

Selective Ultrafast Excitation and Dephasing of Gap Plasmons into Hot Carriers in Structural Color Generation

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Cite This: <https://doi.org/10.1021/acsnano.6c12999>



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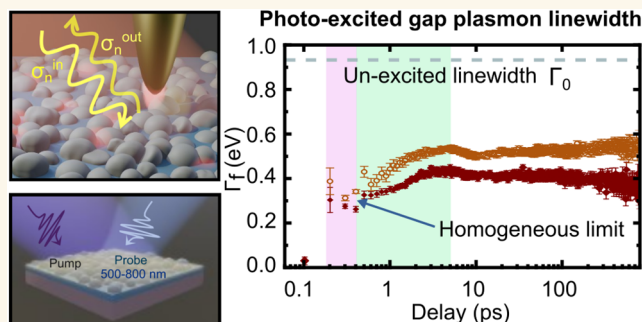
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ABSTRACT: Plasmon-induced hot-carriers generated through Landau damping underpin applications in plasmonic optoelectronics, energy conversion, and photocatalysis. However, it remains unclear whether these carriers retain the spatial localization of their parent plasmon modes or rapidly lose this spatial memory through ultrafast scattering and transport. Here, we experimentally probe the spatial and temporal dynamics of plasmon-induced hot-carriers in a strongly confined plasmonic structural color consisting of disordered aluminum nanoparticle ensembles on near-field cavities. Strong interparticle coupling produces hybridized and localized gap plasmon modes with intense nanoscale electromagnetic confinement, which we directly visualize using scattering-type scanning near-field optical microscopy. Ultrafast pump–probe measurements selectively excite a homogeneously broadened sub-ensemble of plasmonic modes, enabling indirect tracking of pump-generated, plasmon-induced hot-carrier dynamics. We observe that hot-carriers undergo only partial spatial delocalization and retain signatures of the initial plasmonic localization for hundreds of picoseconds. The perturbed sub-ensemble reaches maximum line widths of 0.54 ± 0.06 eV (0.36 ± 0.05 eV) under 630 nm (700 nm) excitation. On a phenomenological localization scale from 0 (localized) to 1 (fully delocalized), this corresponds to 0.35 ± 0.10 and 0.09 ± 0.08 for 630 and 700 nm excitation, respectively. The wavelength-dependent fraction shows that the degree of preserved localization is optically tunable, set by the carrier energy. This persistence of spatial memory, likely arising from disorder-induced scattering within the nanoparticle ensemble, reveals an unexpected spatial dimension of hot-carrier dynamics and highlights the role of plasmonic confinement and structural disorder in governing nanoscale energy flow, with implications for hot-carrier-based optoelectronics.

KEYWORDS: Near-field imaging, hot-carrier dynamics, spatial memory, plasmonic localization, structural colors, ultrafast spectroscopy



INTRODUCTION

The non-radiative decay of surface plasmons generates energetic, non-equilibrium charge carriers through Landau damping, wherein the collective oscillation of conduction electrons transfers its energy to individual electron–hole pair excitations in the material. These plasmon-induced hot carriers have attracted significant attention in optoelectronics due to their potential applications in light-to-energy conversion¹ and photocatalysis.² Following plasmon excitation, the generated hot carriers undergo a sequence of ultrafast relaxation and transport processes through which their excess energy is gradually dissipated into the lattice and the surrounding environment. First, hot carriers undergo rapid carrier–carrier scattering (10s fs to 100 fs), followed by electron–phonon

interactions (few ps) that transfer energy to the lattice and lead to a progressive reduction in carrier temperature on the picosecond time scale.³ Concurrently, hot carriers can undergo spatial transport, including ballistic and diffusive motion, resulting in the redistribution of carriers from the generation region toward neighboring areas with lower carrier temperatures.^{4,5}

Received: July 8, 2026

Revised: September 23, 2026

Accepted: September 24, 2026

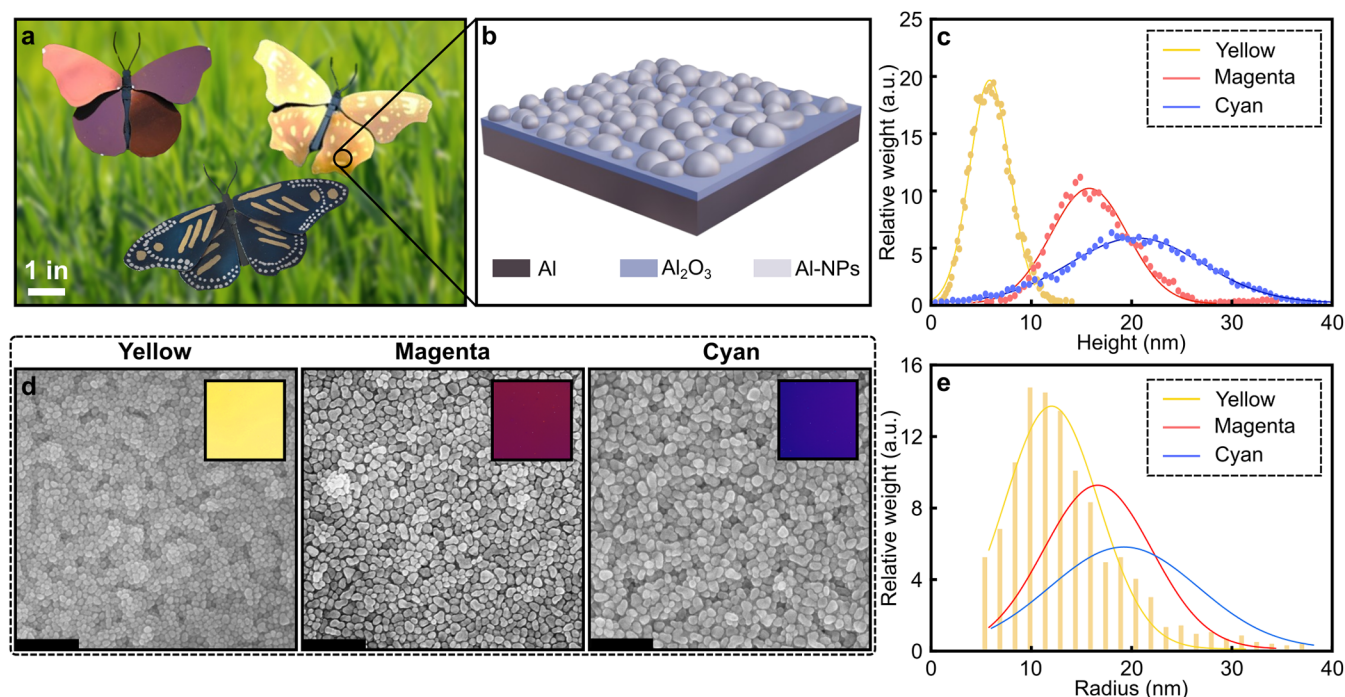


Figure 1. Manifestation of gap-plasmons in disordered metal nanoparticles in macro-regime: structural colors (a) Representative colors formed by gap-plasmon dispersion on large area samples (butterflies). (b) Schematic illustration of the nanostructure consisting of an aluminum mirror, Al₂O₃ spacer, and Al-NPs on the surface. (c) Relative weight of heights for yellow, red, and cyan colored NPs. (d) Scanning electron microscopy for yellow, red, and cyan colored NPs. The scale bar is 100 nm. (e) Probability distribution (relative weight) of radii for yellow, magenta, and cyan NPs.

