Radiative Pumping and Propagation of Plexcitons in Diffractive Plasmonic Crystals

Yuriy Zakharoko,†,‡,§ Marcel Rother,† Arko Graf,† Bernd Hähnlein,‡ Maximilian Brohmann,† Jörg Pezoldt,‡ and Jana Zaumseil*†,‡

†Institute for Physical Chemistry, Universität Heidelberg, D-69120 Heidelberg, Germany
‡Institut für Mikro- und Nanotechnologie, Technische Universität Ilmenau, 98693 Ilmenau, Germany

ABSTRACT: Strong coupling between plasmons and excitons leads to the formation of plexcitons: quasiparticles that combine nanoscale energy confinement and pronounced optical non-linearities. In addition to these localized modes, the enhanced control over the dispersion relation of propagating plexcitons may enable coherent and collective coupling of distant emitters. Here, we experimentally demonstrate strong coupling between carbon nanotube excitons and spatially extended plasmonic modes formed via diffractive coupling of periodically arranged gold nanoparticles (nanodisks, nanorods). Depending on the light-matter composition, the rather long-lived plexcitons (>100 fs) undergo highly directional propagation over 20 μm. Near-field energy distributions calculated with the finite-difference time-domain method fully corroborate our experimental results. The previously demonstrated compatibility of this plexcitonic system with electrical excitation opens the path to the realization of a variety of ultrafast active plasmonic devices, cavity-assisted energy transport and low-power optoelectronic components.

KEYWORDS: Plexcitons, strong coupling, carbon nanotubes, plasmonic crystals, light emission, radiative pumping

The nanoscale localization of electromagnetic energy in the vicinity of metallic nanostructures opens a range of possibilities for fundamental studies and manipulation of light-matter interaction.1–3 The large local field intensities and subdiffraction confinement associated with the surface plasmon resonances in such nanocavities is particularly promising for strong coupling with light emitters. In the simplest form, the coupling strength (g) is tuned via the cavity mode volume (V), number of emitters (N) that collectively couple to the nanocavity (if many) and their oscillator strength (f), 

\[ g \propto \sqrt{N/V}. \]

At the extreme limit, i.e., when the coupling between plasmons and emitters exceeds the total damping rate of the system, the strong coupling regime emerges with the formation of new hybrid quasi-particles, plasmon-exciton polaritons (plexcitons for short). The associated excitonic non-linearities and ultrafast energy exchange enable their active high-speed control, which is important for fundamental science and practical all-optical information processing technologies.1,4

Plexcitons can be achieved with various materials, including organic semiconductors,5–12 quantum dots,13,14 quantum wells,15 carbon nanotubes16 and transition metal dichalcogenides.15,17,18 For plasmonic nanocavities, it is common to implement structures supporting localized surface plasmons (LSPs) such as nanoshells,9,14 nanoprisms,12,19 disks,7 spheres,8 nanorods8,10,18 and dimers.11,20 Owing to the ultrasmall mode confinement, even a single plexciton regime under room temperature conditions could be reported.5,13,20 In addition to localized modes, more spatially extended and propagating plexcitons are considered promising for the coupling of distant emitters22 and large spatial coherence of light emission.21 One attractive design involves the collective resonances in one- and two-dimensional periodic metallic structures.4,16,23,24 Due to their hybrid plasmonic–photonic character they possess reasonably high-quality factors (Q ~ 100) and thus longer lifetimes compared to LSPs. Furthermore, the overall plasmon/exciton/polariton composition of the formed plexcitons enables a straightforward tunability of nanoscale confinement, optical non-linearities and quality factors.

Another degree of optimization is possible via tailoring plexiton band structure that defines the relaxation dynamics (via the excitonic part) and anisotropy of the plexciton effective mass (photonic component). These characteristics are crucial for the improved design of macroscopic coherent states, nanoscale lasing,23 long-range and directional energy transport.25 Despite the fundamental and technological implica-

