the TA spectra of AuNPs exhibit a negative bleaching band at \( \sim 528 \) nm and two positive absorption bands centered at 480 and 565 nm, respectively (Figure 5A). The negative TA signal is due to the “bleaching” of the intrinsic Au SPR band; the positive TA signals at 480 and 565 nm are due to the thermal broadening of the SPR band resulting from an increase in the electronic temperature induced by the pulse laser excitation.\(^{18}\) The TA spectra of Cu\(_{2-x}\)Se NCs show a broad negative band located in the NIR (900–1100 nm) region originating from the bleaching of the intrinsic NIR SPR of Cu\(_{2-x}\)Se NCs observable under the 380 nm- or 800 nm-pulse laser. Previous studies suggested that, with the excitation of the pulse laser, Cu\(_{2-x}\)Se NCs followed bleaching behaviors of plasmonic electrons similar to those in noble metal (Au and Ag) nanoparticles.\(^{21}\) Time-resolved TA spectra show the gradual decrease of the TA signals of the intrinsic SPRs of AuNPs and Cu\(_{2-x}\)Se NCs for both 380 nm- and 800 nm-pulse lasers (Figure 5A,B). In addition, we found that the intrinsic TA signal of Cu\(_{2-x}\)Se NCs under the 800 nm-pulse laser was much lower than that under the 380 nm-pulse laser, indicating the much additional contribution from the resonant excitation with the 380 nm-pulse laser. Similarly, both positive and negative TA bands of the Au domain of the Au@Cu\(_{2-x}\)Se nanocrescent with the Cu\(_{2-x}\)Se:Au molar ratio of 0.71 weaken over delay time as well, but their TA signals are much weaker than those of AuNPs (Figure 5C). In addition, we surprisingly found that the intrinsic TA signal of its Cu\(_{2-x}\)Se domain was much stronger in the Au@Cu\(_{2-x}\)Se nanocrescents than that in Cu\(_{2-x}\)Se NCs under both 380 and 800 nm pulse lasers. This indicates the enhanced NIR optical absorption due to the electronic interplay between the plasmonic Au and Cu\(_{2-x}\)Se domains of the Au@Cu\(_{2-x}\)Se nanocrescent.

We further examined the bleaching dynamics of the intrinsic TA signals of Au@Cu\(_{2-x}\)Se nanocrescents of different Cu\(_{2-x}\)Se:Au molar ratios (Figure 6A,B). The excitation with the pulse laser creates a nonthermal distribution of charge carriers (electrons in the Au domain and holes in the Cu\(_{2-x}\)Se domain) and accordingly causes an increase in the carrier temperature, producing a thermalized electron gas (hot electrons) with higher temperature than the lattices.\(^{21,92,90}\) The newly generated distribution of carriers can be reached on a time scale of subpicosecond via strong carrier–carrier scattering, followed by the bleaching of the SPR bands through fast carrier–phonon coupling within few picoseconds and slow phonon–phonon coupling within a few hundred picoseconds. It can be seen that the bleaching amplitude of the intrinsic TA signal of the Au domain exponentially decreases with the increase of the Cu\(_{2-x}\)Se:Au molar ratio under the excitation of 380 nm-pulse laser, while the bleaching amplitude of the intrinsic TA signal of the Cu\(_{2-x}\)Se domain linearly increases with the increasing Cu\(_{2-x}\)Se:Au molar ratio under both 380 nm- and 800 nm-pulse lasers, except for the Au@Cu\(_{2-x}\)Se nanocrescent with the Cu\(_{2-x}\)Se:Au molar ratio of 0.18.
due to the low loading (accordingly too weak NIR SPR absorption) of Cu$_{2-}$Se (Figure 6B(i)). It is worth noting that the bleaching amplitude of the TA signal of the Cu$_{2-}$Se SPR in the nanocrescents is much larger than the Cu$_{2-}$Se NCs over the Cu$_{2-}$Se:Au molar ratio range of 0.71–3.77 regardless of the excitation of the 380 nm- or 800 nm-pulse laser. These results suggest the decreasing electron density in the Au domain due to the transfer of electrons from the Au domain to the Cu$_{2-}$Se domain; the increasing size of the Cu$_{2-}$Se domain could increase the NIR absorption cross-section and thus compensate the neutralization effect of electron transfer to the hole-rich Cu$_{2-}$Se domain, leading to an increase in the bleaching amplitude with the increasing Cu$_{2-}$Se:Au molar ratio.

