Research Article

Plasmonic Coupling in Three-Dimensional Au Nanoparticle Assemblies Fabricated by Anodic Aluminum Oxide Templates

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We investigated optical properties of three-dimensional (3D) assemblies of Au nanoparticles (NPs), which were fabricated by dewetting of thin Au layers on anodic aluminum oxides (AAO). The NP assembly had hexagonal array of repeated multiparticle structures, which consisted of six trimers on the AAO surface and one large NP in the AAO pore (pore-NP). We performed finite-difference time-domain simulation to explain the optical response of the NP assemblies and compared the calculation results with experimental data. Such complementary studies clearly revealed how the plasmonic coupling between the constituent NPs influenced the spectral response of our NP assemblies. In particular, comparison of the assemblies with and without pore-NPs suggested that strong plasmonic coupling between trimers and pore-NP significantly affected the spectra and the field distribution of the NP assemblies. Plasmonic multi-NP assemblies could provide us new platforms to realize novel optoelectronic devices.

1. Introduction

Nanoplasmonics has surfaced as one of the most interesting and important research topics in recent days. Significant increase of the optical extinction and concomitant sub-wavelength confinement of electromagnetic field enabled us to explore the plasmonic nanostructures for various fields, including high-performance light emitting devices, high-efficiency solar cells, and high-sensitive molecular sensors (e.g., surface-enhanced Raman scattering, SERS) [1–18]. The optical spectra can be largely varied depending on the material and size of the metal nanostructures [1–10]. There has been growing research interest in nanoparticle (NP) assembly, whose optical response can be modulated by controlling the interparticle gap separation and the spatial arrangement of NPs. In this regard, three-dimensional (3D) NP assemblies, where NPs do not lie on a single plane and some of them are above/below the plane containing other NPs, multiple plasmonic coupling is expected to give rise to hybridized plasmon mode formation [1]. Fabrication of artificial nanostructures, however, usually requires high-cost and complicated top-down processes [1–8, 18]. Thus, it is rather difficult to find many examples of experimental studies of 3D NP assemblies.

In this work, we investigated how the plasmonic coupling influenced the optical properties of 3D multi-NP assemblies prepared via honeycomb-shaped pore-array templates, consisting of NP-trimer array and additional NP in the pore. Experimental optical spectra showed characteristic dips in visible range, implying excitation of plasmonic modes. Calculation studies clearly revealed that the 3D arrangement induced unique coupling between constituent NPs. The NP in the pore weakened the interaction between adjacent NP trimers and strongly confined the light at the gap between the trimer and the NP in the pore. Such hybridized plasmon modes dominated the overall optical spectra of our 3D NP assemblies.

2. Experimental

Anodic aluminum oxide (AAO) templates with hexagonally arrayed nanopores were used to fabricate the 3D plasmonic nanostructures. Regular array of nanopores (diameter: 72 nm) formed honeycomb structures with average
3. Results and Discussion

Figures 1(a) and 1(b) show schematic diagrams and SEM images of a typical NP assembly prepared by AAO templates. The Au NPs belong to two groups, as illustrated in Figure 1(a). The first group corresponds to a set of trimers located on the top of the AAO surface and the average diameter of NPs in the trimers is 25 nm. The trimers form an array with hexagonal symmetry due to the characteristic morphology of AAO [9, 19]. The second group contains large-sized NPs located in the nanopores of the template. These NPs also have hexagonal symmetry and the average diameter is 60 nm. The average diameter and average depth of the nanopore in AAO are 72 nm and 60 nm, respectively. The thickness of AAO is 70 nm and nonoxidized aluminum layer remains under the AAO layer.

Figures 2(a) and 2(b) show the top-view (xy-plane) and cross-sectional (xz-plane) diagrams of our NP assembly used for the FDTD simulations, respectively. As described above, two kinds of NPs are present in the assembly. The area depicted in Figure 2(a) represents the unit cell of our samples. In the simulation, the light polarization was along the x-axis. To clarify the role of the NP in the nanopore, simulations were also performed for the identical structures without the large NPs in the pores. Hereafter, the large NP in the pore will be called a pore-NP.

