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2D Arrays of Gold Nanoparticles Immobilized on Large-area Substrate towards Nanophotonics Applications

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Abstract **-**Near-field light sources made it possible to go beyond the diffraction limit. Innovative nanophotonics offers potential throughout the field of photonics, including industrial applications such as high-efficiency solar cells. These applications require a novel technique for generating not a nanometer-scale point but a large-area (mm^2–m^2) near-field light source. Here, we report the first large-area near-field light source that is densely constructed of uniform-size (1-100 nm) gold nanoparticles (AuNPs) two-dimensionally arrayed with regular interparticle gaps (within 1-3 nm), which eventually has tunable localized surface plasmon resonance (LSPR) bands (600–1100 nm). The light source is attached by means of chemical coating on 1×1 cm^2 substrates such as Au thin film or ITO film on quartz substrates, but there is no limitation on the size.

Keywords**:** Metal Nanoparticle, Plasmonics, Near Field Light, Au Nanoparticle, Nanoparticle 2D array.

1. Introduction

The fabrication of large-area nanostructured materials with tunable properties is crucial for further development of nano- to macro-scale science and technology. Gold nanoparticle two-dimensional (AuNP 2D) arrays (Wang, 2007) exhibit highly enhanced electromagnetic fields called "hot spots", and have thus attracted attention for electronic (Park 2008), optoelectronic (Liao 2010), and highly sensitive sensor materials (Félidj, 2003). In order to tune the intensity of such hot spots, which are generated by coupling localized surface plasmons of metal nanoparticles, it is necessary to control the size, shape, and interparticle distance (Jain 2007).

In the last two decades, two main types of bottom-up approaches of forming AuNP 2D-arrays on solid surfaces have been reported. One approach is organizing AuNP 2D-arrays onto various types of substrates using an external field such as Langmuir (Liao 2010), and etc.. Although these methods have succeeded in producing excellent ordering of AuNP 2D-arrays over large areas with high coverage and few defects, they lack the mechanical strength required for application to device materials. The other approach is chemical immobilization using covalent bonds between AuNPs and substrates (kaminska 2008). Although AuNP 2D-arrays covalently attached to substrates have successfully been produced by various chemical techniques, high coverage and density have not been achieved. To overcome these shortcomings, we propose a hybrid method (Isozaki 2010, Miki 2013, Ochiai, 2013 & 2014,) consisting of three elemental technologies: chemical modification of both AuNPs with alkylthiol and the surface of the Au layer with alkyldithiol; electrophoresis; and solvent evaporation. Our hybrid synthesis method makes best use of the respective advantages of the three technologies: (1) Chemical modification enables

us both to order the AuNPs in hexagonal phase with a correlation to the third neighbors, and hence to tune the plasmonic properties of the AuNP 2D-arrays. The properties are coarse-adjusted by changing the size of the AuNP and fine-adjusted by changing the length of the alkylthiol. (2) Chemical modification followed by annealing immobilizes the AuNP 2D-arrays on the Au layer, attaining sufficient mechanical strength for application to device materials. (3) The combination of electrophoresis and solvent evaporation gives excellent high coverage of AuNP 2D-arrays in comparison with each method.