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To investigate the propagation features of plexcitons in 2D plasmonic crystals, we designed and fabricated a sample schematically shown in Figure 1a. It consists of a glass substrate, periodically arranged plasmonic particles (nanodisks or nanorods), supporting LSPs (array area $100 \times 100 \mu m^2$), and a thin but dense layer ($\sim 40−50$ nm) of aerosol-jet printed polymer-wrapped (6,5) single-walled carbon nanotubes (CNTs) covered by a 250 nm PMMA film that homogenizes the dielectric environment (see the Supporting Information for details of sample fabrication). In contrast to our previous studies on plexcitons with a relatively thick 300 nm CNT layer,16 we employed a thinner but denser and homogeneous printed CNT layer that ensured a similar degree of collective coupling between the plasmonic crystal and CNTs. The plexciton generation scheme involves laser excitation of the randomly, in-plane oriented carbon nanotubes at a position $S \mu m$ from the edge of the plasmonic crystal. The typical absorption and emission spectra of noncoupled (6,5) single-walled carbon nanotubes are shown in Figure 1b (see the photoluminescence-excitation map in the Supporting Information, Figure S1). Due to their small Stokes shift, the photons emitted from the photoexcited CNTs will be absorbed upon in-plane propagation (over $5 \mu m$) and only those with wavelengths above $\sim 1050−1100$ nm can reach the plasmonic crystal and excite plexcitons. In this configuration, the radiative decay of propagating plexcitons is less prone to the distortion imposed by the laser excitation profile.

Due to the hybrid plasmonic–photonic nature of the modes occurring in plasmonic crystals, they are intrinsically mediated by the LSPs of the constituting particles. To test the potential impact of the particles’ aspect ratio on the plexciton propagation characteristics, different structures were fabricated, such as nanodisks ($D = \sim 165$ nm), and two types of nanorods.
with a length \( \times \) width of 380 \( \times \) 180 nm (“small”) and 620 \( \times \) 200 nm (“large”), as shown in Figure 1c. The height was fixed to 25 nm and periodicity along X and Y directions was set to 600 and 765 nm, respectively. The size of the particles (which tunes LSPs spectral position) and their periodicity (which defines the photonic modes, i.e., diffraction orders)\(^{34}\) were tailored to support high-quality modes extending along the Y-axis and spectrally close to the excitonic transitions of the (6,5) CNTs. At the same time, the generation of plexcitons propagating along the X-axis was less efficient, due to the large detuning between the longitudinal LSPs and the associated diffraction orders (see Supporting Information, Figure S2).

Upon coupling of the carbon nanotubes to the plasmonic crystals, the formed plexciton states are mostly defined by the dispersion relation of the diffraction orders, as shown in Figure 1d. To reconstruct the band structure, the coupling strengths propagating along the X-axis and spectrally close to the excitonic transitions of the (6,5) CNTs. At the same time, the generation of plexcitons propagating along the X-axis was less efficient, due to the large detuning between the longitudinal LSPs and the associated diffraction orders (see Supporting Information, Figure S2).

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line in Figure 4a) help to gain further insights into the wavelength dependence of the propagation, as shown in Figure 5a. For the $\lambda = 1050$–1200 nm spectral range, one can clearly see the increased propagation for longer wavelengths. It is
important to note that although beyond this range (\( \lambda > 1200 \) nm) plexcitons seem to decay faster, the trend is only apparent due to the lower plexciton population that follows the emission spectrum of CNTs. As for the angular distribution of the plexciton radiative decay, it is mostly dominated by the state associated with a single \((0,+1)\) di
correlates with the higher photon fraction of plexcitons for shorter/positive rods) show similar trends. Slight deviations are evident at the corresponding velocities and photon fractions of the plexcitons estimated from the coupled-oscillator model, as shown in Figure 5c. Note that although the energy flow, and thus plexcitons group velocity is directed into the plasmonic crystal, the phase velocity (characterized by the emission angle) can be along \((\lambda < 1170 \) nm) or in the opposite \((\lambda > 1170 \) nm) direction. Comparable hyperspectral and angular emission features are observed for nanodisk and large nanorod arrays (see Supporting Information, Figures S6 and S7). Additional simulations of local field distribution (Figure 5b) and far-field emission patterns (Figure 5d) show an excellent agreement with the experimental data.

