Loop Formation of Au Nanopaticles Adsorbed on Langmuir Monolayers

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A hybrid monolayer of Au nanoparticles and dioctadecyl-dimethylammonium chloride (DODAC) was formed at the air–water interface. The Au nanoparticles were found to form loop structures. The loops were 0.1–1 µm in size with a width of around 5 nm, and consisted of single particle strings. The loop formation depended on the density of the DODAC monolayers, but not on the size distribution of the particles.

Metal nanoparticles have been intensively investigated in recent years because of their numerous potential applications.[1–6] The most valuable property of metal nanoparticles, electronic quantum confinement, can be used practically only under certain conditions, that is by the formation of quantum dots which need to be regularly arranged one-, two-, or three-dimensionally.[7–10] Highly ordered structures of 2-D assemblies of ligand-stabilized nanoparticles have been spontaneously prepared by drying the respective nanoparticles in a volatile solvent on flat substrates.[7,8] In several systems,[11–14] micrometer-scale ring structures have been obtained from solutions of nanoparticles on solid substrates. This is a very important finding because the mechanism of the formation of these unique assemblies can be used for new strategies to fabricate well-ordered arrays of microsized objects.

In a previous paper,[15] we reported the formation of 2-D arrays of Au nanoparticles using electrostatic interaction between anionic-stabilized Au particles and a cationic amphiphile monolayer which spread on an aqueous solution of Au particles. Electrostatic interaction instead of covalent bonding between particles and organic compounds allows for the adsorbed molecule to be easily removed or exchanged for modification for further processing after a well-defined macroscopic structure is built. In this paper, we show that self-organized unique patterns of particles can also be created by an adsorption process from the bulk solution onto cationic monolayers at the air–water interface.

Dioctadecyldimethylammomium chloride (DODAC, obtained from TCI) was recrystallized three times from an acetone solution. $HAuCl_4$ (Nacalai), trisodium citrate dihydrate (Cica), tetrakis(hydroxymethyl)phosphonium chloride (THPC, TCI), and mercaptoacetic acid sodium salt (ASP, Aldrich) were used without further purification. Au nanoparticles were prepared in water by the reduction of $HAuCl_4$ with THPC at room temperature. To make anionically stabilized Au nanoparticles, a freshly prepared aqueous solution of ASP was added to the nanoparticles under vigorous magnetic stirring. A chloroform solution of DODAC was spread on the Au sol solution, and DODAC monolayers were compressed to a desired area after solvent evaporation. The DODAC monolayers were allowed to stand for 7 days to prepare Au nanoparticles/DODAC films via interaction between anionic Au nanoparticles and cationic DODAC molecules. The Au nanoparticle/DODAC films were deposited on formvar-covered copper grids for TEM by drawing the grids, at an approximately horizontal angle, through the film/air interface. The specimens were examined using an H-9000 HITACHI transmission electron microscope operating at 200 kV. TEM examination showed that the Au particles were spherical with a mean diameter of about 5.3 ± 2.5 nm with a root-mean-square deviation of 47%. The size distribution histogram based on a count of 400 particles is shown in Figure 1.

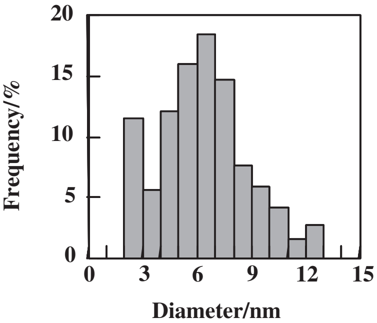

Figure 1. Histogram of the size distribution of Au nanoparticles obtained from TEM observations.