A central question in hot-carrier research concerns the spatial characteristics of carrier generation and transport. It is assumed that hot carriers are generated locally at plasmonic hot spots, such that the generation rate scales with the local electromagnetic field intensity, $G(r) \propto |E(r)|^2$.⁶ However, ultrafast scattering processes can rapidly redistribute carriers in both energy and momentum space. Consequently, whether the generated carriers retain the spatial localization of the plasmonic excitation, the spatial memory depends sensitively on carrier energy, relaxation time scales, and nanostructure geometry. For efficient device operation, hot carriers must be extracted before their excess kinetic energy is dissipated to the lattice through electron–phonon interactions. While minimizing lattice thermalization is therefore desirable, hot carrier diffusion can have contrasting implications depending on the target application. In hot-carrier photodetectors and photovoltaic devices, carrier diffusion toward interfaces can facilitate efficient extraction.⁴ In contrast, for nanoscale photocatalysis, strong spatial localization of carriers near plasmonic hot spots is often advantageous because it enhances charge transfer to adsorbed molecules.^{2,7} Despite extensive investigations of hot-carrier dynamics, the spatial evolution of plasmon-induced carriers remains relatively poorly understood. Most previous studies have primarily focused on temporal dynamics, providing essentially one-dimensional descriptions of hot-carrier relaxation. Consequently, the impact of plasmonic spatial confinement – specifically whether the generated hot carriers preserve the spatial localization of the excitation – remains an open question. A notable experimental effort by Cortés and co-workers introduced a spatially resolved chemical probing technique that revealed reaction products localized near plasmonic hot spots, suggesting localized hot-carrier activity.² However, this approach lacks ultrafast temporal

resolution and therefore reflects the equilibrated spatial distribution after carrier transport and relaxation, rather than directly probing the initial dynamics of hot-carrier generation.

In this work, we investigate the spatial and temporal dynamics of plasmon-induced hot carriers in a strongly localized plasmonic system to address the unresolved question of whether hot carriers retain the spatial memory of their parent plasmon modes. Such a study requires a platform that supports extreme electromagnetic confinement. Recently, we demonstrated that ensembles of aluminum nanoparticles (Al-NPs) assembled on engineered near-field cavities exhibit strong in-plane coupling between neighboring particles.⁸ This interaction leads to hybridization of localized surface plasmon resonances and the formation of intense electromagnetic fields within nanoscale interparticle gaps, producing localized gap plasmon (LGP) modes. The resulting strong light–matter interaction gives rise to vivid structural colors that are largely independent of viewing angle and polarization. This lithography-free self-assembly approach enables ultralight, pigment-free coloration, including one of the lightest structural color coatings reported to date. Using scattering-type scanning near-field optical microscopy (s-SNOM), we directly resolve strongly localized and randomly oriented electric-field hot spots confined within tens of nanometers. Although the structural coloration system consists of an inhomogeneously broadened ensemble of nanoparticles due to size polydispersity, resonant ultrafast excitation with a spectral bandwidth of ~ 20 nm (~ 0.1 eV) induces spectral hole burning, selectively addressing a homogeneously broadened sub-ensemble (line width ~ 0.3 eV) within the broader (~ 1 eV) distribution of LGP resonances. By monitoring the temporal evolution of the spectral hole in a pump–probe configuration, we indirectly probe the dynamics of plasmon-induced hot carriers within

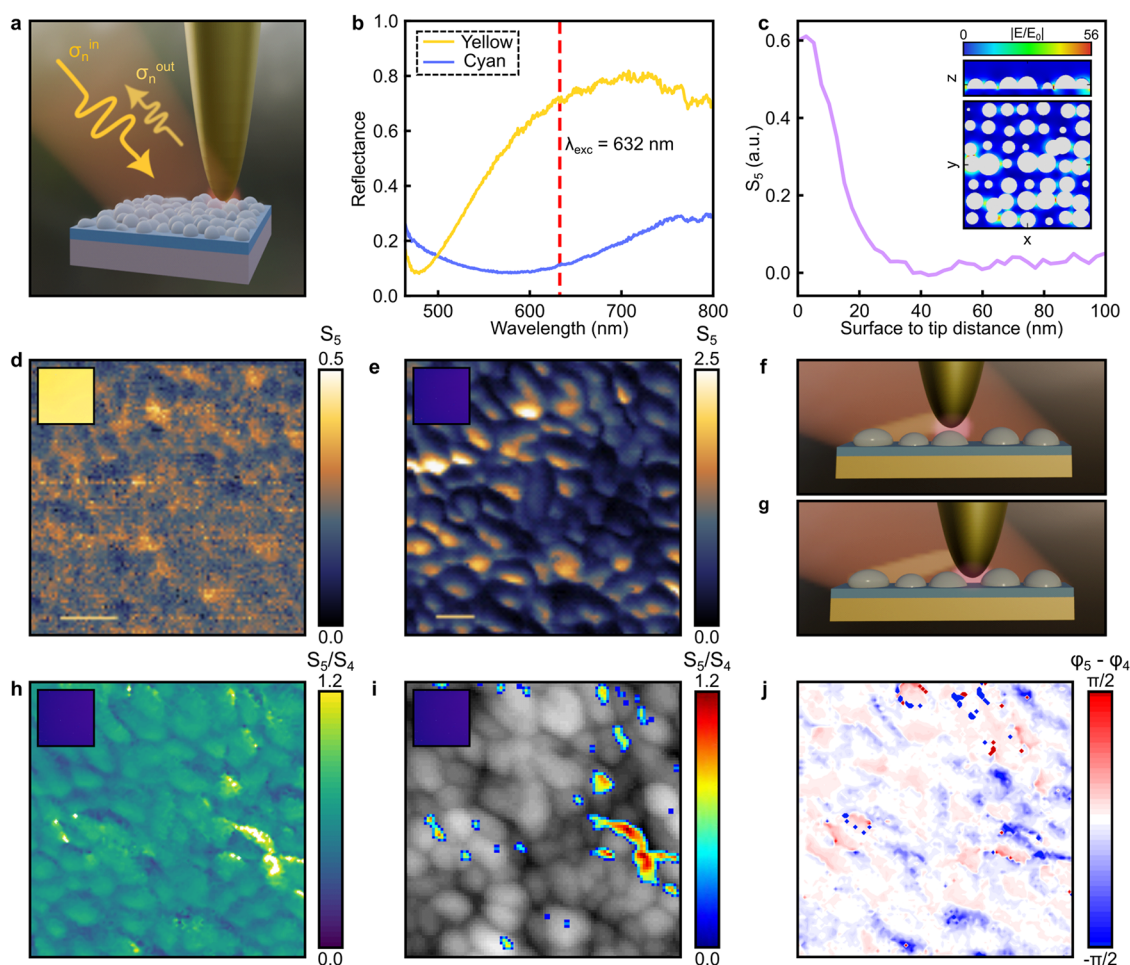


Figure 2. Microscopic view of the gap-plasmons: s-SNOM measurements. (a) Schematic illustration of s-SNOM setup. (b) Reflective spectrum of yellow and blue NPs. (c) 5th order scattered optical field amplitude S_5 from s-SNOM measurement with respect to surface to tip distance. The exponential decay of S_5 indicates a good far-field background subtraction, as the far-field signal variation is near-linear, rather than exponential. The remaining near-field background will be subtracted via postprocessing in Figure 2h, i and j. (d) S_5 of s-SNOM measurement for (d) yellow and (e) cyan NPs. (f) and (g) illustrates the near-field background signal contributed by the scattering from the neighboring NPs. (h) Ratio between the 5th and 4th order amplitude S_5/S_4 which further subtracts the near-field background signal. Gap plasmons are highlighted with brighter intensities. (i) Overlay of the gap plasmons with the AFM height profile. LGPs can be observed as brighter intensities. (j) phase contrast between the 5th and 4th order optical field further shows the localized gap plasmons between NPs.

this highly localized plasmonic landscape. Our measurements reveal that hot carriers undergo only partial spatial delocalization on picosecond time scales and retain signatures of the initial plasmonic localization for hundreds of picoseconds. This behavior contrasts with the commonly expected rapid carrier diffusion following hot-carrier generation. We attribute this persistence to the tunneling-limited connectivity of the disordered nanoparticle network: because the transmission across the interparticle gaps falls exponentially with gap width, the well-coupled gaps form a connected sub-network of finite extent, and hot carriers are confined within it rather than merely slowed. These results demonstrate that plasmon-induced hot carriers can partially preserve the spatial localization of their parent plasmon modes. Notably, the degree of preservation is itself tunable: excitation at 700 nm yields a smaller accessible mode fraction than at 630 nm, indicating that the reach of the hot carriers can be controlled optically as well as structurally. More broadly, our findings uncover an unexpected spatial dimension of hot-carrier dynamics and highlight the interplay between plasmonic confinement and structural disorder in controlling nanoscale

energy flow, with implications for plasmon-driven photochemistry and energy-conversion processes.