Furthermore, we found that the dynamic TA signal of the intrinsic SPR of Au followed a monoexponential decay over time, while the dynamic TA signal of the intrinsic SPR of Cu$_{2-}$Se showed a biexponential decay process (Figure 6A). Thus, the fast carrier–phonon scattering time constant ($\tau_{c-ph}$) and the slow phonon–phonon relaxation time constant ($\tau_{ph-ph}$) of Au@Cu$_{2-}$Se nanocrescents can be extracted from the function as follows: \(^{46,51}\)

$$f(t) = A_1 \exp(-t/\tau_{c-ph}) + A_2 \exp(-t/\tau_{ph-ph}) + A_0$$

where the first term corresponds to the carrier–phonon scattering process, and the second term and the constant term ($A_0$) represent the phonon–phonon relaxation process; $A_1$ and $A_2$ are the corresponding constant coefficients for the first and second terms, respectively. The fitting of the dynamic TA curve was performed in the range from the delay time with the SPR bleaching maximum to the delay time when the TA signal is almost constant over time. The electron–phonon scattering time constant ($\tau_{c-ph}$) and hole–phonon scattering time constant ($\tau_{ph-ph}$) can be obtained from the dynamic curves of the TA signals of Au and Cu$_{2-}$Se, respectively. Because Cu$_{2-}$Se has a carrier behavior similar to that of noble metals,\(^{11,46}\) we assume that the relaxation processes of excited carriers in Cu$_{2-}$Se have the same physical origin as those of noble metals. Thus, we can achieve two time-constants from the fitting results and assign the small and large time-constants as the $\tau_{c-ph}$ and $\tau_{ph-ph}$, respectively. The monoexponential decay of the TA signal of the Au SPR indicates the constant phonon–phonon relaxation time constant involved in the constant term ($A_0$).\(^{51}\) Results show that the $\tau_{c-ph}$ value exponentially decreases with the increasing Cu$_{2-}$Se:Au molar ratio, and becomes almost constant when the Cu$_{2-}$Se:Au molar ratio exceeds 0.71; the $\tau_{ph-ph}$ value that varies insignificantly with the Cu$_{2-}$Se:Au molar ratio is much larger under the 380 nm-pulse laser than that under the 800 nm-pulse laser over the Cu$_{2-}$Se:Au ratio range of 0.71–3.77. In addition, the hole–phonon relaxation of the Cu$_{2-}$Se SPR in the nanocrescents is much faster than Cu$_{2-}$Se NCs over the Cu$_{2-}$Se:Au molar ratio range of 0.71–3.77 under both 380 nm- and 800 nm-pulse lasers. The $\tau_{ph-ph}$ value linearly increases with the increase of the Cu$_{2-}$Se:Au molar ratio over the range investigated for both 380 nm- and 800 nm-pulse lasers. The $\tau_{ph-ph}$ value of Cu$_{2-}$Se NCs is much larger than those of the nanocrescents with the Cu$_{2-}$Se:Au molar ratio of 0.71 and 1.96, but smaller than that of the nanocrescents with the Cu$_{2-}$Se:Au molar ratio of 3.77, regardless of the 380 nm- or 800 nm-pulse laser. Unfortunately, we were unable to obtain the $\tau_{c-ph}$ and $\tau_{ph-ph}$ values for Au@Cu$_{2-}$Se nanocrescents of a Cu$_{2-}$Se:Au molar ratio of less than 0.71 because of the low TA signal of the intrinsic SPR of Cu$_{2-}$Se. It is worth noting that both bleaching amplitude and $\tau_{c-ph}$ of the Au SPR follow the similar change trend with the Cu$_{2-}$Se:Au molar ratio. The rationale is that the electron transfer from the Au domain to the Cu$_{2-}$Se domain decreases electron density and thus accelerates the electron–phonon relaxation in the Au domain. Similarly, both the bleaching amplitude of the Cu$_{2-}$Se SPR and the phonon–phonon relaxation time-constant increase with the Cu$_{2-}$Se:Au molar ratio. The electron transfer from the Au domain to the Cu$_{2-}$Se domain decreases the hole density in the Cu$_{2-}$Se domain, but the increasing Cu$_{2-}$Se domain size results in the increase of the extinction cross-section of the NIR SPR band, which slows the phonon–phonon relaxation process.

