Optical Observation of Plasmonic Nonlocal Effects in a 2D Superlattice of Ultrasmall Gold Nanoparticles

Hao Shen, † Li Chen, † Lorenzo Ferrari, ‡ Meng-Hsien Lin, § N. Asger Mortensen, ¶ Shangjr Gwo, § and Zhaowei Liu * †, ‡, §

† Department of Electrical and Computer Engineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0407, United States
‡ Materials Science and Engineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0418, United States
§ Department of Physics, National Tsing-Hua University, Hsinchu 30013, Taiwan
¶ Department of Photonics Engineering, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

Supporting Information

ABSTRACT: The advances in recent nanofabrication techniques have facilitated explorations of metal structures into nanometer scales, where the traditional local-response Drude model with hard-wall boundary conditions fails to accurately describe their optical responses. The emerging nonlocal effects in single ultrasmall silver nanoparticles have been experimentally observed in single-particle spectroscopy enabled by the unprecedented high spatial resolution of electron energy loss spectroscopy (EELS). However, the unambiguous optical observation of such new effects in gold nanoparticles has yet not been reported, due to the extremely weak scattering and the obscuring fingerprint of strong interband transitions. Here we present a nanosystem, a superlattice monolayer formed by sub-10 nm gold nanoparticles. Plasmon resonances are spectrally well-separated from interband transitions, while exhibiting clearly distinguishable blue-shifts compared to predictions by the classical local-response model. Our far-field spectroscopy was performed by a standard optical transmission and reflection setup, and the results agreed excellently with the hydrodynamic nonlocal model, opening a simple and widely accessible way for addressing quantum effects in nanoplasmonic systems.

KEYWORDS: Surface plasmon resonances, nonlocal effect, hydrodynamic Drude−Lorentz model, 2D superlattice, ultrasmall AuNPs

Plasmonics emerging within the last one to two decades has opened up tremendously new applications owning to its unique capabilities for extreme light control, including nanophotonic lasers and amplifiers, optical metamaterials, or metasurfaces, biochemical sensing, and optical antennas. Recent advances in nanofabrication have successfully shrunk the dimensions of plasmonic device into nanometer or even subnanometer scales, wherein the dynamics and optical response of electrons are subject to intriguing confinement effects. Nanoplasmonic systems, such as sub-10 nm nanoparticles (NPs), NP assemblies such as dimers, or the NP−film system with nanometer to subnanometer spacing, or sharp curvatures, all exhibit abnormal surface plasmon resonances (SPR), where the commonly employed local-response Drude−Lorentz model fails to accurately predict plasmon resonances, and thus, new theories considering electron states as well as electrons interactions to improve and correct classical model, such as QM (quantum mechanism) model, which successfully explain multiple anomalous blue or red shift, especially including the tunneling effect. Another most popular correction, namely, the hydrodynamic Drude−Lorentz model (HDLM), with semiclassical accounts for quantum-plasmonic dynamics, now enables numerical exploration and interpretation of nonlocal plasmon dynamics beyond the classical Drude theory.

Taking single metallic nanoparticle as an example, the classic local optical response of electrons in metals inherently assumes a spatially homogeneous and incompressible free electron gas with an infinite work function (hard-wall boundary). When the size of the nanoparticle drops to sub-10 nm scales, the tight confinement of the electrons promotes the importance of nonlocal quantum-pressure effects as semiclassically accounted for in the HDLM. Nonlocal dynamics influences the spectral position of localized surface plasmon resonance (LSPR), being commonly blueshifted for noble metals with high work.
functions, while redshifts may result when quantum-pressure effects are dominated by pronounced quantum spill-out.48 The theoretical prediction of such quantum nonlocal response in silver (Ag) NPs has been proved by multiple experiments carried out with electron energy loss spectroscopy (EELS).49–52 Unfortunately, such nonlocal effects are inevitably difficult to observe in NPs made by gold (Au, a much more attractive plasmonic material for applications due to its chemical stability and biocompatibility), because the potentially large blueshifts of the LSPR signal would be superimposed on even stronger spectral signatures associated with interband transitions of Au. In addition, acquiring a clear optical spectrum from single sub-10 nm particle is still very challenging, since the small optical dipole moment makes the optical scattering signal too weak to be detected.