RESULTS AND DISCUSSION

Sample Geometry

The strong light-matter interactions in the near-field cavity-coupled Al nanoparticles manifest as vibrant colors. Figure 1a presents a macro-scale example of the structural color coatings applied to flexible substrates shaped like butterfly wings. The structural color assembly consists of a thin layer of self-assembled Al-NPs, deposited via electron-beam (e-beam) evaporation, on a thin (10 nm) dielectric aluminum dioxide (Al_2O_3) spacer layer, which is supported on top of an aluminum reflector, as schematically illustrated in Figure 1b. The detailed sample fabrication process is provided in the Methods section. The dimensions of the Al-NPs, and in turn the generated color, can be adjusted based on the deposition parameters, reported in earlier works.^{8,9} Numerical simulations suggest that when ambient light illuminates the surface, the random orientation and proximity of the nanoparticles above

the tunneling limit allow in-plane mode hybridization due to the capacitive coupling of neighboring nanoparticles.¹⁰ In addition to such planar coupling, the nanoparticles on a mirror with a spacer in-between is essentially a metal-dielectric-metal configuration, allowing out-of-plane coupling between in-plane hybridized modes and cavity modes, resulting in strongly localized gap plasmons. In addition to facilitating mode coupling, the underlying aluminum mirror efficiently reflects broadband white light while the plasmonic resonances of the nanoparticle layer selectively absorb certain wavelengths. This interaction modulates the reflected spectrum, giving rise to angle and polarization independent vivid structural colors.⁸ The electron-beam evaporation based self-assembling technique produces nanoparticles with moderate polydispersity, particularly evident in the larger particle dimensions. Figure 1c,e displays the relative height and size distribution of the fabricated nanoparticles that highlight the size variations. We fabricated three sets of nanoparticle assemblies with average radii ranging from 12 to 20 nm with average heights between 5 and 21 nm, that demonstrate vivid yellow, magenta, and cyan colors. Consequently, the steady-state spectral response (see Figures 2b and S1) reflects an ensemble average rather than the behavior of individual plasmon modes. High-resolution scanning electron microscopy (SEM) images of the fabricated nanoparticle surfaces are presented in Figure 1d, with insets showing photographs of the actual sample colors. We refer to each nanoparticle assembly by its corresponding observed color (cyan, yellow, and magenta).

Near-Field Imaging of the Gap Plasmons

To investigate the localized field enhancement within the nanoparticle ensembles, we employ scattering-type scanning near-field optical microscopy (s-SNOM), which provides a spatial resolution of approximately 20 nm. Figure 2a presents a schematic representation of the s-SNOM configuration: a metal-coated AFM tip operating in tapping mode is illuminated with a visible laser at a 60° incidence angle, with the amplitude (S_n) and phase (ϕ_n) of the near-field scattered light being collected at the 5th harmonic of the cantilever's oscillation frequency (See Methods section for more details). Figure 2c shows the approach curve, where the S_5 value displays a sharp exponential reduction within 20 nm from the surface, confirming a strongly confined near-field. Figure S2 further compares the approach curves for harmonics, $n = 2-4$ which additionally includes far-field backgrounds. Spatial S_5 maps were recorded on both the yellow and cyan samples under continuous-wave 632 nm excitation (Figure 2d,e). At this wavelength, the cyan NP can be excited resonantly, while the yellow NP is strongly blue-detuned (Figure 2b). Accordingly, the cyan sample exhibits pronounced, field enhancements ("hot-spots") localized around the nano-islands. In contrast, the S_5 map of the yellow sample, excited off-resonance, displays a more uniform near-field distribution, indicating minimal confinement. Although the S_5 effectively suppresses far-field background contributions, it does not eliminate near-field background (NFB) scattering originating from adjacent nano-islands. This limitation becomes evident when the tip apex is directly atop a single nano-island the near-field signals scattered from neighboring islands, emitted in all directions, can still reach the tip (illustrated in Figure 2f). For clarity, the illustration shows NFB scattering only from a single neighboring particle. To eliminate the NFB and identify the in-

plane gap plasmon modes, we extract the ratio of the scattering amplitudes (SA), defined as

$$\frac{\sigma_n}{\sigma_{n-1}} = \frac{S_n}{S_{n-1}} e^{i(\phi_n - \phi_{n-1})} \quad (1)$$

which selectively enhances the true, local near-field response.⁶ Accordingly, we extract both the amplitude ratio S_5/S_4 and the corresponding phase difference $\phi_5 - \phi_4$, as displayed in Figure 2h,j. The amplitude ratio map reveals localized regions of enhanced scattering that appeared less prominent in the S_5 map alone. Moreover, the observed π phase contrast at these specific, yet random locations further indicate the presence of strongly confined plasmon modes. For direct correlation with surface morphology, the S_5/S_4 amplitude ratio is overlaid on the AFM height profile in Figure 2i. Interestingly, the highest SA ratio values are consistently located in the interparticle gaps rather than on top of individual nanoparticles. To clarify this further, we overlaid the spatial second derivative of the surface morphology with the hot-spot locations and found a clear correlation between the NP edges and the hot spots (see Figure S3, Supporting Information). We also verified that S_5/S_4 map does not yield noticeable field localization in the yellow sample. Direct nanoscale imaging confirms that the dominant local near-field response arises from resonant excitation of randomly distributed, hybridized gap plasmon modes in the aluminum nanoparticle ensemble. The broad reflectance spectra (Figure 1b) arise from the structural inhomogeneity of the gap-plasmon ensemble, where multiple plasmonic resonances contribute simultaneously. Consequently, the near-field distribution measured by s-SNOM at 632 nm reflects the subset of individual plasmonic modes resonantly excited at this wavelength.

Illumination of the nanoparticle assembly with resonant, single-frequency light therefore produces a unique spatial map of hot spots (USM-h), determined by the locations of nanoscale gaps supporting gap-plasmon modes at the excitation frequency. Consequently, tuning the excitation frequency spatially modifies the USM-h distribution across the nanoparticle assembly. This further implies that the excitation bandwidth is directly related to the degree of hot-spot randomization: broader excitation spectra generate a higher number of spatially randomized hot spots, whereas narrower excitation spectra produce more restrictive localization. Since the excitation line width governs the ensemble of excited gap plasmons and the resulting USM-h distribution, narrowband pump and broadband probe spectroscopy can provide insight into the temporal evolution of spatial localization.

Ultrafast Dynamics of the Nanoparticles

To explore the ultrafast dynamics, we utilize broadband transient reflection spectroscopy, where we excite the material with wavelength-tunable, narrowband (<20 nm) pump pulse and probe with a broadband supercontinuum pulse spanning 500–800 nm with temporal resolution ~150 fs. We acquire time- and spectrally-resolved differential change in reflectance ($\frac{\Delta R}{R}$). Further details on instrumentation, data acquisition, and modeling are provided in the Methods section.

