Enhancement of self-assembly of large (>10 nm) gold nanoparticles on an ITO substrate

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Received March 24, 2014; accepted April 10, 2014; published online May 13, 2014

Densely arraying gold nanoparticles (AuNPs) immobilized on substrates is still a challenge. For the arraying, surface modification of AuNPs with alkanethiols is a key technology. However, if the particle size is larger than 20 nm, short-chain alkanethiols have very weak interparticle interaction such that self-assembly is not realized, whereas long-chain alkanethiols have very strong interaction such that self-aggregation is induced in solution. One solution is their combination. Eventually, a HexT:DodT = 4:1 mixture gave a dense array of 55 nm AuNPs on an ITO substrate with a coverage of approximately 80%. Our approach provides high-performance plasmonic optics with a resonance wavelength of more than 700 nm. © 2014 The Japan Society of Applied Physics

G old nanoparticle (AuNP) two-dimensional (2D) arrays have been attracting much attention as plasmonic substrates because they localize light below diffraction limits and generate enhanced electromagnetic fields in the gap between closely spaced AuNPs owing to the localized surface plasmon resonance (LSPR). To develop plasmonic substrates, much effort has been devoted to fabricating AuNP 2D arrays to date. Top-down methodologies based on lithography techniques, such as nano-space,1) electron beam lithography,2) and consequent thermal dewetting,3,4) are applied to produce 2D arrays of large AuNPs of more than 100 nm diameter with high resolution and accuracy, but require large, expensive equipment and therefore are impractical for large-scale synthesis. In contrast, bottom-up approaches based on external-field-induced self-assembly methods can be used to fabricate dense and large-area 2D arrays with small AuNPs of less than 20 nm diameter.5–13) reports on intermediate-sized AuNPs using resorcinarene tetrathiol14,15) or CTAB16) as surface-capping molecules are limited. However, these self-assembled AuNP 2D arrays are only physiosorbed, and thus lack mechanical durability required for device materials. Another method, the chemical immobilization method through covalent bonds, gives large-area 2D array substrates with high mechanical durability, but essentially lacking high density owing to the repulsion between AuNPs during the immobilization reaction.17,18) To solve these problems associated with fabricating large-area AuNP 2D arrays with high density and mechanical durability, we have recently reported a hybrid fabrication method consisting of three elemental technologies: chemical modification of both the AuNPs with alkanethiol and the surface of the conductive layer with thiol-terminating agents, electrophoresis, and solvent evaporation.19) By the hybrid method, large-area, dense, regular ordered AuNP arrays with high mechanical durability have been achieved and used for catalytic,20) photochemical,21,22) and photocatalytic applications.23) However, similarly to other self-assembly-based methods,5–13) our hybrid method using only one type of alkanethiol could not control well the self-assembly of AuNPs larger than 20 nm and thus failed to give a high coverage of AuNP arrays owing to two essential reasons. One is due to the strong interparticle hydrophobic interaction arising from the increasing number of alkanethiols involved in inducing self-aggregation in solutions rather than self-assembly on the substrate, in the case of alkanethiols bearing long alkyl chains such as C12 and C16 (Fig. 1). The other is due to the weak interparticle interaction that prevents self-assembly between AuNPs, in the case of alkanethiols bearing short alkyl chains such as C6, which form rigid self-assembled monolayer (SAM) on the AuNP surface. To induce self-assembly of large AuNPs suitable for fabricating 2D arrays, we need to design a new type of optimum hydrophobic interface showing moderate interparticle interaction. For that purpose, we focused on a mixed alkanethiol-SAM. Jiang and coworkers have reported that two types of alkanethiol, namely, those bearing short alkyl chains less than C8 and those bearing long alkyl chains, form a homogeneous mixed SAM on the solid surface without phase separation.24) Thus, the combination of long- and short-chain alkanethiols is expected to form homogeneous SAM on large AuNPs, showing that moderate interparticle interaction is suitable for the hybrid method. Note that the combination of the two alkanethiols without a sufficient difference in alkyl chain length resulted in a low coverage of AuNP arrays, e.g., a 45% coverage with the combination of C8 and C12 alkanethiols. Hence, we focused on the combination of C6 and C12 alkanethiols as candidates for mixed alkanethiol-SAM on large AuNPs. Here, we report, using this mixed alkanethiol-SAM functionalization concept (Fig. 1), an improved hybrid method suitable for 55 nm AuNPs to fabricate large-area (1 × 1 cm2), dense (ca. 80%), and regular ordered 2D arrays of AuNPs (Fig. 2).