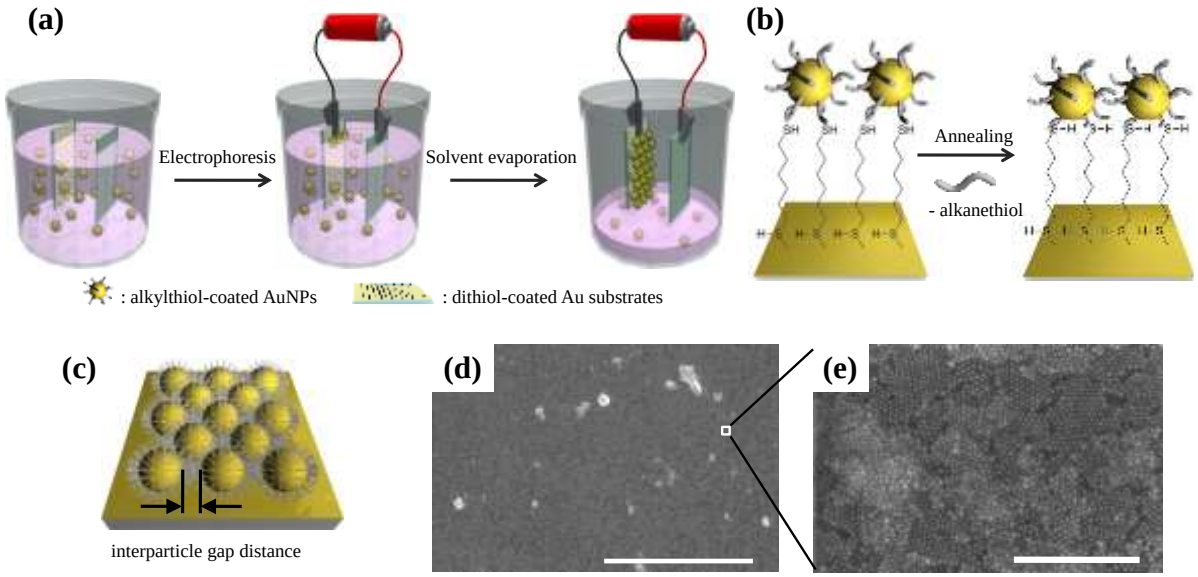

Fig. 1. Schematic illustration of (a) process of fabricating AuNP 2D-arrays, and (b) annealing process to immobilize AuNPs covalently onto substrates. (c) 10Dod 2D-array. (d) SEM images of 10Dod 2D array fabricated on 1,6-hexanedithiol-coated gold substrates by the hybrid method. (e) High magnification.

2. Propose of New Synthesis Method

The hybrid method was performed using alkylthiols as surfactants to assist the self-organization of gold nanoparticles into 2D-arrays. Dodecanethiol-coated gold nanoparticles (10Dod) were prepared by mixing an aqueous colloidal solution of gold nanoparticles (10 nm, 5.7×10^{12} /mL, Funakoshi Corporation) and acetone solution of dodecanethiol (1.7×10^{-2} M), and purified by repeating centrifuging, followed by decanting and redispersion of the precipitated particles into acetone. The substrates for AuNP 2D-arrays were prepared by two steps: (1) deposition of a 10 nm-thick Cr layer and then a 40 nm-thick Au layer onto quartz plates (10×10×0.60 mm) with an E-gun type evaporator; (2) immersion of the gold-coated quartz substrates into 1,6-hexanedithiol solution in EtOH (3.3×10^{-1} M) to functionalize the surface with thiol-group terminations. The thiol-terminated substrate and a PFC (plastic formed carbon, 10×10 ×1.0 mm) plate were immersed into the 10Dod colloidal solution in *n*-hexane (5.7×10^{13} /mL) and used as a cathode and an anode for electrophoresis. Electrophoresis was carried out by applying a voltage of 1.0 V at RT (Figure 1a). The electrophoresis vessel was opened to enhance solvent evaporation proceeding in the vessel until the solution level reached the base of the cathode. To immobilize AuNPs onto the substrates by substitution of the thiols (Nakanishi 1997), the thiol-terminated substrate used as the cathode was then annealed on the hot plate at 50 °C for 24 h, and washed by sonication in *n*-hexane for 1 min (Figure 1b). SEM observation of the substrate showed high coverage (>95%) and high density 10Dod 2D-arrays with hexagonal order (Figure 1d, e). Further SEM observations at several different points revealed that uniform coverage was achieved over the whole area of the substrate. The mechanical strength of the 10Dod 2D-array was investigated by ultrasonication in *n*-hexane having high affinity for alkylthiol-coated AuNPs. SEM observations were carried out at the same positions of the substrates both before and after subjecting the samples immersed in *n*-hexane to sonication for 5 min. The 10Dod 2D-array fabricated by the hybrid method was resistant to sonication. The SEM observations revealed a

moderate decrease of the coverage from 90% to 71%, indicating the retention of 79% of AuNPs after sonication for 5 min.