Resonant ultrafast excitation generates localized plasmons that decay on ultrashort time scales (~fs) into free charge carriers with excess kinetic energy through direct interband absorption, electron-defect scattering, and/or Landau damp-

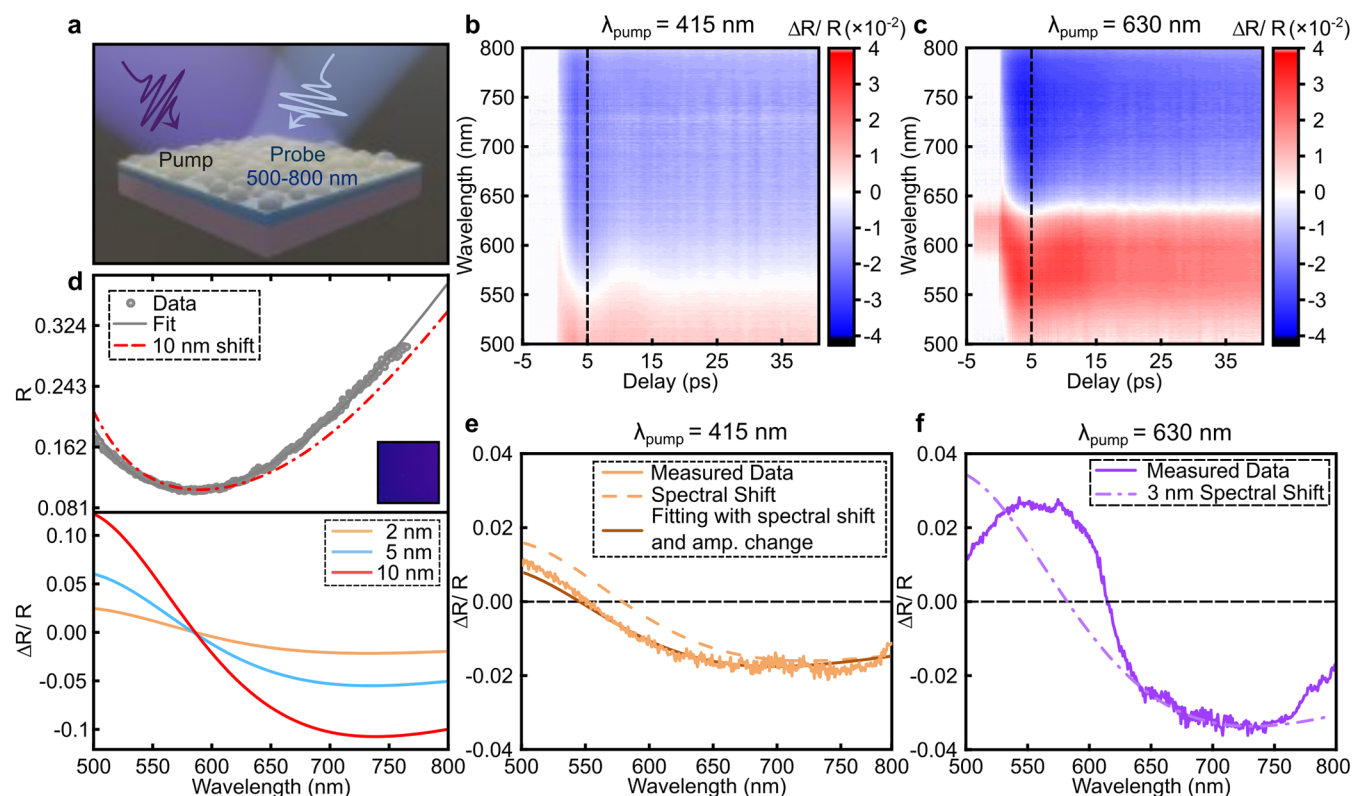


Figure 3. Schematic representation of the transient reflectivity measurement on the cyan nanoparticles. (a) 415 nm pump (off-resonance), and a broadband probe (500–800 nm). Transient differential reflectance (TDR) spectrum, $\left(\frac{R_{\text{probe}}^{\text{pump}}(\lambda, t)}{R_{\text{probe}}^{\text{no pump}}(\lambda)} - 1\right)$ is abbreviated as $\frac{\Delta R}{R}$ in the labels, where $R = (R_{\text{probe}})$ is the reflectance measured through the broadband probe in the presence ($R_{\text{probe}}^{\text{pump}}(\lambda, t)$) or absence of the pump excitation ($R_{\text{probe}}^{\text{no pump}}(\lambda)$). TDR is obtained for (b) 415 nm and (c) 630 nm pump. (d) Explanation on the origin of the spectral shape of the reflectance; First panel: scattered plot (solid line) denotes the measured (fitted) steady state reflectance, red dashed line is numerically red-shifted reflectance spectrum. Second panel: numerically obtained TDR when the LSPR absorption band is shifted by 2, 5, and 10 nm. Experimentally measured TDR at 5 ps probe delay in the presence of (e) 415 nm and (f) 630 nm pump excitation. The dashed lines are numerically fitted spectra with optimized spectral shifts of the LSPR. The thick solid line in (e) indicates the numerically fitted spectrum considering spectral shift, as well as oscillator amplitude change.

ing.³ The resulting non-thermal electron distribution subsequently undergoes electron–electron scattering over tens of femtoseconds, leading to energy redistribution among quasiparticles and the establishment of a Fermi–Dirac distribution. Since our temporal resolution is ~ 150 fs, our measurements probe the population of hot carriers generated by the pump pulse, whereas plasmon dephasing and plasmon–plasmon interactions cannot be directly resolved.

Figure 3a shows a schematic illustration of the utilized pump–probe reflectance spectroscopy. We focus on the cyan colored Al-NPs sample that exhibits broad LGP resonance across the visible spectrum. Aiming to understand the origin of the broad spectral response and its relationship with USM-h, we perform transient reflectance experiments using three distinct pump wavelengths: 415, 630, and 700 nm. The 415 nm pump is non-resonant to LGPs and introduces uniform inter- and intra-band transitions in the aluminum particles¹¹ (no USM-h), whereas the 630 and 700 nm ultrafast excitations are within the LGP resonance, thus introducing random field localizations/USM-h corresponding to the resonant LGP modes. This leads to transient changes in the material permittivity at the unique nano-locations of the ensemble. By systematically varying the probe-delay, we capture the temporal evolution of pump-induced modulations that eventually affect the broadband probe reflectance stemming

from the full ensemble of LGP modes. Figure 3b,c shows the transient differential reflectivity (TDR) maps under 415 and 630 nm excitation. In both cases, a clear differential response is observed, enhanced reflectance at lower wavelengths and reduced reflectance at higher wavelengths, indicative of a photo-induced spectral red-shift. To explain the spectral signature, in Figure 3d, we illustrate $\Delta R/R$ spectra corresponding to spectral shifts of 2, 5, and 10 nm of the entire ensemble from that of the steady-state resonance (see Methods). Figure 3e presents the measured (solid yellow) and fitted (dashed yellow) TDR spectrum at 5 picoseconds (ps) delay under 415 nm excitation. A fit based solely on a red-shift in reflectance reproduces the general trend but deviates at shorter wavelengths, indicating that photo-induced changes in oscillator strength also play a role. Incorporating both a spectral red-shift and an increase in oscillator strength produces a simulated spectrum (brown solid line) that matches the experiment much more closely, confirming the involvement of both energy renormalization and oscillator-strength modification in the ultrafast response. We thus conclude that 415 nm excitation generates free carriers throughout the sample and red-shift the entire LGP ensemble (global redshift).