On the basis of the aforementioned analysis, we propose a possible mechanism that elucidates the interactions between the Au and Cu$_{2-}$Se domains of the Au@Cu$_{2-}$Se nanocrescents, schematically illustrated in Figure 6C. Both interband transition and SPR excitation would induce the generation of hot electrons, which could subsequently transfer from the Au domain to the Cu$_{2-}$Se domain. The increasing Cu$_{2-}$Se domain size enhances the extraction of hot electrons from the Au domain, which decreases the electron density in the Au domain. Despite the charge neutralization in the Cu$_{2-}$Se domain, the increasing Cu$_{2-}$Se size causes the increase of the NIR extinction cross-section and thereby increases the bleaching amplitude of the TA signal of the intrinsic SPR of Cu$_{2-}$Se. The hot electrons and holes transfer to the surrounding lattices through the electron–phonon and hole–phonon interactions, which enhance the phonon–phonon relaxation process, and weaken both the electron–phonon scattering in the Au domain and the hole–phonon scattering in the Cu$_{2-}$Se domain of the nanocrescents. Therefore, this work presents new physical insights into the coupling interactions existing in the Au@Cu$_{2-}$Se nanocrescents, and thereby an in-depth understanding of their optical properties, benefitting the design of Au–Cu$_{2-}$Se hybrids of optimal optical properties for a diversity of plasmon-based applications.

**CONCLUSIONS**

In summary, a selenium-mediated two-step synthetic approach has been developed to prepare high-quality dual-plasmonic Au@Cu$_{2-}$Se nanocrescents, which allows tuning the Cu$_{2-}$Se domain size and the plasmonic properties in the NIR-II region by changing the concentration of the SeO$_2$ precursor. Cu$_{2-}$Se grows unidirectionally on the Au core with more addition of the SeO$_2$ precursor, forming the asymmetric crescent structure responsible for the unique plasmonic properties of Au@Cu$_{2-}$Se nanocrescents. The Au@Cu$_{2-}$Se nanocrescents exhibit two characteristic SPR bands positioned at the visible and NIR-II regions that originate from the collective oscillation of free electrons and free holes in the Au and Cu$_{2-}$Se domains of the nanocrescents, respectively. With the increasing Cu$_{2-}$Se domain size, the NIR SPR band of the Cu$_{2-}$Se domain becomes more intense with a slight red-shift. The theoretical modeling shows the asymmetric electric field distributions arising from the asymmetric structure of the nanocrescents. Both experimental results and theoretical calculation confirm the strong coupling between the Au and Cu$_{2-}$Se domains of the nanocrescents, accounting for their enhanced optical...
properties with respect to AuNPs and Cu$_2$−Se NCS. TA measurements suggest the Cu$_2$−Se domain size-dependent bleaching amplitude and carrier dynamics of the intrinsic SPRs corresponding to the Au and Cu$_2$−Se domains with variations of the carrier–phonon and phonon–phonon coupling interactions. A coupling mechanism between the Au and Cu$_2$−Se domains of the nanocrescents is proposed to explain the Cu$_2$−Se-dependent plasmonic properties. This work presents not only a synthetic method for the high-quality dual-plasmonic Au@Cu$_2$−Se nanocrescents but also generates new physical insights into the interplay between their Au and Cu$_2$−Se domains. We foresee a huge potential of this type of dual-plasmonic hybrids for NIR-II plasmonic applications in photovoltaics, photocatalysis, and biomedicine.

**MATERIALS AND METHODS**

**Chemicals and Materials.** All chemicals and solvents were of analytical grade and used as received unless otherwise specified. Sodium borohydride (NaBH$_4$, >98%), copper(II) sulfate pentahydrate (CuSO$_4$·5H$_2$O, ≥99%), ascorbic acid (VC, ≥99%), and sodium dichromate (Na$_2$Cr$_2$O$_7$·2H$_2$O, ≥99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Chloroauric acid (HAuCl$_4$·4H$_2$O, 99% trace metals basis) was ordered from Shanghai Civi Chemical Technology Co., Ltd. Hexadecyltrimethylammonium chloride (CTAC, 97%) was purchased from Aladdin Chemistry Co., Ltd. Gold standard solution (1000 μg/mL) containing 1.5 M HCl, copper standard solution (1000 μg/mL) containing 1.0 M HNO$_3$, and sodium standard solution (1000 μg/mL) containing 2.0 M HNO$_3$ were obtained from Guobiao (Beijing) Testing and Certification Co., Ltd. Ultrapure water with a resistivity of 18.2 Ω cm (at 25 °C) was produced with a Millipore Direct-Q3 UV system (Molshein, France) and used in the entire experiment. All glassware used in this work was cleaned with aqua regia, rinsed thoroughly with ultrapure water, and then air-dried prior to use throughout all experiments.