Herein, we present a new quantum nanosystem, a superlattice monolayer formed by monodispersed ultrasmall Au NPs, with which the nonlocal effects were successfully detected in a traditional optical-spectroscopy system. The Au NPs are chemically synthesized and stabilized with a thin molecular shell, and then self-assembled to a uniform 2D hexagonal Bravais lattice monolayer, with Au NPs controllable in size (diameter <10 nm) and gap (~1.22 nm). Taking advantage of a large number of NPs in the monolayer and the strong
plasmonic couplings between NPs, the LSPRs are spectrally shifted away from the interband-transition region, thereby allowing quantum-plasmonic effects (nonlocal effects) to exhibit clearly in the optical response. In our experiments, we found that the optical spectrum dramatically blueshifts compared with classical Drude–Lorentz model, while fully agreeing with the HDLM-based nonlocal theory. Our work represents pure optical confirmation of quantum-originating nonlocal effects for an ordered system of completely sub-10 nm system in terms of diameter size of NPs and interspace length between NPs. This new foundation in our understanding of sub-10 nm Au NPs is opening up potential applications ranging from 2D/3D quantum metamaterials to an optics based sensor and detector.

Results. Experimental Demonstration: Fabrication and Optical Characterization. Single-crystal Au NPs are chemically synthesized in toluene and stabilized with a thin molecular shell of dodecanethiols (inset of Figure 1a). By means of a self-assembling process detailed in Section 1 of Materials and Methods, the Au NPs are coated on a quartz substrate into a monolayer with the in-plane symmetry of a 2D hexagonal Bravais lattice. Figures 1a and b show respectively a schematic representation and a scanning electron microscope (SEM) image of the Au NP monolayer, which can be distinguished by the naked eye from the bare quartz substrate due to its characteristic violet color appearance (inset of Figure 1b).

The accurate geometrical parameters, including Au NPs diameter and the interparticle spacing between Au NPs, are measured by means of a high-resolution scanning transmission electron microscope (STEM) (Figure 2a). The average particle diameter (obtained from an arbitrary ensemble of 600 randomly chosen NPs) of the three samples is 4.32, 5.64, and 6.45 nm, respectively, and the size distributions are restricted within a narrow (<1 nm) fluctuation range (see Figure S1 of Supporting Information for the size distributions). The interparticle gap is measured to be 1.22 nm ± (≤0.1 nm) from more than 200 sampling locations of each monolayer samples. The stiffness and the chemical binding force of the dodecanethiol shell stabilize around the particle surfaces, maintaining rather well-controlled and constant gaps between NPs.

The optical characterization of transmission and reflection spectra was experimentally captured through a Carl Zeiss optical microscope with a broadband halogen lamp and a confocal spectrometer (see Section 2 of Materials and Methods for optical experiment methodology). Each transmission spectrum (black curves in Figure 2b, c, and d) exhibits a characteristic minimum transmittance (“dip”) with an inverted Gaussian-like profile at the vacuum wavelength of 571, 587, and 594 nm, respectively. The corresponding reflectivity spectra (red curves in Figure 2b, c, and d) are accordingly peaked at almost the same spectral locations, and the absorptivity spectra (blue curves in Figure 2b, c, and d) are consequently obtained as \( A = 1 - T - R \), where \( A \), \( T \), and \( R \) stand respectively for absorptivity, transmissivity, and reflectivity. The features observed in the optical spectra can be intuitively understood from the resonant absorption of the incident light, which initialize and sustain collective oscillations of the electron gas of the Au NPs, i.e., LSPRs.

Simulation Demonstration. In order to illustrate the concept of the HDLM-based generalized nonlocal optical response (GNOR) theory and better support the interpretation of our experimental results, we first neglect nonlocal effects and turn to the classical Drude–Lorentz model to simulate the interaction between light and a Au NP monolayer on a quartz substrate with the commercial software COMSOL Multiphysics (see Section 3 of Materials and Method for the classical Drude–Lorentz model simulation setting with COMSOL 4.3b). The colorful background of Figure 3a shows the mapping result of Au NPs diameter-dependent transmission spectrum of a monolayer of Au NPs on quartz, for the case in which the equation of motion of the electron gas in the metal follows the classical Drude–Lorentz model. The transmission is plotted in color scale as a function of the vacuum wavelength (530–700 nm) and the Au NP diameter (2.5–7.5 nm), and the white dashed line is used to highlight the wavelength of...
minimum transmission evolving as the particle diameter is varied. The electric-field distribution of the resonant collective eigenmode is influenced both by the Au NP diameter and by the interparticle gap size, i.e., collective coupled dipolar resonance of the monolayer is overlaid to this simulation plot, they appear blueshifted with respect to the white-dashed line. This confirms that the traditional Drude–Lorentz model cannot accurately predict the behavior of extremely small metallic NPs, and in order to explain our experimental results we must resort to the HDLM. We next include the above-described nonlocal corrections (see Section 3 of Materials and Methods for the principle of HDLM based GNOR theory) and simulate again the transmission of light through such Au NPs monolayer on quartz. In comparison of traditional classic Drude model (Figure 3b II), the dips of transmission, as shown in Figure 3b III, respectively obtained at the vacuum wavelengths of 567, 582, and 591 nm are now remarkably better aligned with the experiments. We attribute the slight discrepancy in spectral peak location and in full width at half maximum (fwhm) to the dislocation of nonperfectly uniform lattice and the misplaced defects in samples, which may potentially induce both spectral shifts and broadening. The Decisive Role of NP Superlattice for Optical Observation. The critical importance of utilizing an ordered monolayer of Au NPs to enable the optical observation of nonlocal effects is illustrated in Figure 4. The LSPR of the Au NPs dispersed in toluene (insert picture in Figure 4a) is completely determined by individual particles due to negligible optical coupling effects. As the NP size decreases, the LSPR is concealed by interband transitions, and therefore its LSPR dependence on particle size can be revealed and further explored (blue dots). As a comparison, no discernible LSPR shift is observed (green dots) in the dispersion of Au NPs in toluene due to the inevitably strong interband absorption.