Next, we analyze the spectral signature of TDR with resonant, 630 nm pump excitation. As shown in Figure 3c,f, the observed TDR spectra display positive (negative) $\Delta R/R$ in

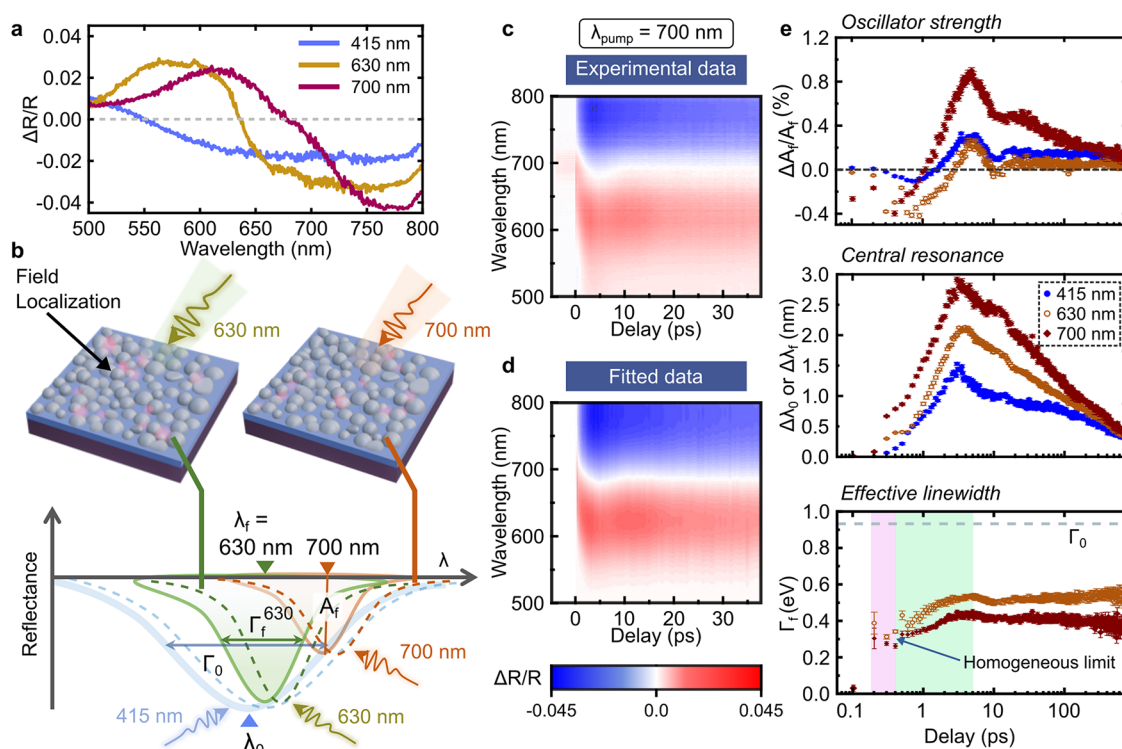


Figure 4. Ultrafast excitation of fractional ensemble. (a) Differential reflectance at 5 ps delay corresponding to three different pump wavelengths. (b) (top panel) pedagogical explanation of the selective plasmon excitation and field localization between the random gaps of nanoparticles following 630 and 700 nm excitation. Red highlights indicate the USM of gap plasmons. (bottom panel) selective plasmon excitation introduces spectral changes (e.g., red-shift) of a fraction of the LSP modes around the excitation wavelength. The solid blue line is the steady-state broadband reflectance of the entire ensemble; green and brown curves indicate the fraction of ensemble excited by 630 and 700 nm; dashed green and brown lines indicate spectral alteration of the fractional ensemble upon the mentioned pump excitation. (c) Experimentally measured (d) numerically fitted $\Delta R/R$ spectrum as a function of probe delay and probe wavelength corresponding to 700 nm pump excitation. (e) Numerically extracted (panel 1) change of the LSPR oscillator strength, (panel 2) spectral shift, (panel 3) line width of the excited ensemble (only for 630 and 700 nm pump) with probe delay following different pump excitations, as indicated. The dashed line indicates the equilibrium line width of the entire ensemble (~ 0.98 eV).

lower (higher) wavelengths. The overall spectral shape of the TDR resembles the positive-to-negative trend corresponding to 415 nm pump, yet it is spectrally narrower. A model based solely on a global redshift (dashed line in Figure 3f) fails to capture this spectral narrowing. Also, the inclusion of other parameters (e.g., oscillator strength, line width) changes does not improve the quality of spectral reproduction. This discrepancy and observed narrowness in TDR suggest a fundamentally different pump-induced modulation of the LSP probe than that of 415 nm pumping. The 630 nm pump, being on-resonance, only selectively couples to resonant gap plasmon modes, not the whole ensemble. Consequently, the probe encounters spatially-localized pump-induced changes at the hot-spots corresponding to 630 nm, and the spectral alteration of the probe is therefore confined to the relevant, narrower spectral window, reflecting the selective excitation of resonant plasmonic sub-population within the ensemble. This indicates a selective plasmonic excitation similar to spectral-hole burning (SHB) effects.¹² Figure 4a compares the TDR spectra at a 5 ps delay for three pump wavelengths. A clear red-shift and narrowing of the TDR spectral features are observed while the pump excitation is tuned from 415 to 700 nm, confirming selective excitation of the localized gap plasmons through resonant pump excitation. The resonant narrowband pump does not perturb the entire LSP distribution but instead excites a fractional sub-ensemble. The bandwidth of the excited

LSPs is expected to be governed by the homogeneous line width (Γ_{hom}) convoluted with the excitation line width. $\Gamma_{\text{hom}} \sim \frac{2\hbar}{T_2}$ where T_2 is the plasmon dephasing time. Since the pump line width is relatively narrow (~ 20 nm), it contributes minimally compared to the broader Γ_{hom} . As indicated in literature, the fastest dephasing mechanism, plasmon–electron scattering, sets the scale of this homogeneous line width, while slower processes such as interband Landau damping,¹³ plasmon–phonon interactions, and surface scattering contribute insignificantly to the observed spectral width.¹⁴

To model the TDR spectra for resonant pump, we assume that only a fraction of the LSP modes centered at the excitation wavelength undergoes changes in oscillator strength (A_f), spectral red-shift ($\Delta\lambda_f$) and contributes to the transient response. The key parameter governing this fractional contribution is the modified line width, denoted as Γ_f which characterizes the excited sub-ensemble. If Γ_f is ~ 1 eV, this indicates the entire LSP ensemble is perturbed through the pump. In an attempt to display the wellness of our approximation, Figure 4c displays experimental $\Delta R/R$ spectrum upon 700 nm excitation, up to a delay of ~ 40 picoseconds and Figure 4d shows the corresponding fitted 2D spectra that well reproduce using three adjustable parameters (A_f , $\Delta\lambda_f$, Γ_f) at each probe-delay. Figure 4e compiles the temporal evolution of the probe's overall plasmonic absorption

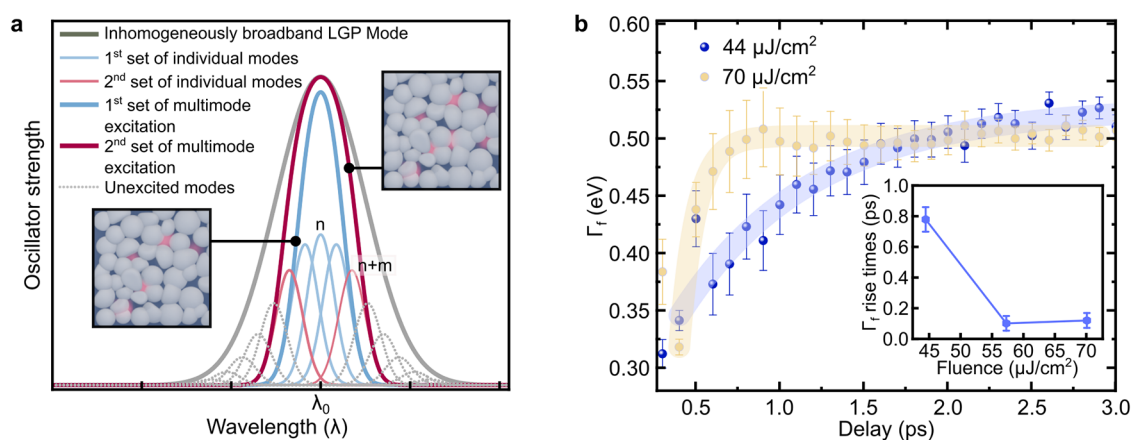


Figure 5. Illustration of effective LGP excitation line width and spatial confinement of hot carriers. (a) Pedagogical illustration of spatially localized hot-spots for a narrow (blue thick line) and a broad (red thick line) plasmonic ensemble being excited. The insets show the corresponding USM-h maps. For a narrower (broader) excitation, less (more) hot-spots (shown by red areas) are observed. (b) Initial effective LGP line width dynamics as observed for different pump fluences at 630 nm excitation. The inset shows the rise-times as a function of the pump fluence.

