J|A|C|S
COMMUNICATIONS

Published on Web 02/14/2003

Light-Induced Coherent Interactions between Silver Nanoparticles in Two-Dimensional Arrays

Serhiy Malynych and George Chumanov*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Received November 22, 2002; E-mail: gchumak@clemson.edu

Silver particles reduced to nanometer dimensions exhibit unique optical properties in the visible spectral range due to the excitation of the collective oscillations of conducting electrons known as plasmon resonances or surface plasmons.[1] The resonance frequency of surface plasmons strongly depends on the size, shape and dielectric environment of nanoparticles, thus providing an effective way for tuning of their optical properties. The optical excitation of plasmon is the most efficient process by which light interacts with matter; in fact, a single silver nanoparticle interacts with light more efficiently than the particle of the same dimension composed of any known organic or inorganic chromophore. Such high efficiency together with the tunability of the optical properties makes silver nanoparticles very attractive for a variety of optical and photonic applications. Especially interesting are one-, two-, and three-dimensional arrays of closely spaced nanoparticles in which short- and long-range interactions between plasmons may lead to new optical properties. Here we describe the light-induced, coherent interaction between silver nanoparticles arranged in two-dimensional arrays. This phenomenon results in the formation of a plasmon mode with an extremely sharp and strong resonance representing the cooperative interaction of several particles with light. The resonance is very sensitive to interparticle distance, incident angle, and the polarization of light.

The extinction spectrum of noninteracting, 100-nm silver particles is characterized by two distinctive features: an intense broad band at 545 nm due to the dipolar component of the plasmon and a somewhat weaker band at 430 nm representing quadrupolar electron oscillations resulting from the phase retardation of incident wave within a single particle (Figure 1, red curve).[1] When such particles form random aggregates, both bands broaden and shift to the red spectral range due to the strong electronic coupling between particles.[2]

In this work, 100-nm silver particles were self-assembled on glass or silicon surfaces modified with poly(vinylpyridine). Poly(vinylpyridine) is an efficient surface modifier for immobilization of metal nanoparticles because it is capable of simultaneous interaction with various substrates via hydrogen bonding and with metal particles through metal−ligand interactions of the nitrogen atom on the pyridyl group.[3] The modified substrates were exposed to a suspension of silver nanoparticles in deionized water at low ionic strength. Low ionic strength is required to maintain substantial long-range electrostatic repulsion between particles and, consequently, for the formation of 2D arrays in which particles are not in direct contact with each other. By changing the exposure time, arrays can be obtained with different density of particles on the surface.[4]

When the average interparticle distance in the arrays becomes comparable to the particles' diameter, the extinction spectrum undergoes dramatic change: a new sharp band appears at 436 nm (Figure 1, black curve). Surprisingly, the electron microscopy revealed no long-range order within the assembly of nanoparticles (Figure 1, inset). Lack of long-range order was further confirmed by two-dimensional Fourier analysis of these images. Because the long-range order does not appear to be an important factor, the sharp band most likely originates from short-range interactions between particles.

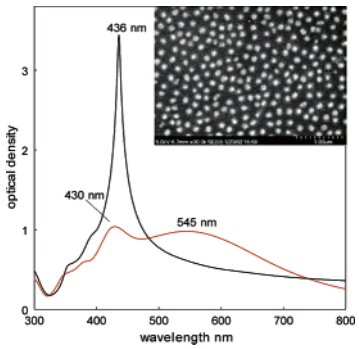

Figure 1. Extinction spectra of 100-nm Ag particles in water (red curve) and the same particles assembled into a closely spaced 2D array imbedded in poly(dimethylsiloxane) (PDMS) (black curve). Inset: electron microscopy image of this 2D array. The spectrum (black curve) corresponds to the image in the inset. Measurements of the 2D array were performed in the dry state. Placing the film in water resulted in the red shift of the maximum to 439 nm without noticeable change in the shape of the spectrum.

The excitation of plasmon resonances leads to the oscillating local field surrounding silver nanoparticles. The local field extends from the particle surface to a distance smaller than the wavelength of light (near field) and is enhanced as compared to the field of the incident light. When particles are closely spaced so that the local fields from individual particles overlap, the near-field interaction takes place, and the system becomes coupled. This coupled system has a new optical mode, termed cooperative plasmon mode (CPM), that is characterized by coherent electron oscillations in adjacent particles and is represented by the sharp band observed in the extinction spectrum of the two-dimensional arrays. The excitation of the CPM corresponds to the simultaneous interaction of several particles with light; however, it is not clear what the coherence length is or what the minimum number of particles required to establish the observed narrow band is.

It was reasoned that the coherent coupling between nanoparticles could be effectively controlled by varying the interparticle distance in the array. For this purpose, the nanoparticle array was imbedded into a transparent elastomeric film of PDMS.[5] The film was continuously stretched along two axes, and the extinction spectra were simultaneously measured (Figure 2, inset).