**Synthesis of Au Nanoparticles (AuNPs).** The spherical AuNPs were synthesized according to the well-established protocol described in the literature.$^5$ First, 0.3 mL of 10 mM ice-cold NaBH$_4$ aqueous solution was added to a solution containing 2.5 mL of 0.15 M CTAC solution and 0.025 mL of 50 mM HAuCl$_4$. After being vigorously stirred for 2 min, the solution was kept still at room temperature for 1 h, producing the Au seed solution. Next, 3.2 mL of 0.2 M CTAC solution was mixed with 0.8 mL of 10 mM HAuCl$_4$ solution at room temperature, followed by successive addition of 35 mL of ultrapure water and 3.8 mL of 0.1 M VC solution under gentle stirring, producing the growth solution. Ten microliters of the Au seed solution was added to the growth solution at room temperature. After being vigorously shaken for 1 min, the reaction solution was aged at 30 °C for at least 8 h. Finally, the reaction solution was centrifuged at 7500 rpm, and the pellet was the AuNP products with an optical extinction peak of 524 nm, which were dispersed in ultrapure water with a final concentration of 2.0 nM for further use.

**Synthesis of Cu$_2$−Se Nanocrystals.** 200 μL of 0.1 M VC aqueous solution was added into 3 mL of 20 mM CTAC aqueous solution followed by the addition of 1.5 mL of SeO$_2$ with a final concentration of 2.44 mM. After being stirred for 10 min, a freshly prepared mixture consisting of 80 μL of 0.2 M CuSO$_4$·5H$_2$O and 0.4 mL of 0.1 M VC aqueous solution was added under vigorous stirring. The reaction was allowed to continue until a dark green solution was observed, indicating the formation of Cu$_2$−Se NCS.

**Synthesis of Au@Cu$_2$−Se Nanocrescents.** Two milliliters of the 20 mM CTAC aqueous solution was added to 1 mL of 2.0 nM AuNP suspension under vigorous stirring at 30 °C. Next, 200 μL of 0.1 M VC aqueous solution was added, followed by the addition of a given amount of SeO$_2$ aqueous solution to get a final SeO$_2$ concentration of 0.083, 0.33, 1.00, 1.33, or 2.00 mM. After being stirred for 10 min, a solution containing 30 μL of 0.2 M CuSO$_4$·5H$_2$O and 0.4 mL of 0.1 M VC aqueous solution was added. The mixture was allowed to react under vigorous stirring at room temperature for overnight. The resulting products were purified by successive centrifugation and washing, and then redispersed in 1 mL of ultrapure water for further use.

**Characterization and Instrumentation.** Transmission electron microscopy (TEM) images were taken using an FEI Tecnai G2 F20 transmission electron microscope (FEI, U.S.) operating at 200 kV; high-resolution TEM (HRTEM) images, high-angle annular dark-field scanning TEM (HAADF-STEM) images, and energy dispersive X-ray (EDX) elemental mapping were obtained on an FEI Titan G2 80-200 transmission electron microscope equipped with a spherical aberration corrector, allowing it to reach a spatial resolution of ~0.7 Å at 300 kV. The geometric parameters of all samples were measured from the TEM data using the ImageJ analysis software. At least 100 nanoparticles were counted for each type of sample, and Gaussian fitting was carried out to obtain the average size of nanoparticles. UV–vis−NIR extinction spectra were measured in the wavelength range from 175 to 330 nm using a Cary 5000 UV–vis−NIR spectrophotometer (Agilent Technology, U.S.). The crystal structures were determined by a SmartLab3 kW X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5406 Å) operating at 40 kV and 30 mA. The elemental composition of samples was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on an Agilent 7500 inductively coupled plasma–optical emission spectrometer (Agilent Technologies, U.S.). Samples for the ICP-OES measurements were digested in concentrated nitric acid, followed by dilution with ultrapure water.