properties (absorption strength, resonance energy, and line width) following three different pump excitations ($\lambda_{\text{pump}} = 415, 630, 700$ nm). The second panel of Figure 4e displays the temporal dynamics of spectral shift. The red-shift of LGPs is dictated by the local change in material permittivity due to the pump-induced hot carriers. The higher is the carrier temperature, the higher is the redshift. Maximum energetic shift is observed around 4 ps probe delay: ~ 10 meV ($\lambda_{\text{pump}} = 415$ nm), ~ 7 meV (630 nm) and ~ 6 meV (700 nm). The decay dynamics of $\Delta\lambda$ is fitted with a bi-exponential decay and two major time scales are revealed: (i) 20–30 ps (ii) 300–500 ps (see the Supporting Information). The faster time scale is associated with hot carrier cooling, while the longer decay indicates recombination of free carriers. We observed from the top panel of Figure 4e that irrespective of excitation wavelength, the plasmonic oscillator strength displays reduction (negative values) within a few picoseconds and increases up to 0.8 % within 5 ps of excitation, followed by the reversion to steady-state values that takes place within a nanosecond. The sign reversal in $\Delta A_f/A_f$ irrespective of resonant or non-resonant excitation is interesting. Initial reduction possibly originates from a high carrier temperature of electrons that destroys coherence and hinders LGP formation. While the carrier temperature reduces with increasing delay, probe-induced LGP formation becomes favorable owing to the newly available (pump-induced) free carriers from Landau process or direct carrier generation. Most importantly, the remaining parameter, the effective line width under resonant excitations explains the sub-ensemble being excited through the SHB. Numerically obtained Γ_f narrows down to 0.3 eV right after excitation irrespective of the excitation wavelength and thereafter, gradually increases to ~ 0.54 eV (~ 0.36 eV) within 4 ps of 630 nm (700 nm) pump excitation (green shaded region in Figure 4e). The lowest value of Γ_f right after pump excitation provides an estimate of homogeneous limit $\Gamma_f(t \rightarrow 0) \sim \Gamma_{\text{hom}}$. We estimate a dephasing time $T_2 \sim 4$ fs of the gap plasmons. This value is similar to the plasmon dephasing times reported in metal nanoparticles.^{15,16} Post the dephasing time, LGPs dissociate and create HCs through Landau damping (including electron-electron scattering) and subsequently transfers the excess energy to the lattice through electron-phonon scattering.¹⁷ The gradual increase in line width up to

0.54 eV ($\Gamma_{f \text{ max}}$) within a few ps originate from either homogeneous or inhomogeneous broadening of the excited plasmon ensemble. Homogeneous broadening can arise from plasmon–carrier or plasmon–phonon scattering processes, where pump-induced free carriers and/or phonons reduce the dephasing time of the (probe-generated) LGPs, thereby increasing the homogeneous line width of the individual modes. Such an effect can be identified by varying the pump fluence, since higher fluence generates larger carrier and phonon populations and should therefore result in reduced dephasing time and eventually an increased maximum effective line width, $\Gamma_{f \text{ max}}$. In addition, any increase in homogeneous line width is expected to recover to its initial value once the excess carrier and phonon populations decay.¹⁸ To investigate these, we performed transient reflectance measurements at different pump fluences for 630 nm excitation. We observe a fluence-independent minimum of Γ_f at 0.3 eV, again highlighting the homogeneous limit (Γ_{hom}). However, as shown in Figure 5b, the effective maximum LGP line width ($\Gamma_{f \text{ max}}$) is constant around 0.5 eV, regardless of pump fluence up to 70 $\mu\text{J}/\text{cm}^2$. Moreover, the enhanced line width does not recover within nanoseconds. These observations rule out homogeneous broadening as the underlying mechanism within the excitation fluence range $< 80 \mu\text{J}/\text{cm}^2$ and instead point toward inhomogeneous broadening of the plasmon ensemble.

A pedagogical illustration on line width and spatial mode distribution is provided in Figure 5a: the broad LGP ensemble is constituted of multiple individual modes arising from the inhomogeneity of the nanoparticle size. Here, we compare two multimode excitations with different line widths, shown by red and blue thick lines. We assume that the pump resonant with λ_0 enables excitation of three adjacent modes (thin blue lines); the resultant effective OS is shown in a thick blue line. The inset image on the left portrays the creation of hot-spots within a sample area at this excitation condition. Next, we allow two more adjacent individual modes (shown by thin red lines) to be excited, and the summed effective OS gets broadened (see the thick red curve). Importantly, in this case, there will be more hot-spots in the sample area. This is illustrated in the inset at the right. Each individual mode corresponds to creation of hot-spots at unique location. Hence, as discussed earlier, a narrower (broader) effective LGP line width indicates

fewer (more) number of hot-spots in a selected area of the nanoparticle assembly. Consequently, the effective line width of excited LGPs depend on the spectral spread of multi-mode excitation (for example, the red solid curve suggests the ensemble of LGPs constituting from $n-m$ to $n+m$ modes). So, an increase in effective probe LGP line width essentially means more individual plasmonic modes are getting modulated through the pump-induced hot carriers. In a densely packed assembly, each particle borders several neighbors and participates in gaps of varying width and resonance. As a result, adjacent modes partially share hot spots, while more distant modes are supported at increasingly distinct locations. Modulating a broader set of plasmonic modes therefore requires pump-induced hot carriers beyond the initially excited regions.

Importantly, although the hot carriers cool within ~ 20 – 30 ps and recombine on time scales of several hundred picoseconds as inferred from the $\Delta\lambda$ dynamics, the effective line width does not recover to the steady-state value (~ 0.98 eV) within these time scales. If complete spatial diffusion and loss of spatial memory had occurred during the hot-carrier lifetime, the SHB line width would be expected to return to its equilibrium value of ~ 0.98 eV. The persistence of a narrowed line width therefore indicates that the pump-generated hot carriers undergo only partial spatial delocalization and retain the spatial localization of the parent plasmon modes even after cooling.

The initial increase of Γ_f up to 0.5 eV can be fitted by a single exponential function to reliably estimate sub-ps diffusion times. The range of G_f rise time (τ_d) varies from 0.8 to 0.1 ps with pump fluence increasing from 44 to 70 $\mu\text{J}/\text{cm}^2$, as depicted by the inset in Figure 5b. The τ_d values below 0.15 ps are the upper limits given the instrument response function of 150 fs. This observation is in line with the fact that higher fluence generates higher carrier densities and hotter carrier temperatures, which generally enhances the effective diffusion coefficient during the hot-carrier regime.¹⁹ Moreover, this trend also argues against contributions from plasmon–carrier or plasmon–phonon scattering processes, since τ_d would be expected to increase with increasing excitation fluence in such scenarios.²⁰