The aqueous 55 nm Au colloidal solutions were synthesized by the reported seed-mediated growth method.25,26) The extinction spectra of the colloidal solutions are shown in the online supplementary material (available at http://stacks.iop.org/APEX/7/065001/mmmedia). The aqueous colloidal solution of 55 nm AuNPs (15 mL, 0.39 mM) and mixed alkanethiol of hexanethiol (HexT) and dodecanethiol (DodT) with molar ratios ranging from 1:1 to 19:1 in acetone (0.55% v/v in 15 mL) were mixed and stirred at RT overnight. Then, mixed-alkanethiol-capped AuNPs were extracted with n-hexane and purified by sequential centrifugation and redispersion into acetonitrile three times and n-hexane twice.

To avoid the irreversible attachment of alkanethiol-capped AuNPs, we prepared fluoroalkyl-surface-functionalized PMMA cuvettes. Oxygen plasma treatment was carried out prior to functionalizing the walls with fluoroalkyl silane SAM. The surface of each PMMA cuvette was treated with O2...
plasma (50 sccm, 200 W) for 2 min, and then terminated with trimethoxy-(1H,1H,2H,2H-nonafluorohexyl)silane by the vapor method in Ar atmosphere for 1 d at 40 °C in a sealed vessel. Then, the PMMA cuvette was dried using a heat gun for 3 min and used for solution-phase UV–vis–NIR extinction measurement. To observe UV/vis spectra of the AuNP solution with high concentration, a baseline correction method was employed by putting a 2 × 1 mm² slit to the reference side for a double-beam-type UV/vis spectrometer (JASCO V-670). Sonication for 1 min was carried out before taking UV–vis–NIR extinction spectra of mixed-alkanethiol-capped AuNPs with various mixing ratios as a function of gold concentration. All spectra were fitted with Multi-Peak fitting version 2.0 packages in Igor Pro 6.32A. A cubic baseline and two peaks with a Voigt peak function were used to separate overlapping peaks between 500 and 700 nm in the spectra. The goodness of the fitting was characterized by reduced chi-square values, which were in the range of 1.0–1.3.

The effect of mixed alkanethiol-SAM on reducing the interparticle interaction to induce the self-aggregation of large AuNPs was examined by concentration-dependent UV–vis–NIR extinction analyses with various mixing ratios of HexT and DodT. With increasing AuNP concentration in n-hexane, all 55 nm AuNPs used in this experiment showed increasing redshifted shoulder LSPR peaks based on the formation of AuNP aggregates (Fig. 3). The LSPR peak shift of the AuNP aggregates is plotted as a function of the AuNP colloid concentration in Fig. 3(a). DodT-capped 55 nm AuNP colloids show a gradual redshift of the LSPR peak of aggregates from ca. 2.0 × 10⁻² mM and reached saturation at ca. 1.0 × 10⁻¹ mM [Figs. 3(a) and 3(b)], indicating a typical noncovalent interaction-based self-aggregation behavior, similar to that of previously reported DodT-capped 10 nm AuNP colloids. Mixed-alkanethiol-capped 55 nm AuNPs with the HexT : DodT ratios of 2 : 1 and 4 : 1 show the same starting and final LSPR wavelengths of their aggregates arising from the same interparticle distance with the contribution of some content of DodT, but the self-aggregation starts from ca. 5.0 × 10⁻² mM and saturates at ca. 3.0 × 10⁻¹ mM, indicating a lower interparticle interaction, as expected [Figs. 3(a), 3(c), and 3(d)]. In the case of mixed-alkanethiol-capped 55 nm AuNPs with the HexT : DodT ratio of 9 : 1, the LSPR peak of the aggregates gradually redshifted and did not reach saturation in this concentration range, indicating very weak interparticle interaction [Figs. 3(a) and 3(e)]. A similar profile was observed for HexT-capped 55 nm AuNP colloids; the longer LSPR wavelength is based on the shorter interparticle distance with HexT [Figs. 3(a) and 3(f)]. From these results, we found that the mixed alkanethiol-SAM can reduce the interparticle interaction, as expected, and there is an optimal mixing ratio for inducing the efficient self-assembly of large AuNPs.
concentrations, 2.5
© arrays, the interparticle gap distances with HexT and DodT angle X-ray scattering (SAXS) analyses of 10 nm AuNP
1.388. The interdipole spacing was set to 0.5 nm. From our
Fig. 3. Self-aggregation property of 55 nm AuNPs (in n-hexane) with various molar ratios of HexT and DodT. (a) Concentration dependence of peak wavelength of 580–700 nm as a function of molar ratio, (b)–(f) UV–vis–NIR extinction spectra of HexT/DodT-capped 55 nm AuNPs at various concentrations, 2.5 × 10−5, 5.0 × 10−5, 7.5 × 10−5, 1.0 × 10−4, 2.0 × 10−4, 3.0 × 10−4, 5.0 × 10−4, 7.5 × 10−4, 1.0, and 2.0 nM (concentration based on Au atom mole) in n-hexane. HexT : DodT = (b) 0 : 1, (c) 2 : 1, (d) 4 : 1, (e) 9 : 1, and (f) 1 : 0.