**Transient Absorption Measurements.** The TA measurements were performed at room temperature on the ExciPro femtosecond pump–probe system (CDP Systems Corp.), equipped with a regeneratively amplified Ti:sapphire ultrastar laser system for the excitation (Coherent Astrella).$^{55}$ The incident pump pulses with the wavelength of 380/800 nm and pulse width of 100 fs were generated by an ultrastar optical parametric amplifier (Coherent Opera Solo). The probe beams were produced from a thin CaF$_2$ plate, which were focused into a fiber-coupled multichannel spectrometer with complementary metal oxide semiconductor sensors at a frequency of 1 kHz. The power of the pump pulses was adjustable with a series of neutral density filter wheels. The delay between the pump and probe pulses was controlled by a motorized delay stage. The TA spectra and dynamic data were collected over a broad spectral range in a transmission mode with a 0.3 mW pump power and a ~300 μm focused spot size of pumping beam on the aqueous suspension of samples, which were placed in a 10 mm-thick quartz cuvette. The concentration of the samples was controlled to have the same power density for the excitation, which allows for the comparison of the bleaching amplitude between samples.

**Theoretical Modeling of the Plasmonic Properties.** Both extinction spectra and electric field distribution were calculated by the Finite-Difference Time-Domain (FDTD) method using the commercial software Lumerical FDTD Solutions 8.19.1584 (Lumerical Solutions, Inc., Canada). For the simplicity of Au@Cu$_2$−Se nanocrescents, we modeled an AuNP core with a sphere of 25 nm in diameter, conformally coated with a 2 nm-thick Cu$_2$−Se layer and then deposited with an additional asymmetric Cu$_2$−Se shell of various sizes, schematically shown in Figure S2. The dimensional parameters of the Au and Cu$_2$−Se domains were statistically measured from the TEM data and used for the model creation. The dielectric function of Au was taken from the measured data by Johnson and Christy,$^{55}$ while the dielectric function ($\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$) of Cu$_2$−Se with various Cu$_2$−Se domain sizes was calculated by the Drude model:

$$\varepsilon_1 = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

$$\varepsilon_2 = \frac{\omega_p \gamma}{\omega^2 + \omega_p^2}$$

where $\varepsilon_\infty$ is the high frequency dielectric permittivity, and $\omega_p$ and $\gamma$ are the plasma frequency of free carriers of the nanoparticles and the...
free carrier damping, respectively. The background dielectric constant \( \varepsilon_{\text{bg}} \) is due to the presence of interband transitions at higher photon energy, for example, \( \varepsilon_{\text{bg}} = 1 \) for Au, \( \varepsilon_{\text{bg}} = 7 \) for \( \text{Cu}_2x\text{Se} \) at \( x \approx 0.2 \).

The background refractive index of the surrounding medium (water) was set to be 1.33. A total-field scattered-field was employed as the incident source for calculations of both electric field distribution and extinction spectra in the wavelength range from 400 to 2000 nm. The mesh size of the box containing a geometric structure was set as 0.25 nm. The calculated extinction cross-section \( (\sigma_{\text{ext}}) \) from the FDTD simulations was converted to the theoretical molar extinction coefficients \( (\varepsilon_{\text{theory}}) \) by the following equation:

\[
\varepsilon_{\text{theory}} = \frac{N_A}{2.3 \times 10^3} \sigma_{\text{ext}} \left( \text{M}^{-1} \text{cm}^{-1} \right) \tag{7}
\]

\( N_A \) is Avogadro’s number.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b04100.

Calculation of the concentration of the particulate size of nanoparticles, unit cell structures of cubic Au and cubic berzelianite \( \text{Cu}_2x\text{Se} \), crystallographic parameters of the unit cells of cubic Au and cubic berzelianite \( \text{Cu}_2x\text{Se} \), schematic of the model of the \( \text{Au@Cu}_2x\text{Se} \) nanocrystals for the FDTD simulations, TEM image and size distribution of as-synthesized \( \text{Cu}_2x\text{Se} \) NCSs, size distribution of \( \text{Au@Cu}_2x\text{Se} \) nanocrystals, and \( \text{Cu}_2x\text{Se} \) domain size-dependent electric field \( (\log(E_f^3)/E_f^3) \) distributions at the calculated SPR wavelengths corresponding to the Au and \( \text{Cu}_2x\text{Se} \) domains (PDF)

**AUTHOR INFORMATION**

*Corresponding Authors*

E-mail: liming0823@gmail.com, liming0823@csu.edu.cn.

E-mail: chenr@sustech.edu.cn.

**ORCID**

Rui Chen: 0000-0002-0445-7847

Ming Li: 0000-0002-2289-0222

**Notes**

The authors declare no competing financial interest.

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