Figure 2 shows a typical TEM micrograph of a nanoparticle/DODAC film prepared at a surface area per DODAC molecule (*As*) value of 0.40 nm^2/molecule. It was observed that Au particles formed loop structures with a diameter of 0.1–1 µm and a width of ca. 5 nm. Loops of smaller dimensions were also present inside some of the larger ones. The widths of the loops correspond to the average particle diameter, and the higher magnification micrograph in Figure 2 shows that the loops were made of single particle strings. The size of the particles making up the loops was 5–7 nm, which is in the middle of the size distribution shown in the histogram, while most of the particles inside and outside the loops were smaller than 5 nm.

In order to examine the effects of the surface density of DODAC on loop formation, Au particle/DODAC films created at various *As* values were examined in the TEM. For $As <$ 0.40 nm^2/molecule, the size of the loops decreased and the widths of the loops increased with decreasing *As*. However,

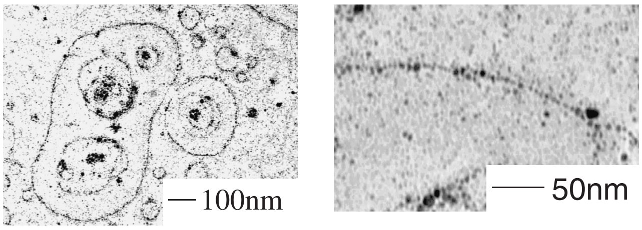

Figure 2. TEM images of Au nanoparticles prepared at $As =$ 0.40 nm^2/molecule.

for $As > 0.45\,\text{nm}^2$/molecule, the particles were randomly dispersed with no loop formation, as shown in Figure 3. Furthermore, it was found that the initial As value, i.e. the As value prior to the compression of DODAC monolayer, also showed the same effect on loop formation. In other words, the decrease in the initial As value from $1.0\,\text{nm}^2$ to $0.5\,\text{nm}^2$/molecule brought about a shrinkage in the loop and an enlargement of the width, while no loop formed in a larger initial $\text{As} > 2.0\,\text{nm}^2$/molecule. Thus, both initial and final densities of the DODAC monolayer play a crucial role in the formation of the particle loops.

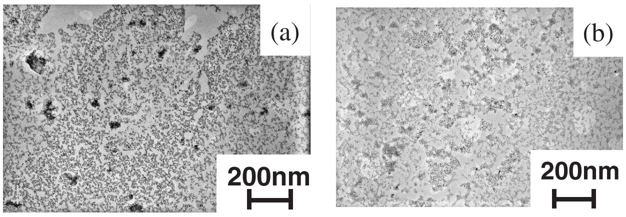

Figure 3. TEM images of Au nanoparticles at (a) $As = 0.45\,\text{nm}^2$/molecule and (b) $As = 0.60\,\text{nm}^2$/molecule.

Similar ring formation of nanocrystals, including those of Au, Ag, CdS, and barium hexaferrite, has been reported by several research groups.[12] These were made by evaporating a drop of nanocrystals-dispersed volatile solvents on TEM. Ohara et al.[14] proposed that the rings are formed owing to holes opening up in the liquid film on drying, and pushing the particles into the rims. Thus, as per this hypothesis, the formation of the rings depends mainly on the drying process of particle suspensions.

In our system, there are two processes involved in preparing hybrid particle/DODAC films. One is the evaporation of chloroform which is the solvent, and the second is the adsorption of particles to DODAC monolayers at the air–water interface. The loop formation in our study is likely independent of the evaporation process, because it takes a week to form the hybrid particles/DODAC films, and the loop formation depends on the initial and final As values. In addition, a domain structure of the DODAC monolayer at the air–water interface, created by the evaporation of the solvent, is another possible reason for the loop formation. We showed in a previous paper[15] that large particles with a narrow size distribution never form loops. Thus, even if a domain structure of DODAC monolayer exists, the loop structure is probably not induced by the domains. In conclusion, in our study, the adsorption process should be of primary importance to the loop formation.

The size distribution of particles may also influence the loop formation. To test this, we used a mixture of THPC particles and citric particles,[17] which has a broader particle size distribution, and prepared hybrid monolayers of Au particles and DODAC. As seen in Figure 4, the resulting monolayers show a size-dependent phase separation structure, which organizes large particles (ca. 15-nm diameter) positioned at the center surrounded by successively smaller particles. This structure was little affected by changes in the relative fraction of citric particles.