3. Structural and Optical Characterization

Analyses of the structures and optical properties could clarify the optical tunability of AuNP 2D-arrays by means of the hybrid method. The 2D-arrays of 10Hex, 10Dod, and 10Hexd were fabricated by the hybrid method using hexanethiol, dodecanethiol, and hexadecanethiol as functionalizing agents. SAXS (small-angle X-ray scattering) measurements of the 10Hex, 10Dod, and 10Hexd 2D-arrays showed ordering with a correlation to the third neighbors with the periodic spacings of 9.31, 9.47, and 10.24 nm, respectively (Figure 2a). Considering the hexagonal closed-packed lattice, the distances between the centers of the nearest neighboring particles were calculated to be 10.8, 11.0, and 11.8 nm, which correspond well with those obtained from the SEM images, 10.6, 11.4, 12.0 nm, respectively. SEM images revealed the average size of gold clusters to be 9.00 nm as shown in Figure 2c, thus interparticle gap distances of 10Hex, 10Dod, and 10Hexd 2D-arrays were identified to be 1.59, 2.45, and 2.99 nm, respectively. The interdigitation ratio showed a logarithmic relationship with the carbon chain number of alkylthiols. The extinction spectra of 10Hex, 10Dod, and 10Hexd 2D-arrays exhibited red shifts of surface plasmon resonance (SPR) bands at 630, 606, and 599 nm depending on the interparticle gap distances, respectively (Figure 2b). The shifts of SPR bands from the starting gold nanoparticle solution as purchased showed decay curves with increasing interparticle gap distance, similar to previous reports (Jain 2007, Härtling 2008). Larger AuNP 2D-arrays were also fabricated to demonstrate further optical tunability. SAXS measurements of 30Dod and 50Dod 2D-arrays, made by chemical modification of 30 nm or 50 nm sized AuNP colloids with dodecanethiols, yielded the periodic spacings of 27.8 and 43.9 nm, which indicate distances between the centers of nearest neighboring particles of 32.1 and 50.7 nm, as expected (Figure 2a). SEM images exhibited similar values of interparticle distance, 32.8 and 49.1 nm, to the SAXS results, and interparticle gap distances, 2.38 and 2.70 nm, to those of the 10Dod 2D-array. Extinction spectra of 30Dod and 50Dod AuNP 2D-arrays showed higher red shifts of SPR bands at 894 and 1103 nm than that of the 10Dod AuNP 2D-array, as expected (Figure 2b). These results clearly demonstrate the advantage of the hybrid method, which directly enables us to tune the optical properties of AuNP 2D-arrays which coarse-adjusted by changing the size of the AuNP and fine-adjusted by changing the length of the alkylthiol.

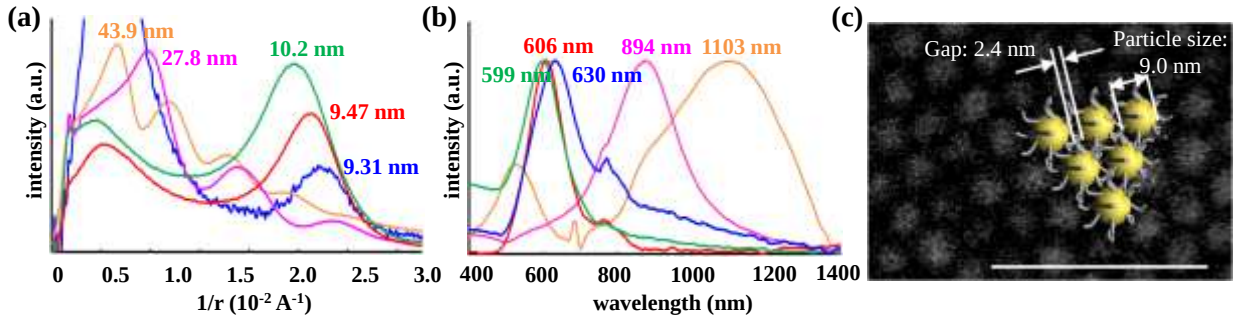

Fig. 2. (a) SAXS patterns and (b) UV-Vis-NIR extinction spectra of the 10Hex (blue), 10Dod (red), 10Hexd (green), 30Dod (magenta), and 50Dod (orange) 2D-arrays. (c) Representative illustration of the 10Dod 2D-array showing interparticle gap distance and particle size. The scale bar is 50.0 nm.