The relationship between LSPR wavelength and aggregate structure was investigated by DDA simulation [see online supplementary material (available at http://stacks.iop.org/APEX/7/065001/mmedia)]. The DDA simulation was carried out using the DDSCAT 7.3 code (http://code.google.com/p/ddsca t/). We used simple models consisting of 50 nm AuNPs and n-hexane as ambient medium because of the difficulty in making models taking into account the alkanethiols on AuNP surfaces and the small difference (about 5%) in refractive index among n-hexane (n = 1.388), HexT (n = 1.45), and DodT (n = 1.459). The value reported by Johnson and Christy was used as the refractive index of Au, and the refractive index of the ambient medium (n-hexane) was set to 1.388. The interdipole spacing was set to 0.5 nm. From our previous scanning electron microscopy (SEM) and small angle X-ray scattering (SAXS) analyses of 10 nm AuNP arrays, the interparticle gap distances with HexT and DodT were estimated to be 1.6 and 2.4 nm, and thus roughly equal gap values of 1.5 and 3.0 nm were applied to the simulation, respectively. Extinction spectra of 50 nm AuNP, dimer, and tetramer aggregates with 1.5 and 3.0 nm gaps in n-hexane were calculated under two perpendicularly polarized incident light conditions [see online supplementary materials (available at http://stacks.iop.org/APEX/7/065001/mmedia)]. The calculated extinction spectrum of 50 nm AuNP shows 534 nm LSPR absorption under both incident light polarizations, in accordance with that of the experimental value
[see online supplementary materials (available at http://stacks.iop.org/APEX/7/065001/mmedia)]. In the case of the 50 nm AuNP dimer, the LSPR absorption appears at 616 and 656 nm depending on the interparticle gap distances of 3.0 and 1.5 nm, respectively, with parallel incident light polarization, whereas the LSPR absorption was almost not shifted at 534 nm with the incident light perpendicular to the interparticle axis, similarly to that in previous reports. In contrast, the 50 nm AuNP tetramer, having a highly symmetric aggregate structure, shows almost the same LSPR absorption under both incident light polarizations at 616 and 656 nm depending on their interparticle gaps of 3.0 and 1.5 nm, respectively. These calculated LSPR wavelengths of 616 and 656 nm with 3.0 and 1.5 nm gaps, respectively, roughly correspond to the observed LSPR wavelengths of over 660 nm for HexT-capped 55 nm AuNP aggregates and 620 nm for mixed-alkanethiol-capped 55 nm AuNP aggregates (Fig. 3). Furthermore, the calculated LSPR wavelengths of the tetramer are almost the same as those of the dimer with parallel incident polarization, indicating that 50 nm AuNP aggregates larger than the tetramer show sufficiently strong plasmonic coupling between neighboring AuNPs under unpolarized incident light condition. These calculation results confirm that alkanethiol-capped 55 nm AuNPs self-assemble in n-hexane to form aggregates larger than the tetramer, and their LSPR wavelengths are redshifted depending on the molecular length of surface-capping alkanethiols.