In order to quantify the plexciton dynamics and spatial coherence of light emission, first, we estimated the group velocity\(^{35}\) of the plexcitons \(v_g(k) = \frac{1}{\hbar} \frac{dE}{dk}\) from their dispersion along the Y- and X-axes as a function of k-vector (Figure 6, parts a and c). In addition, to improve quality of the calculations and as a guide to the trends, we included the corresponding velocities and photon fractions of the plexcitons estimated from the coupled-oscillator model that was fitted to the experimental dispersions. One can clearly see that the absolute values differ significantly for the two orthogonal directions, with velocities reaching the speed of light in a medium \((c/n, \text{with } n = 1.5)\) for the dominant propagation direction (Y-axis). This increase in the group velocity correlates with the higher photon fraction of plexcitons for negative k-vector values (or angles in Figure 5c). Surprisingly, all three nanoparticle geometries (i.e., nanodisks and nanorods) show similar trends. Slight deviations are evident at shorter/positive k-values for the large nanorod plexcitons that are more matter-like due to their higher admixture of localized surface plasmons (Figure 6a). Further, the propagation distances are calculated from the group velocities and dispersion linewidth \(\Delta E\) of the plexciton mode (i.e., corresponding to lifetime, \(\tau = 2\hbar/\Delta E\)),\(^{36}\) as shown in Figure 6, parts b and d. Here again the larger propagation lengths correspond to the plexcitons with higher photon fraction due to the simultaneous contribution of higher group velocity and plexciton lifetime. Owing to the coherent coupling of carbon nanotubes across the plasmonic crystal via extended plasmon-photonic modes, the spatial coherence of light emission can be deduced from the dispersion linewidth \(\Delta k\) as \(L(k_x, k_y) = 2/\Delta k_y\).\(^{36}\) A very good agreement between coherence and propagation lengths for the Y-axis is observed. The smaller values for the array consisting of large nanorods relate to their shorter lifetime (see Supporting Information, Figure S7a). As for the orthogonal direction, the discrepancies appear for all nanoparticle arrays at small k-vectors, most likely originating from the plexciton energy relaxation and/or the spatial extension of the excitation region seen in Figure 4a.

Given the very good agreement between group velocities calculated from the experimental data and the coupled-oscillator model, we can easily generalize our approach for all in-plane directions (see schematics in Figure 6e). To facilitate the calculations and for clarity, the polar plot was chosen with \(k_\parallel\) (in-plane k-vector component) and \(\varphi\) (polar angle) coordinates that define the corresponding Cartesian projections: \(k_x = k_\parallel \sin(\varphi)\) and \(k_y = k_\parallel \cos(\varphi)\). First, the group velocities in Figure 6f show a complex direction and k-vector dependence reaching \(c/n\) values mainly along the Y-axis as discussed before. This ballistic motion of plexcitons with several micrometers propagation distance are of high practical importance for devices where the exciton diffusion is a main transport mechanism (i.e., with a typical diffusion length about tens or hundreds of nanometers).\(^{35}\) Furthermore, our findings can be easily generalized beyond the carbon nanotubes to other materials that support strong coupling regime. Second, the propagation speed is connected to the effective inertial
mass $^{35}$ of the plexcitons $m_{\text{eff}}(k, \varphi) = \hbar^2 k \left( \frac{dE}{dk} \right)^{-1}$ and shown in Figure 6h (normalized to the electron mass $m_e$). The very low mass (7 orders of magnitude lower than $m_e$) highlights the great potential of plasmonic crystals to reach low-threshold plexcitonic $^{33}$ or plasmon-polariton $^{37}$ lasing. The critical density of bosons (plexcitons or polaritons) necessary for the condensation in such an extended 2D systems scales approximately as $n \propto m^{-1}_{\text{eff}}$. It is important to note that a stopgap opening in the dispersion is not pronounced in our samples (see Figures 3, S3, S4, and S7). However, for arrays with larger particle polarizability, $^{38}$ it is expected that the stopgap will appear leading to a higher effective mass at the band edge.

Apart from these anisotropic properties of effective mass and velocity, it is also advantageous to calculate direction and propagation speed for plexcitons at specific wavelengths. Toward this end, the velocity was deduced for several band edge.

A stopgap will appear leading to a higher effective mass (7 orders of magnitude lower than Figure 6h, normalized to the electron mass $m_e$).

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Sample fabrication, characterization, and theoretical analysis, photoluminescence excitation map of the CNT layer, localized surface plasmons of nanodisks and nanorods, angular dispersion (reflectivity and photoluminescence) of samples with large nanorods and nanodisks, and spectrum-integrated and hyperspectral and angular distribution of radiative decay and propagation of the plexcitons (PDF).

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**NOTES**

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**ASSOCIATED CONTENT**

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**AUTHOR INFORMATION**

*Corresponding Authors

(Y.Z.) E-mail: yuriy.zakharko@pci.uni-heidelberg.de, yuzak@fysik.dtu.dk.

(J.Z.) E-mail: zaumseil@uni-heidelberg.de.

**ORCID®**

Yuriy Zakharko: 0000-0001-8087-0951
Jana Zaumseil: 0000-0002-2048-217X

**Present Address**

*Department of Physics, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
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