4. Summary

In conclusion, we succeeded in developing a novel hybrid method consisting of three elemental technologies: chemical modification of both AuNPs with alkylthiol and the surface of the Au layer with alkyldithiol; electrophoresis; and solvent evaporation. Our method enabled the easy fabrication of immobilized large AuNP 2D-arrays with high coverage possibly exceeding 95% and high tunability of the plasmonic properties by controlling the size and interparticle distances of AuNPs. We demonstrated the

tunability of the local plasmon resonance wavelength of the AuNP arrays in the range 600–1100 nm. These AuNP 2D-arrays enable the development of nanophotonics applications such as optical sensors having high sensitivity or photo reactors (Pincella, 2013 & 2014) and even for catalsys (Taguchi 2012).

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References

Félidj N., Aubard J., Lévi G. (2003). Appl. Phys. Chem., 82, 3095.

Härtling T., Alaverdyan Y., Hille A., Wenzel M. T., Käll M., Eng L. M. (2008). Optically controlled interparticle distance tuning and welding of single gold nanoparticle pairs by photochemical metal deposition. Optics Express, 16, 12362.

Isozaki K., Ochiai T., Taguchi T., Nittoh K., Miki K. (2010). Chemical coating of large-area Au nanoparticle two-dimensional arrays as plasmon-resonant optics. Appl. Phys. Lett., 97, 221101.

Jain P. K., Huang W., El-Sayed M. A. (2007). On the Universal Scaling Behavior of the Distance Decay of Plasmon Coupling in Metal Nanoparticle Pairs: A Plasmon Ruler Equation. Nano Lett., 7, 2080.

Kaminska A., Inya-Agha O., Forster R. J., Keyes T. E. (2008). Chemically bound gold nanoparticle arrays on silicon: assembly, properties and SERS study of protein interactions. Phys. Chem. Chem. Phys., 10, 4172.

Liao J., Agustsson J. S., Wu S., Schönenberger C., Calame M., Leroux Y., Mayor M., Jeannin O., Ran Y.-F., Liu S.-X., Decurtins S. (2010). Cyclic Conductance Switching in Networks of Redox-Active Molecular Junctions. Nano Lett., 10, 759.

Miki K., Isozaki K., Ochiai T., Taguchi T., Nittoh K. (2013). Gold Nanoparticle 2D-Arrays Chemically Immobilized as Large-Area Near-Field Light Source. ECS Trans. 50, 205-213.

Nakanishi T., Ohtani B., Uosaki K. (1997). Construction of Semiconductor Nanoparticle Layers on Gold by Self-Assembly Technique. Jpn. J. Appl. Phys., 36, 4053.

Ochiai T., Isozaki K., Nishiyama S, and Miki K. (2014). Enhancement of self-assembly of large (> 10 nm) gold nanoparticles on an ITO substrate. Appl. Phys. Express 7, in print.

Ochiai T., Isozaki K., Pincella F., Taguchi T., Nittoh K., Miki K. (2013). Plasmon-resonant optics on an indium-tin-oxide film exciting a two-photon photochromic reaction. Appl. Phys. Express 6 102001.

Park Y.-K., Yoo S.-H., Park S. (2008). Three Dimensional Pt-coated Au Nanoparticle Array: Applications for Electrocatalysis and Surface-Enhanced Raman Scattering. Langmuir, 24, 4370.

Pincella F., Isozaki K., Miki K. (2014). Visible light-driven plasmonic photocatalyst. Light: Science & Applications, 3, e14.

Pincella F., Isozaki K., Taguchi T., Song Y., Miki K. (2014). Selective Two-Photon-Absorption-Induced Reactions of Anthracene-2-Carboxylic Acid on Tunable Plasmonic Substrate with Incoherent Light Source. Journal of Nanoscience and Nanotechnology, in print.

Taguchi T., Isozaki K., Miki K. (2012). Enhanced Catalytic Activity of Self-Assembled-Monolayer-Capped Gold Nanoparticles. Adv. Mater., 24, 6462.

Wang W., Wang Y., Dai Z., Sun Y., Sun Y. (2007). Nonlinear optical properties of periodic gold nanoparticle arrays. Appl. Surf. Sci., 253, 4673.