Construction of 2D Superlattices of Gold Nanoparticles at an Air/Water Interface Based on Hydrogen-Bonding Networks

Hiroshi Yao,* Hiroyuki Kojima, Seiichi Sato, and Keisaku Kimura
Department of Material Science, Graduate School of Science, Himeji Institute of Technology,
3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297

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Two-dimensional (2D) superlattices of mercaptosuccinic acid-modified gold nanoparticles were constructed at an air/water interface in the presence of 4-pyridinecarboxylic acid (PyC). Hydrogen-bonding interaction caused the incorporation of PyC into the surface-functionalized gold nanoparticles, suggesting that the interparticle spacing in the superlattices is controllable with an intercalating molecule.

Construction of nanoparticle superlattices is of great interest because it is expected to provide new architectures of nanoelectronic and optical devices based on the collective physical properties of assembled arrays.[1,2] In the past few years, a significant effort has been made toward the controls of self-assembly of surface-modified metal nanoparticles into 2D or 3D superlattices.[2–5] In the superlattices, each nanoparticle is separated from every other by an insulating barrier of the surface modifier. Since the barrier thickness directly affects the exchange coupling or dipole interactions between metal nanoparticles, fine tuning of the interparticle spacing is of crucial importance for the electronic structure design of the superlattice.[6,7] So far, most of the superlattices have been constructed via van der Waals interaction because the constituent metal nanoparticles are commonly passivated with long-chain alkanethiols. The interparticle spacing can be changed by controlling the length of the alkanethiols.[6]

On the other hand, we have developed syntheses of uniform-sized water-soluble gold nanoparticles.[8,9] Application of water-soluble nanoparticles is one of the new fields for the construction of 2D or 3D superlattices not by weak van der Waals interactions but by hydrogen-bonding and/or electrostatic interactions.[10] In particular, hydrogen-bonding interaction is attractive, directional and selective,[11] and expected to work quite effectively at an air/water (hydrophobic) interface.[12] In this letter, we report construction of a 2D gold nanoparticle superlattice at an air/water interface based on the hydrogen-bonding network strategy. For the first time, we found that interparticle spacing could be controlled by incorporating a rigid hydrogen-bonding molecular unit among surface-functionalized gold nanoparticles.

Water-soluble, mercaptosuccinic acid (MSA)-modified gold nanoparticles (abbreviated as MSA-Au) were prepared by the similar method reported earlier.[8] Briefly, 0.5 mmol of $HAuCl_4$ dissolved in water (0.121 M) and 1.5 mmol of MSA were at first mixed in methanol (100 mL), followed by the addition of a freshly prepared 0.2 M aqueous $NaBH_4$ solution (25 mL) at a rate of 2.5 mL/min under vigorous stirring. A dark-brown crude precipitate was produced. The precipitate was then thoroughly washed with water/ethanol (1/4) and methanol. Finally, after dissolving the precipitate into water (10 mL), dialysis was continued for 24 h, followed by freeze-drying.

For constructing gold nanoparticle superlattices, 2 mL of an aqueous MSA-Au mother solution (40 mg in 20 mL water) containing 4-pyridinecarboxylic acid (PyC; 9 mg) and HCl (12 M; 6 μL) was stored in a sealed vessel for about 3–5 days to allow self-assembling of gold nanoparticles at the air/water interface. It is well-known that carboxylic acid and pyridine are good hydrogen-bonding partners.[13] Moreover, the pyridine group plays a role of the explicit marker for various analyses. Therefore, we selected PyC as a rigid molecular unit that might be incorporated between MSA moieties on gold nanoparticles. Formation of the superlattice film could be detected by the light reflection at the interface. Note that both PyC and HCl are indispensable for superlattice formation, indicating that the suppression of carboxylic acid dissociation is essential. The superlattice films were scooped on a carbon-coated Cu grid, and examined by using a transmission electron microscope (TEM). Attenuated total reflectance IR (ATR-IR) spectra were measured by placing the superlattice film on a ZnSe internal reflection trapezoid prism. The film was washed with methanol before the IR measurements to remove impurities.

Figure 1a shows a typical TEM image of a gold nanoparticle 2D superlattice representing a long-range ordered structure, where it can be clearly seen that hexagonal close-packed structures are formed. The mean particle core diameter (d_{core}) and the standard deviation are 5.7 and 0.81 nm, respectively. Because no superlattices were generated in the absence of PyC under the condition,[14] the formation of 2D superlattices at an air/water interface suggests that hydrogen-bonding interactions between PyC and MSA moieties would drive the particle assembling.[12,13] Interparticle attraction due to van der Waals dispersional interactions is also considered to contribute the self-assembling.[15,16]

The interparticle spacing distance in the 2D nanoparticle

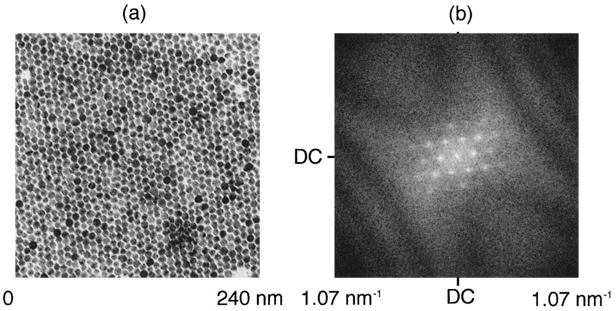

Figure 1. (a) TEM micrograph of a 2D superlattice of gold nanoparticles. (b) Fourier transform (FT) pattern of (a).