Conclusion. In conclusion, we have demonstrated a well-controlled monolayer superlattice of ultrasmall Au NPs on quartz substrate, enabling the optical detection of nonlocal effects, which would otherwise be extremely challenging to achieve from individual metallic NPs. By means of optical transmission and reflection measurements, we observed a size-dependent blueshift in the collective resonance of the NP array, as predicted by the HDLM. Unlike EELS, which is based on the electron-plasmon interaction in single NPs, our method directly probes a statistical ensemble-averaged photon-plasmon interaction of ordered ensembles of NPs. Our study further confirms the validity of the HDLM for the design of sub-10 nm scale optical and optoelectronic devices, opening up new possibilities for quantum plasmonic applications.

Materials and Methods. Assembling Process of 2D Superlattice Monolayers of Ultrasmall Au NPs. The superlattice monolayers of ultrasmall Au NPs on quartz substrates are self-assembled via a pull-coating method, adopting the following process: First, the 2 mg of dodecanethiol-stabilized Au NPs powder (AES0287-IXW0108, JCP1176-ECP1080 in nanoComposix, and AuP-06-25 in Ocean Nanotech) was diluted into 2 mL of toluene solvent, slightly shaking to complete dissolution. The Au NPs solution was then water-bath heated to 55 °C and kept during the whole assembling process. Second, the clean quartz substrate, perpendicular to the surface of Au NPs solution, was quickly dipped into Au NPs solution and slowly pulled out at a constant speed of 20 μm/sec. While the toluene rapidly evaporated at the interface of quartz substrate and Au NPs solution, the Au NPs automatically assembled to an ordered structure due to the lowest energy principle. Finally, waiting 5–10 min after pulling-coating, the sample was dried enough and ready to use.

Measurement of Optical Spectrum. The optical scattering spectra were measured in a confocal microspectroscopy system, Carl Zeiss inverted microscope (Axio Observer D1m), and a Czerny–Turner spectrograph (Andor Shamrock 303i). A broadband light source from a halogen lamp passed through a numerical aperture (N.A.) controllable condenser and illuminate the sample at nearly normal incident angle (N.A. = 2237 DOI: 10.1021/acs.nanolett.6b04849 Nano Lett. 2017, 17, 2234–2239
0.1). A direct transmission signal from the samples in the forward direction was collected by an optical objective (50X magnification, N.A. = 0.55) and analyzed by a diffraction grating of 150 lines mm⁻¹ (blaze wavelength at 500 nm) and a charge coupled device (CCD) camera (Andor Newton CCD) equipped inside the Czerny–Turner spectrograph. The confocal configuration was used between microscope and spectrometer, so that specific field of view can be selected for the measurement. The reflection spectrum was captured by the same microscope system with a slightly different configuration. The illumination light and the reflection signal were sent and collected by a same objective. Also, an additional aperture was added to control the illumination light as the normal incident angle in reflection mode to keep the consistency as transmission spectrum.

Electromagnetic Simulations of Optical Spectra. Classical Drude–Lorentz Model. The full-wave numerical simulation for the EM wave transmitting through or reflected by a 2D superlattice monolayer of ultrasmall Au NPs on the quartz substrate was carried out in a three-dimensional x–y–z space by using a commercial available finite-element method, COMSOL Multiphysics (V4.3b). Plane waves with TE mode were incident normally onto one unit cell of a superlattice Au NPs array, where the periodic boundary condition was set to describe the real structure. Two probe ports parallel to sample were respectively positioned at opposite sides of sample plane detecting the reflection and transmission signal. The permittivity of Au is taken from ref 58 (Johnson & Christy, 1972), and the molecular shell was modeled as a dielectric shell with refractive index,59,60 n = 1.5.