Figures 3(a) and 3(b) show experimental and simulative optical reflectance spectra, respectively. In the calculation, the following three types of NP assemblies are compared as shown in Figure 3(b): trimers only, pore-NPs only, and trimers with pore-NPs. The results in Figure 3(b) are obtained for linearly polarized light along the x-axis and the simulation data for the y-polarization are almost invariant. The trimers belong to the $D_{3h}$ point group, and the plasmon hybridization does not have polarization dependence [6]. The calculation reveals that all the NP assemblies have similar optical spectra with broad dips in the wavelength range from 400 nm to 600 nm. Although there is overall shift of the spectra, the experimental result looks similar to the calculation results. Thus, the shape of the spectra alone cannot clarify the physical origin of the optical characteristics.

To achieve better understanding of the 3D arrangement of NPs, optical spectra of an isolated heptamer consisting of seven Au NPs with identical size were studied. The six outer NPs form hexagon (oNPs) and the last one is located at the center of the hexagon (cNP). The diameter of all the NPs is 100 nm and the gap between the oNPs is 10 nm. The calculation results show double peaks in the extinction cross-section, as shown in Figure 4(a). At the local maxima of the extinction spectra, the electric field components along the light polarization direction of all the NPs have the same sign. In contrast, the field components of some NPs have the opposite sign at the local minima of the spectra. It has been known that the bonding (super radiant) mode and the antibonding (subradiant) modes are formed at the former cases and the latter cases, respectively [1-4]. Figure 4(a) also shows the extinction spectra of the heptamers whose cNP is moved upward or downward from the plane containing other six heptamers, as illustrated in Figures 4(b) and 4(c). The double peaks, the signature of the Fano resonance, become less noticeable when the vertical displacement of the central NP is increased. This means that increase of the cNP’s vertical displacement weakens the coupling between oNPs and cNP. Thus, the result in Figure 4(a) clearly shows that cNP plays a key role in the Fano resonance [2]. It should be noted that the two peaks exhibit distinct dependence on the vertical movement of cNP. The position of the short-wavelength peak does not change much, and the intensity is slightly increased, since the interaction between oNPs
Figure 2: (a) Top-view (xy-plane) and (b) cross-sectional view (zx-plane) of the unit cell in our NP assembly used for FDTD optical simulations.

Figure 3: (a) Experimental and (b) simulation results of the optical reflectance of NP assemblies.

is much stronger than that between cNP and oNPs. In contrast, the long-wavelength peak moves toward short-wavelength region and its intensity is reduced, because the interaction between cNP and oNPs is stronger than that between oNPs in the specific mode. This suggests that the dipole interaction between the constituent NPs should depend not only on the interparticle spacing but also on the direction between the dipoles in the 3D configuration. The results in Figure 4(a) show that the 3D arrangement of NPs can provide an alternative way to modulate the optical spectral response of the plasmonic NP assembly. The considered NPs have somewhat simple structures, but this study gives us an insight into understanding more complicated 3D NP assemblies.

If oNPs in the heptamer are replaced with trimers and cNP is moved along the vertical direction from the plane containing oNPs, then such 3D NP structure will look similar to our NP assembly (see Figures 1 and 2). In addition, our 3D NP assembly consists of multisized NPs. The size of pore-NP (diameter: 60 nm) is larger than that of NPs in the trimers (diameter: 25 nm). The degree of the interaction between NPs depends on both the interparticle spacing and the NP diameter. Large-sized NP can enhance the coupling strength due to the large dipole moments. Our NP assembly forms a hexagonal array with the aid of the periodic AAO template. Thus, NPs can interact with NPs in nearby unit cells as well as NPs in an identical unit cell. The dielectric constant of AAO (alumina) is somewhat large, and hence the electric field due to pore-NP is confined in the nanopore. As a result, the interaction between neighboring pore-NPs is not so strong enough to cause serious array effects. In contrast, the trimers in adjacent unit cells are located so close that they can induce notable coupling.