Finally, the effect of mixed alkanethiol was investigated by fabricating and analyzing mixed-alkanethiol-capped 55 nm AuNP arrays. AuNP arrays were fabricated by our hybrid method using mixed-alkanethiol-capped 55 nm AuNPs with various mixing molar ratios of HexT : DodT = 0 : 1, 1 : 1, 2 : 1, 3 : 1, 4 : 1, 6 : 1, 9 : 1, and 19 : 1, and 1 : 0. The fabricated 55 nm AuNP arrays were analyzed on the basis of SEM images, extinction spectra, and SAXS patterns (Fig. 4). SEM observations revealed that the mixed-alkanethiol-capped 55 nm AuNPs gave higher coverage values of 2D arrays than those with only DodT of 38% and HexT of 23%, as expected (Fig. 4(b)). The highest coverage value of 60% was obtained from a 4 : 1 mixing ratio as the optimum ratio (Figs. 4(a) and 4(b)). The formation of a close packing structure of AuNP arrays was confirmed from the SAX patterns and extinction spectra (Figs. 4(c)–(f)). The SAXS patterns of mixed-alkanethiol-capped 55 nm AuNP arrays show the almost same interparticle distance of 3.0 nm [Figs. 4(c) and 4(d)], corresponding very well to the results of extinction spectra of colloidal mixed alkanethiol-capped AuNP aggregates (Fig. 3), revealing that interparticle gap distances are strongly dependent on the long-alkyl-chain thiols. In the extinction spectra of mixed-alkanethiol-capped 55 nm arrays, with the increase in HexT content, the LSPR wavelength redshifted [Figs. 4(e) and 4(f)]. In particular, the AuNP array with the 4 : 1 ratio gave the most redshifted LSPR wavelength. This redshift profile depending on the HexT content coincides well with the averaged coverage value profile observed by SEM [Fig. 4(b)]. Thus, this redshift is considered to originate from the long-range plasmon coupling between large AuNPs with the increased structural regularity based on the optimized interparticle interaction with the mixed alkanethiol-SAM.

In conclusion, we found that the surface functionalization with mixed alkanethiol-SAM can control the self-assembly...
Coverage was found to be large-area and dense 2D arrays of large AuNPs using mixed-alkanethiol-SAM-capped AuNPs succeeded in length of alkanethiol. Finally, the hybrid fabrication method particle distance in the AuNP aggregates on the alkyl chain from more than four AuNPs and the dependence of interparticle distance in the AuNP aggregates is predominantly determined by the long-chain alkanethiol. Although the interparticle distance in the AuNP aggregates is short-chain alkanethiol to long-chain alkanethiol as expected, interparticle interaction is weakened with increasing ratio of mixed-alkanethiol-SAM-capped AuNPs revealed that the property of large AuNPs. Dilution experiments of colloidal mixed-alkanethiol-SAM-capped AuNPs revealed that the interparticle interaction is weakened with increasing ratio of short-chain alkanethiol to long-chain alkanethiol as expected, although the interparticle distance in the AuNP aggregates is predominantly determined by the long-chain alkanethiol. DDA simulation supported the formation of AuNP aggregates from more than four AuNPs and the dependence of interparticle distance in the AuNP aggregates on the alkyl chain length of alkanethiol. Finally, the hybrid fabrication method using mixed-alkanethiol-SAM-capped AuNPs succeeded in fabricating large-area and dense 2D arrays of large AuNPs with a high coverage of over 60%. From SEM observations, the best mixing ratio of HexT and DodT to give the highest coverage was found to be 4 : 1. SAXS analysis and extinction spectra clarified that 2D arrays of large AuNPs maintain the same interparticle distance as the aggregate from colloidal solutions, but show highly redshifted LSPR originating from the long-range plasmon coupling. In this work, we demonstrate that the simple mixed-alkanethiol-capping method can be used to expand the plasmonic applications on the basis of the bottom-up self-assembly of metallic nanoparticles.

**Acknowledgments** We thank the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) for financial support [Grant-in-Aid for Challenging Exploratory Research (K.M., 24650404), Grant-in-Aid for Scientific Research on Innovative Areas “Integrated Organic Synthesis” (K.M., 22106545 and 24106746), and Grant-in-Aid for Young Scientists (K.L., 30455274)], and the Japan Science and Technology Agency (JST) for financial support of e-ASIA JRP. Also, part of this research was supported by the Research Foundation for Opto-Science and Technology, Yazaki Memorial Foundation for Science and Technology, and the Sumitomo Foundation. SAXS measurements were performed at BL40B2, SPring-8, with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Grant Nos. 2010B1744, 2012A1575, and 2012B1705).

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**Fig. 4.** Fabrication of optimized HexT:DodT-capped 55 nm AuNP array. (a) SEM image of optimized 55 nm AuNP array capped with HexT : DodT = 4 : 1 ratio. (b) Averaged large-area coverage of 55 nm AuNP arrays as a function of HexT content. Normalized SAXS patterns (c) and UV–vis-NIR extinction spectra (d) of 55 nm AuNP arrays with various molar ratios of HexT : DodT = 0 : 1, 1 : 1, 2 : 1, 3 : 1, 4 : 1, 6 : 1, 9 : 1, 19 : 1, and 1 : 0. (d) Interparticle distance calculated from SAXS patterns of 55 nm AuNP arrays as a function of HexT content. (f) Peak wavelength of extinction spectra of 55 nm AuNP arrays as a function of HexT content.