As the film is stretched to different degrees, the intensity of CPM resonance rapidly decreases, and a new band appears at approximately 505 nm. The color of the film changes from intense yellow to pale pink. Remarkably, after stretching by only 50% the sharp band nearly disappears, and the extinction spectrum of the film resembles that of noninteracting particles where bands at 430 and 505 nm represent the quadrupolar and dipolar components of the surface plasmon of individual particles, respectively. The strong

10.1021/ja029453p CCC: $25.00

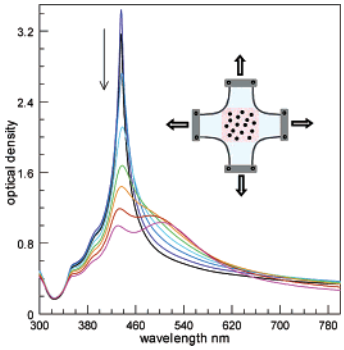

Figure 2. Extinction spectra of 2D array of Ag nanoparticles imbedded into PDMS as a function of the degree of stretching. All curves are normalized to the same number of particles probed by the beam. Red curve represents the film stretched 50% from its original, nonstretched state (black curve). Inset: schematic of the biaxial stretching.

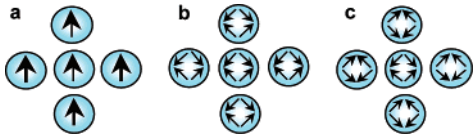

Figure 3. Model for dipolar (a) and quadrupolar (b, c) couplings between plasmon resonances in nanoparticle array. Arrows indicate the direction of the electric polarization induced by incident light. Repulsive (b) and attractive (c) quadrupolar interactions are shown.

distance dependence of the CPM resonance further emphasizes the near-field character of the coupling.

A distinctive feature of the CPM resonance is that it evolves gradually from the quadrupolar component of the plasmon for noninteracting particles (Figure 2). As the interparticle distance becomes smaller, the quadrupole band progressively increases in intensity and sharpens, whereas the dipole band gradually disappears. Such behavior indicates that the coupling between these particles has quadrupolar character. The predominance of quadrupolar coupling can be qualitatively explained by the following symmetry considerations. Each silver particle in the array is surrounded by several closely spaced neighbors. Ideally, each particle is indistinguishable and should interact in the same way with all its neighbors. Consider one particle symmetrically surrounded by four neighbors (Figure 3). In the case of the dipolar coupling (Figure 3a), particles that are lined-up in the vertical direction interact head-to-tail, whereas particles lined-up in the horizontal direction experience different, head-to-head and tail-to-tail interactions. Clearly, the requirement for each particle to interact with all neighbors in the same way is not fulfilled, resulting in the dipolar coupling being symmetry-forbidden for this arrangement. However, for the quadrupolar component of the plasmon, the interaction between particles becomes the same in both directions (Figure 3, b and c).[6] It will remain the same even if more particles are added to the system, forming a two-dimensional square lattice The quadrupolar coupling is symmetry-allowed in this case. Two possible couplings can be envisioned: repulsive (Figure 3b) and attractive (Figure 3c). In both instances, the electron oscillations in adjacent particles are coherent, being in-phase for repulsive and alternating in-phase/out-of-phase for attractive couplings. Conceivably, the arrangement of particles with six close neighbors will support hexapolar coupling. The general outcome from this rationale is that a two-dimensional arrangement of silver nanoparticles, in which each particle is surrounded by more than two in-line neighbors, favors multipolar coupling of plasmon resonances over the dipolar one. Yet, it is necessary to take into account that the induced dipole−dipole interaction is 4 orders of magnitude stronger

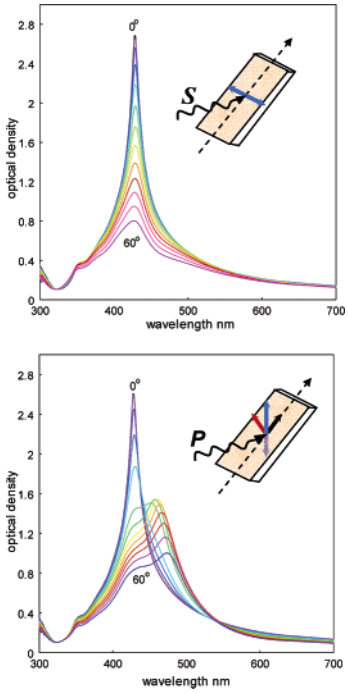

Figure 4. Extinction spectrum of the silver nanoparticle array as a function of incident angle for s- and p-polarized light. All curves are normalized to the same number of particles probed by the beam. Insets: blue arrow indicates the direction of the electric vector of incident light. Red and black arrows indicate normal and in-plane components of electron oscillations in nanoparticles.

at a given distance than the induced quadrupole-quadrupole interaction[7] that, in turn, is much stronger than the induced hexapole−hexapole interaction. Weakness of the hexapolar interaction on one hand and the symmetry restriction for dipolar coupling for normal incidence of light on the other hand results in quadrupolar coupling being the optimum plasmon coupling in two-dimensional arrays of silver nanoparticles.