superlattice can be obtained by analyzing the Fourier transform (FT) power spectrum of the image. Figure 1b shows the FT pattern of Figure 1a, which demonstrates the long-range nanoparticle ordering and its hexagonal symmetry. The observed spots in the FT pattern reflect the spacing periodicity of the nanoparticle arrays. The center-to-center distance between nearest neighbor particles (D_{cc}) was calculated to be 7.6 nm. Considering that the 2D superlattice was composed of 5.7-nm nanoparticles in core diameter, we can estimate the interparticle gap (D_{gap}: $D_{cc} - d_{core}$) of 1.9 nm. Because the obtained D_{gap} is about three times larger than the thickness of MSA modifier (ca. 0.6 nm), it is expected that PyC (molecular length: ca. 0.6 nm) is incorporated between nanoparticles. The results indicate that the interparticle gap in nanoparticle superlattices is controllable with a rigid intercalating molecule.

Hydrogen bond formation in the superlattice film was identified by ATR-IR spectroscopy. Figure 2a shows the IR absorption spectrum of a superlattice film, along with that of PyC and MSA. The spectrum of the superlattice film has characteristic features of both PyC and MSA. A broad band around 2800–3500 cm^{-1} is assigned to the carboxylic acid O–H stretching of MSA molecules.[8] The peaks at 1603 and 1406 cm^{-1} are assigned to ring vibrations of pyridine groups. The absorption bands around 1900–2000 and 2400–2500 cm^{-1} are attributed to the O–H stretching bands based on hydrogen-bonding between pyridine and carboxylic acid groups in a splitting pattern.[17] Note that pure PyC possesses similar splitting bands. Therefore, in addition to the detection of hydrogen-bonded O–H groups, observation of the peak shift (1723 cm^{-1}) assigned to the C=O stretching vibration was the essential evidence for hydrogen-bonding interactions between MSA and PyC moieties; the peak position was different from that of pure MSA (1695 cm^{-1}) or PyC (1710 cm^{-1}). We conclude that strong hydrogen-bonding between MSA on the surface of gold nanoparticles and PyC is present in the superlattice films.

Hydrogen-bonding interaction between pyridine and carboxylic acid groups is influenced by the degree of dissociation of the acids used, which directly relates to the solution pH. The pH of the solution in which the nanoparticle superlattice was formed was measured to be 1.8. According to the literatures,[18] the pKa of succinic acid in aqueous solution is 4.00 and 5.24 whereas that of PyC is 1.79 and 4.78 (these acids are dibasic). At pH = 1.8, the pyridine group in PyC is protonated, and other carboxylic acid groups in PyC or MSA are scarcely dissociated. By taking these conditions into accounts, we optimized a stable geometry, which shows that one PyC is incorporated between two MSA molecules through hydrogen-bonding, by using a MOPAC software. The result is shown in Figure 2b. This molecular geometry indicates that the distance (arrow line in Figure 2b) which corresponds to D_{gap} is 1.93 nm (Note that hydrogen bond distance is ca. 0.16 nm). This distance is consistent with D_{gap} obtained from Figure 1b, implying that the existence of hydrogen-bonding networks between PyC and MSA in the 2D superlattices are reasonable. The incorporation of single PyC molecule between two MSA moieties is probably due to the energy differences in hydrogen-bonding interactions; the hydrogen-bonding interaction between PyC and MSA might be stronger than that between two PyC molecules. Future research in our group includes the arbitrary controls of the core size of constituent nanoparticles and the interparticle spacing in the nanoparticle superlattices by incorporating a various sized hydrogen-bonding molecular unit.

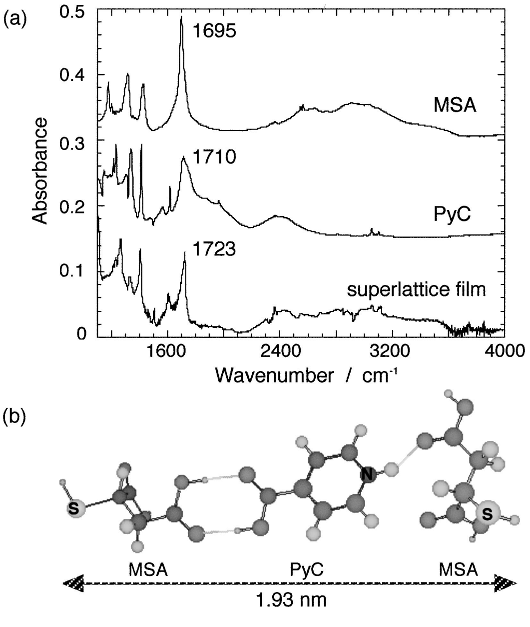

Figure 2. (a) FT-IR absorption spectra of a superlattice film, PyC, and MSA. (b) Optimized molecular geometry of PyC incorporated between two MSA molecules via hydrogen bond.

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References and Notes

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