Similar size-selective phase separation has been observed in samples created by evaporating a drop of Au-particles-in-hexane on an amorphous carbon-coated TEM grid.[16] The largest particles crystallize first owing to the size dependence of van der Waals-type dispersional attraction between particles. These then serve as seeds for further crystallization. In our system, the same mechanism may act as a driving force to make the phase separation structures at the air–water interface. Thus, the degree of van der Waals-type dispersional attraction between particles is important to the loop formation, but not the size distribution of particles. Complete details of the loop formation mechanism are still not fully understood. To clarify the mechanism, we need to examine time dependence of the particle adsorption. This may be difficult since it requires TEM observations at very early reaction times. The current investigation, however, suggests that the density of the DODAC monolayer clears plays a critical role.

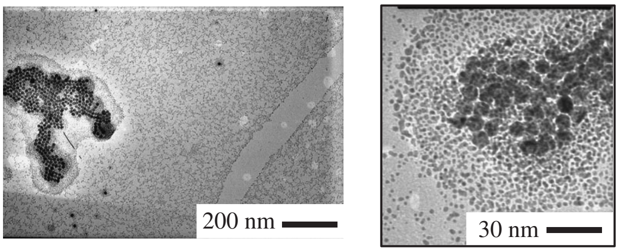

Figure 4. TEM images of a monolayer prepared from a mixture of THPC and citric particles.

References and Notes

1 Y. Dirix, C. Bastiaansen, W. Caseri, and P. Smith, *Adv. Mater.*, **11**, 223 (1999).
2 M. Quinten, A. Leitner, J. R. Krenn, and F. R. Aussenberg, *Opt. Lett.*, **23**, 1331 (1998).
3 H. Wohltjen and A. W. Snow, *Anal. Chem.*, **70**, 2856 (1998).
4 J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin, and R. L. Letsinger, *J. Am. Chem. Soc.*, **120**, 1959 (1998).
5 C. A. Mirkin, R. L. Letsinger, R. C. Mucic, and J. J. Storhoff, *Nature*, **382**, 607 (1996).
6 I. I. Moiseev and M. N. Vargaftik, *New J. Chem.*, **22**, 1217 (1998).
7 L. Motte, F. Billoudet, E. Lacaze, J. Douin, and M. P. Pileni, *J. Phys. Chem. B*, **101**, 138 (1997).
8 J. F. Sampaio, K. C. Beverly, and J. R. Heath, *J. Phys. Chem. B*, **105**, 8797 (2001).
9 S. Nakao, K. Torigoe, K. Kon-No, and T. Yonezawa, *J. Phys. Chem. B*, **106**, 12097 (2002).
10 S. Wang, S. Sato, and K. Kimura, *Chem. Mater.*, **15**, 2445 (2003).
11 K. V. P. M. Shafi, I. Felner, Y. Mastai, and A. Gedanken, *J. Phys. Chem. B*, **103**, 3358 (1999).
12 M. Maillard, L. Motte, A. T. Ngo, and M. P. Pileni, *J. Phys. Chem. B*, **104**, 11871 (2000).
13 L. V. Govor, G. H. Bauer, G. Reiter, E. Shevchenko, H. Weller, and J. Parisi, *Langmuir*, **19**, 9573 (2003).
14 P. C. Ohara and W. M. Gelbart, *Langmuir*, **14**, 3418 (1998).
15 T. Kawai, D. J. Neivandt, and P. B. Davies, *J. Am. Chem. Soc.*, **122**, 12031 (2000).
16 P. C. Ohara, D. V. Leff, J. R. Heath, and W. M. Gelbart, *Phys. Rev. Lett.*, **75**, 3466 (1995).
17 Citric particles were the same as Ref. 15 and its average diameter was 15 nm.