The redistribution of pump-induced hot carriers in our nanoparticle assembly proceeds through two distinct channels. Within an individual nanoparticle, transport is ballistic rather than diffusive, since the hot-carrier mean free path in aluminum is comparable to the particle dimensions; equilibration across a particle requires only $l/v_F < 20$ fs and is therefore complete well within our temporal resolution. Because each particle borders several neighbors and participates in several gaps of differing width and resonance, this channel alone renders spectrally distinct LGP modes non-disjoint in space. It cannot, however, account for the observed dynamics: the measured rise of Γ_f (~ 0.8 ps at 44 $\mu\text{J}/\text{cm}^2$) is far slower than intraparticle equilibration, and a $\Gamma_{f\text{max}}$ ceiling set solely by the number of gaps a particle borders would be independent of excitation photon energy, contrary to the observed difference between 630 and 700 nm excitation. A second, interparticle channel must therefore be operative. In a continuous metal film this channel would be fast: with $D = 1/3v_F^2\tau \approx 100$ cm^2/s , comparable to the value measured directly in gold films by ultrafast thermomodulation microscopy,¹⁹ carriers would spread ~ 280 nm ($\sim \sqrt{4Dt}$) within the first two picoseconds and Γ_f would approach $\Gamma_0 \approx 0.98$ eV almost immediately. It

does not. In our assembly, the particles are separated by dielectric gaps, so interparticle transport proceeds by tunneling and is limited by interfacial transmission rather than by the intraparticle mean free path. Because the gap-width distribution is broad and the transmission falls exponentially with gap width, the well-coupled gaps form a connected sub-network of Al NPs with a finite characteristic size, and carriers halt at its poorly coupled boundary.²¹ Transport is thus confined to a bounded domain, within which the diffusion coefficient governs only how rapidly the plateau is reached and not its height—carriers stop at the same boundary whether they arrive at 0.1 or 0.8 ps. This accounts for the two observations that a simple diffusive picture cannot reconcile: $\Gamma_{f\text{max}}$ is fixed by the connectivity of the particle network, and is therefore independent of pump fluence, while the rise time is not. The wavelength dependence of Γ_f dynamics follows from the same picture: a carrier at energy ΔE above the Fermi level experiences an effective barrier $\Phi_{\text{eff}} = \Phi_B - \Delta E$, so higher photon energy raises the critical gap width that remains traversable by the charges and enlarges the connected cluster, giving the larger accessible mode fraction observed at 630 nm.

Since Γ_f reflects the extent of the plasmonic sub-ensemble perturbed by the pump, and each plasmonic mode corresponds to a distinct spatial hot-spot distribution, the increase in Γ_f provides an indirect measure of the spatial spread of the hot-carrier population. We introduce a phenomenological measure,

$$S = \frac{\Gamma_{f\text{max}} - \Gamma_{\text{hom}}}{\Gamma_0 - \Gamma_{\text{hom}}}, \text{ where } S = 1 \text{ indicates full delocalization and } S = 0 \text{ suggest completely localized.}$$

Experimental values of $\Gamma_{f\text{max}} = 0.54 \pm 0.06$ eV (0.36 ± 0.05 eV) corresponding to 630 (700) nm pump excitation yields $S = 0.35 \pm 0.1$ (0.09 ± 0.08) indicating a localized behavior. At 700 nm, the uncertainty on S is comparable to its value, so this measurement establishes an upper bound rather than a resolved degree of delocalization; the wavelength dependence is therefore established more robustly by comparing $\Gamma_{f\text{max}}$ directly, where the common terms Γ_{hom} and Γ_0 cancel. The fraction of the excited ensemble can be estimated by the ratio of the integrals using the stretched

$$\text{Gaussian function: } S' = \frac{\int \alpha(\lambda; A_0', \lambda_0', \Gamma_{f\text{max}}) d\lambda}{\int \alpha(\lambda; A_0, \lambda_0, \Gamma_0) d\lambda}, \text{ which yields } 0.64 \pm$$

0.07 and 0.42 ± 0.05 corresponding to 630 and 700 nm excitation. The ratio of the excited maximum effective line width to that of the total line width ($S' = \frac{\Gamma_{f\text{max}}}{\Gamma_0}$) also provides an approximation of the fractions: $S' = 0.55 \pm 0.08$ and 0.37 ± 0.05 for 630 and 700 nm, respectively.

CONCLUSIONS

In this work, hybridized gap plasmon modes in disordered nanoparticles are explored for the first time using spatial, temporal, and spectrally resolved spectroscopic techniques. Near-field imaging allows direct visualization of the randomly located plasmon “hot-spots” within nanoparticle gaps, revealing the out-of-plane coupling between the hybridized localized plasmons and the metallic mirror. Such randomized and strong field-localization in sub-diffraction volumes of metallic nanoparticles explains the observed high oscillator strength of LGPs in these systems. The inherent spatial randomness of the plasmonic excitation is exploited through ultrafast spectroscopy, where a narrowband pump allows selective excitation of a homogeneously broadened sub-ensemble of the entire plasmon modes without coupling to the remaining ensemble even after a nanosecond of excitation (spectral hole burning).

Following LGP excitation, the plasmon modes rapidly dephase and transfer their energy to generate hot carriers through Landau damping, as evidenced by the transient redshift of the probe resonance. Ultrafast tracking of the pump-modulated LGP line width reveals that the generated hot carriers retain signatures of the initial plasmonic localization for hundreds of picoseconds, indicating only partial ($\sim 0.35 \pm 0.1$; 0.09 ± 0.08 out of 1 for 630 and 700 nm pump) spatial delocalization. This behavior likely arises from the interplay between strong plasmonic confinement within nanoscale gaps and percolation of the disordered nanoparticles, which limit long-range carrier diffusion and preserves the spatial memory of the parent plasmon modes. The extent of preserved localization is not fixed by the sample alone but can be tuned in situ through the excitation wavelength, offering an optical handle on how far plasmon-generated carriers spread through the network. These spatiotemporal insights into hybridized localized gap plasmons in disordered metallic nanoparticle systems address a key open question regarding the spatial memory of plasmon-induced hot carriers. Beyond advancing the fundamental understanding of hot-carrier dynamics, our results highlight the potential of such strongly confined plasmonic systems for application in efficient sensing,^{22–24} displays technologies,^{9,25,26} plasmonic memory,²⁷ plasmonic photochemistry²⁸ and a broad range of hot-carrier based energy harvesting^{29,30} applications.

MATERIALS AND METHODS

Fabrication of Self-Assembled Structural Color Stack

A 100 nm thick aluminum layer was first deposited as a reflective back mirror using an electron beam evaporator (AJA International) at a base pressure of $\sim 1 \times 10^{-7}$ Torr and a deposition rate of 0.1 nm/s to ensure uniform film formation. Next, a dielectric spacer layer of aluminum oxide (Al_2O_3) was deposited using atomic layer deposition (Savannah 200, Cambridge Nanotech) with alternating pulses of trimethylaluminum (TMA) and water at a substrate temperature of 100 °C. Finally, a thin aluminum layer was evaporated using the same AJA e-beam system to facilitate the self-assembly of aluminum nanoparticles. The morphology of the nanoparticles, and consequently the structural color, was tuned by controlling the substrate temperature (100 °C), chamber pressure ($< 5 \times 10^{-8}$ Torr), and deposition rate (~ 0.1 Å/s) to enable controlled nucleation and growth of the nanoparticles.

Scattering-Type Scanning near Field Optical Imaging (s-SNOM)

We use a commercial s-SNOM set-up (Neaspec, Attocube systems) for the near-field imaging of the structural colors. A monochromatic, continuous-wave laser (632 nm) illuminates the nanoparticles in the presence of a Pt-coated AFM tip that operates in tapping mode. The out-of-plane electric field beneath the nanoscale tip apex is significantly enhanced due to the elongated shape of AFM tip, which allows stronger vertical dipole. However, the 60° incidence angle of the input beam allows a minimal enhancement of the in-plane electric-field. This near-field signal is subsequently coupled to far-field scattering and reflectivity for detection. In this tapping mode s-SNOM, the tip to sample distance is varied sinusoidally ($d(t) = d_0(1 - \cos(\Omega t))$) with tapping frequency Ω (~ 155 kHz) and the resulting time-varying scattering is demodulated in the frequency domain at higher harmonics ($n = 1, 2, \dots, 5$) of scattering, $\sigma: \sigma_n^{\text{out}} = \sigma_n e^{i\phi_n}$; n being the demodulation order. A nonlinear variation of the near-field scattering amplitude (SA) with tip-to-surface distance ($d(t)$) results in strong anharmonicity in the time-domain signal ($\sigma(t)$), leading to higher-order components in the frequency domain ($S_n(\omega)$). Far-field components, being nearly linear with tip-sample distance, are ignored in the higher harmonics. Therefore, a higher demodulation order ensures sizable suppression of the far-field background contributions.