Figures 5(a) and 5(b) show top-view (xy-plane) electric field distribution of the NP assemblies with and without pore-NPs, respectively (wavelength of incident light: 633 nm). The field map is obtained at the plane containing the center of NPs in the trimers. The strong field confinement is clearly seen at the gap between NPs of the trimers. In particular, the dipole-dipole interaction is much stronger between NPs located along the light polarization (i.e., x-axis) [1]. At the gap between NPs placed perpendicular to the light polarization (i.e., y-axis), the dipoles of the neighboring NPs are oppositely directed, and hence the superposed field intensity is very small. Field enhancement is also seen between the neighboring trimers, which are placed along the x-axis.

The existence of pore-NPs drastically influenced the field distribution. Overall field intensity in Figure 5(a) is smaller than that in Figure 5(b). This indicates that the plasmonic coupling between NPs becomes weak due to pore-NPs. Brandl et al. theoretically investigated the hybridized plasmonic modes of trimers and predicted multipolar...
resonances [6]. Alegret et al. fabricated Ag NP trimers using electron beam lithography and experimentally observed the hybridized plasmon modes [7]. In both of these studies, in-plane symmetry adapted coordinates (SACs) for allowed dipolar modes of trimers can be found. The in-plane SACs are classified in two types: one with vanishing total dipole moment and the other with a finite moment. The latter is known to dominate the optical response and belongs to the $E'$ representation of the $D_{3h}$ point group [7]. The $E'$ SACs are twofold degenerate, and they are called bonding (low-energy) and anti-bonding (high-energy) dipolar oscillations. The dipole configuration in Figure 5(a) cannot be found in the $E'$ SACs but that in Figure 5(b) cannot. This indicates that the trimers on pore-NPs behave more like isolated trimers. This is well explained by the reduced field intensity around the trimers, as aforementioned. The NP assemblies without pore-NP, that is, hexagonal array of trimers, exhibit plasmon hybridization modes quite different from the isolated trimers, due to the strong coupling between the neighboring trimers.

The cross-sectional filed distributions of the NP assemblies with and without pore-NP are shown in Figures 6(a) and 6(b), respectively. As discussed above, the near-field intensity near the pore-NP is strongly confined in the AAO pore due to the large dielectric constant of AAO. Hot spots can be found at the gap between the trimer and pore-NP as well as the pore-NP vicinity. In the NP assembly without pore-NP, strong field can be formed at the gap between adjacent trimers. Comparison of these two distributions shows that the pore-NP weakens the coupling between trimers, as expected from Figures 5(a) and 5(b). The pore-NP has a larger size than the NPs in the trimers, producing strong field nearby pore-NP. The dipole field from the pore-NP is oppositely directed to that from the trimers. As a result, the plasmonic coupling between the trimers is drastically suppressed. This explains well the reason why the reflectance spectrum of our 3D NP assembly looks more or less similar to that of pore-NP array, rather than that of trimer array.

4. Conclusions

We investigated optical properties of 3D Au NP assemblies fabricated with the aid of AAO templates. The unit cell of the NP assembly consisted of six trimers on the AAO surface forming hexagonal shape and one large NP in the AAO pore (pore-NP) under the center of each hexagon. The optical reflectance spectra showed broad dips in the visible range, indicating excitation of resonant plasmonic modes. In order to clarify the plasmonic coupling, we performed FDTD simulations for several NP assemblies, including heptamers (2D and 3D), trimer arrays, and pore-NP arrays. All these results showed that the direction of dipoles in each NP as well as the interparticle gap spacing could influence the optical spectra of the 3D NP assemblies. The plasmonic coupling

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(a) Calculated extinction spectra of 3D heptamers whose central NP is moved along the vertical direction, as illustrated in (b) and (c). The white dashed lines and the red arrows indicate the planes containing the center of oNPs and the direction of the incident light, respectively.}
\end{figure}
Figure 5: Top-view (xy-plane) electric field distributions of the 3D NP assemblies (a) with and (b) without pore-NPs (wavelength of incident light: 633 nm).

Figure 6: Cross-sectional view of the field distributions in the 3D NP assemblies (a) with and (b) without pore-NPs.
between trimers and pore-NP dominantly affected the optical properties and the field distribution of our 3D NP assemblies.

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