The coherent character of the coupling was further concluded from the extinction measurements for light polarized perpendicular (s-polarized) and parallel (p-polarized) to the plane of incidence as a function of the incident angle (Figure 4). As the angle of incidence increases from 0° (normal incidence) to 60°, the intensity of CPM resonance decreases for both s- and p-polarized light. For p-polarized light, an additional band appears in the 460−470-nm spectral region. The decrease in intensity of CPM resonance with incident angle results from the dephasing of the electron oscillations in adjacent particles. At oblique angles, the adjacent particles experience different phases of incident wave and thus less efficient coherent coupling. Whereas for s-polarized light, the electric vector of the radiation at any incident angle is parallel to the plane of the array thereby exciting only in-plane electron oscillations, an additional normal component appears at oblique incident angels for p-polarized light. This component of the electric vector excites electron oscillations normal to the plane of the array. The normal oscillations are coupled too; however, the character of the coupling is dipolar rather than quadrupolar. Dipolar coupling prevails over the quadrupolar one in this case because the dipole−dipole interaction is stronger and no symmetry restrictions are imposed for normal component of electron oscillations. The growth of the new band in the 460−470 nm spectral region with increase of the incident angle is an indication for the dipolar coupling of the electron oscillations normal to the plane of the array (Figure 4).

The coherent coupling in silver nanoparticle arrays is a very efficient process. A remarkably high extinction of light (ca. 2000-

fold at the maximum) was measured for only one monolayer of coupled nanoparticles (Figure 1). An intriguing observation is that the integrated area under the curve in the extinction spectra (total oscillator strength of the system) decreases with the increase of the incident angle (Figure 4). This behavior can be rationalized from two alternative perspectives. At normal incidence, the polarizability of individual particles in the array is enhanced, or at oblique incident angles, the polarizability of the particles in the array is suppressed as compared to noncoupledparticles. The enhancement could result from the fact that each particle experiences the local fields from all neighbors. Because all neighboring particles have the same resonance frequency and oscillate with phase coherency, they mutually enhance each other's polarizability. As the incident angle increases, the particles in the array start behaving more like independent oscillators, and their polarizability decreases, approaching the value for noncoupled particles. In an alternative scenario, the dephasing that takes place at oblique incident angles could hinder the electron oscillations in individual particles, thereby decreasing overall the oscillator strength as compared to the same number of noncoupled particles.

It is important to emphasize that the physical nature of the coherent coupling described here is different from that responsible for optical mode localization in photonic gap materials[8] even though both phenomena result in a sharp resonance in the extinction spectra. Whereas the former is due to the near-field interactions between silver particles, the latter results from Bragg diffraction of light from dielectric periodicities. The following arguments can be used to support the different origin of these two phenomena. First, the coherent coupling was observed for nanoparticle arrays lacking long-range order (Figure 1, inset), in contrast to the requirement for long-range periodicity in the case of Bragg diffraction. Second, the spectral position of the transmission minimum in colloidal crystals, a typical band gap material, depends on the distance between dielectric periodicities in the characteristic way for diffraction phenomena.[9,10] It shifts to the red, retaining essentially the same intensity as the distance increases. On the contrary, the sharp CPM resonance in the coupled arrays of silver nanoparticles experiences hardly any spectral shift with increase of interparticle distance. Instead, a sudden decrease of the intensity is observed due to the steep decline of the near-field interaction between particles (Figure 2).

The coherent coupling of plasmons represents a new class of optical phenomena originated from light-induced, near-field interactions between metal nanoparticles. Further exploration of these interactions will result in the discovery of novel principles of both fundamental and practical importance. A generic approach will be developed on the basis of controlling near-field interaction between metal nanoparticles organized in various one-, two-, and three-dimensional structures to engineer materials and devices with desired optical properties.

Acknowledgment. We thank the National Science Foundation for financial support of this work.

References

(1) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Verlag: Berlin, Heidelberg, 1995.
(2) This phenomenon is well-known and extensively described in the literature, e.g.: (a) Storhoff, J. J.; Lazarides, A. A.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L.; Shatz, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4640. (b) Lazarides, A. A.; Shatz, G. C. *J. Chem. Phys*. **2000**, *112*, 2987.
(3) Malynych, S., Luzinov, I., Chumanov, G. *J. Phys. Chem. B* **2002**, *106*, 1280.
(4) Chumanov, G.; Sokolov, K.; Cotton, T. M. *J. Phys. Chem*. **1996**, *100*, 5166.
(5) Malynych, S.; Robuck, H.; Chumanov, G. *Nano Lett.* **2001**, *1*, 647.
(6) Born, M.; Wolf, E. *Principles of Optics*; Pergamon Press: Oxford, New York, Seoul, Tokyo, 1993; Chapter 13.
(7) Jackson J. D. *Classical Electrodynamics*; J. Wiley & Sons: New York, Chichester, Brisbane, Toronto, Singapore, 1975; p 138.
(8) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059.
(9) Asher, S. A.; Holtz, J.; Weissman, J.; Pan, G. *MRS Bull.* **1998**, *23*, 44.
(10) Foulger, S. H.; Jiang, P.; Ying, Y.; Lattam, A. C.; Smith, D. W., Jr.; Ballato, J. *Adv. Mater*. **2001**, *13*, 1898.

JA029453P