The strongly confined nature of the near-field response from the sample surface is observed from the variation of SA S_3 as a function of tip-to-surface distance (the highest possible harmonic is limited by the speed of data acquisition electronics and weak signal to noise ratio).

Ultrafast Pump–Probe Transient Reflection Measurements

A 50 fs Ti: sapphire regenerative amplifier (LIBRA, Coherent) of central wavelength 808 nm and a repetition rate of 1 kHz has been used to perform the ultrafast pump–probe transient reflection spectroscopy for the sample. A significant part of the laser (808 nm center wavelength) beam goes into an Optical Parametric Amplifier (OPA) generating a tunable (250–1900 nm) pump pulse, and the other part is focused onto a 3 mm CaF_2 crystal, generating a super-continuum pulse that acts as the broadband probe pulse. The probe pulse passes through a set of retro-reflectors placed on a mechanical delay-stage to probe the sample absorption at different delays up to a maximum of 8 ns after the excitation pump pulse. An optical chopper of frequency 500 Hz (half of that of the laser repetition rate) is employed in the pump beam path to compare “pump-on” and “pump-off” situations. Pump and probe beams spatially overlap at the sample holder position in a non-collinear fashion. The pump beam, after transmission through the sample, is blocked and the transmitted probe beam is dispersed into a linear Si-CCD array attached with a spectrometer (Oriel MS 260i) through a fiber-coupler. The spectrometer is synchronized with the master laser through a square wave signal of frequency 1 kHz from the laser so that it only integrates in the temporal vicinity of the laser pulse. The spectrometer data is acquired through a programmable hardware interface (National Instruments PCI-6132 DAQ). To check for the artifacts from pump-induced sample heating or any optical damage, the differential reflection spectra acquired through sequential and random delay progressions have been compared. Although the delay stage has a time resolution < 10 fs, the temporal resolution of the setup is limited by the cross-correlation of the pump and probe pulses, commonly known as the “Instrumental Response Function” or IRF which is ~ 150 fs. The spatial resolution of the setup is limited by the probe spot size, which is ~ 200 μm . During data acquisition, an average was performed over one second, i.e., 1000 shots, and therefore, the signal-to-noise ratio is of the order $\sim \sqrt{N} \approx 32$. A minimum and maximum signal-to-noise ratio of ~ 10 and 40, respectively, have been maintained, corresponding to the pump intensities used in the experiment. For measurements, a low excitation power density (< 80 mW/cm²) has been maintained to avoid optical damage of the structural colors. The damage threshold is found to be ~ 100 mW/cm².

Data Acquisition

The instrument acquires differential absorption $\Delta\alpha = \log\left(\frac{R_{\text{probe}}^{\text{no pump}}}{R_{\text{probe}}^{\text{pump}}(t)}\right)$, where $R_{\text{probe}}^{\text{no pump}}$ indicates the reflected probe spectra from sample in absence of the pump pulse and $R_{\text{probe}}^{\text{pump}}(t)$ is the reflected probe t time later the pump pulse excitation. The transient differential reflectance (TDR) spectrum is extracted as a function of delay between the pump and probe pulses (t)

$$\frac{\Delta R}{R} = 10^{-\Delta\alpha} - 1 \quad (2)$$

defined as the change in probe reflectance with the pump, normalized to the un-excited probe reflection.

Numerical Analysis of the Steady-State Optical Properties of the Structural Color

The steady-state optical reflectance of the structural color is governed by the inhomogeneous nanoparticle layer on the surface, supported by an underlying metal mirror. The back mirror provides a complete reflection, while the Al nanoparticles at the surface serve as the absorbing layer. Owing to the perfect absorption condition, the absorption (α) from the NPs are related with the reflectance (R) through the following equation

$$R_{\text{probe}}(\lambda; A_0, \lambda_0, \Gamma_0) = 10^{-\alpha(\lambda; A_0, \lambda_0, \Gamma_0)} \quad (3)$$

A stretched Gaussian function is utilized to numerically fit the steady-state absorption spectrum of the nanoparticles

$$\alpha(\lambda; A_0, \lambda_0, \Gamma_0) = A_0 e^{-4 \log(2) \left(\frac{\frac{\lambda}{\lambda_0} - \frac{\lambda}{\lambda_0}}{\Gamma_0 + p \lambda} \right)^2} \quad (4)$$

where A_0 is the oscillator strength, λ is the wavelength, λ_0 is the center wavelength, p is the stretch parameter, and Γ is the line width. The broad line width, Γ , and the Gaussian-like profile are attributed to size polydispersity in the nanoparticle ensemble. The stretch parameter is included due to the asymmetry present in the spectra, possibly stemming from various mode hybridizations. Fitted parameter values of the steady-state reflectance spectra of the cyan nanoparticle ensemble are indicated in Table 1.

Table 1. Fitted Parameter Values Obtained for Steady-State Absorption Spectrum of the Cyan Nanoparticles

parameter (units)	value
A_0	0.990 ± 0.001
λ_0 (nm)	580.2 ± 0.3
Γ_0 (eV)	0.98 ± 0.03
p (eV/nm)	0.00009 ± 0.00003

Numerical Analysis of Time-Dependent Sub-Ensemble LGP Mode Excitation through Pump

Experimental TDR from ΔA is numerically fitted from the following expression and eq 2

$$\Delta\alpha(t) = \alpha(\lambda; A_f + \Delta A_f(t), \lambda_{\text{pump}} + \Delta\lambda_f(t), \Gamma_f(t)) - \alpha(\lambda; A_f, \lambda_{\text{pump}}, \Gamma_f(t)) \quad (5)$$

Here, the second term is nothing but the un-excited, resonant sub-ensemble, and the first term corresponds to the pump-induced altered properties of this ensemble. The remaining non-resonant part of the broad spectrum stays unchanged. The equilibrium oscillator strength (OS) is obtained as $A_f = A(\lambda = \lambda_{\text{pump}})$, and the center wavelengths ($\lambda_f = 630$ or 700 nm) are pinned to the excitation wavelengths. There are three parameters, namely, change in oscillator strength (ΔA_f), spectral shift ($\Delta\lambda_f$), and effective line width (Γ_f) that evolve over the probe delay.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.6c12999>.

Reflectance spectra of the structural colors (yellow, magenta, and cyan), approach curves for s-SNOM acquired at different harmonics of tapping frequency, time scales of plasmon red-shift ($\Delta\lambda$) relaxation (Table S1), second derivative of surface topography overlaid with normalized scattering amplitude S_5/S_4 map (PDF)

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Author Contributions

M.K. and D.C. conceptualized and designed the research; M.K. performed the s-SNOM measurements; A.J.K. performed the ultrafast measurements; T.G. and M.S. prepared the samples; M.K. analyzed the experimental data, performed numerical analysis, and interpreted the data; P.C.A. contributed to the interpretation of s-SNOM data; D.C. contributed materials/analysis tools. M.K., A.B., P.K.D., and D.C. co-wrote the paper.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work at the University of Central Florida was partially supported by the National Science Foundation (NSF) under the grant no. ECCS 1920840, National Geospatial-Intelligence Agency (NGA) under the grant no. HM0476-20-1-0010 and Army Research Office (ARO) under the grant No. W36QYT0012457276.

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