Principle of HDLM Based GNOR Theory. Unlike the classical Drude model, in which the dispersion of material is normally accounted for by pure Ohm’s law assuming the permittivity is constant over the entire metallic volume with equation \( \mathbf{J} = \sigma(\omega) \mathbf{E} \), where \( \mathbf{J} \) is the hydrodynamic current density, \( \mathbf{E} \) the electric field, and \( \sigma(\omega) \) the conductivity, the more complicated HDLM, namely, the generalized nonlocal optical response (GNOR), which conversely rely on the effective dispersive permittivity, has been modified in the following equation,36,37

\[
\begin{align*}
\frac{\gamma^2}{\omega(\omega + i\gamma)} \nabla (V \mathbf{J}) + \mathbf{J} &= \frac{i\omega\epsilon_0}{\omega(\omega + i\gamma)} \mathbf{E} \tag{1}
\end{align*}
\]

where \( \gamma \) is the damping constant, \( i \) the imaginary unit, \( \epsilon_0 \) the permittivity in vacuum, \( \omega \) the frequency, and \( \omega_p \) the plasma frequency, the same utilized in the equation of the classical Drude model \( \varepsilon(\omega) = 1 - \omega_p^2 / \omega(\omega + i\gamma) \). The first term in left-hand side of eq 1, describing the integral effects between pressure-driven convective electron flow and disorder- or entropy-driven charge diffusion, indicates the main nonlocal correction. The coefficient \( \frac{\gamma^2}{\omega(\omega + i\gamma)} \), with parameter \( \gamma^2 = \beta^2 + D(\gamma - i\omega) \), where \( \beta \) is proportional to the Fermi velocity \( v_F \) (\( \approx 6.5 \times 10^6 \) m/s, as of fitting parameter) and \( D \) is the charge-carrier diffusion constant (\( \approx 8.8 \times 10^{-4} \) m²/s, as of fitting parameter), combines \( \beta \) related diameter size effect (SE) of NPs and the \( D \) related gap effect (GE) between neighbor NPs.

The diameter size effect associated with \( \beta(\omega + i\gamma) \), which determines the convection length \( \xi_{\text{conv}} \), with the definition \( \xi_{\text{conv}} = \frac{v_F}{\omega} \), strictly links to the size of each NPs. As a consequence, smaller NPs typically at sub-10 nm scales possess stronger nonlocal responded SE. Similar to the convection length of SE, the diffusion length \( \xi_{\text{diff}} = \frac{D}{\sigma(\omega + i\gamma)} \) in the interparticle spacing determined by term \( \frac{D(\gamma - i\omega)}{\omega(\omega + i\gamma)} \) has the same requirement; relying on this, the GE will be detected noticeably.

After incorporating GNOR, the Maxwell equation will be rewritten by,

\[
\nabla \times \nabla \times \mathbf{E} = \frac{\omega^2}{c^2} [\epsilon_D + \xi^2 \nabla^2] \mathbf{E} \tag{2}
\]

where the \( c \) is the constant light speed in vacuum and \( \epsilon_D \) is the Drude dielectric function associated with Ohmic local response (also including the interband effect). The corresponding nonlocal SE and GE will consequently be represented in the optical spectrum, thanks to an average diameter size smaller than 10 nm and a gap size as small as \( \sim 1.22 \) nm in our ultrasmall super lattice AuNPs monolayer system.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b04849.

Size distribution of Au NPs (Figure S1) and principle of quantum size model (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail address: zhaowei@ucsd.edu.

ORCID

Hao Shen: 0000-0002-0063-3153

N. Asger Mortensen: 0000-0001-7936-6264

Author Contributions

H.S. and L.C. contributed equally. H.S and Z.L. conceived the concept. L.C. performed numerical modeling and simulations in details. H.S. prepared the samples and performed optical measurements. M.H.L. and S.G. initiated the sample fabrication. N.A.M. and Z.L. guided the theoretical study. H.S. and L.C. prepared all of the figures. H.S., L.C., L.F., and Z.L. wrote the manuscript. All authors discussed the results and commented on the manuscript. Z.L. supervised the project.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge financial support from a US-Sino-Danish plasmonic network (grant 4070-00157B INP TFJ). The authors thank Yunfeng Jiang for help with STEM characterization.

**REFERENCES**


