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The First Example of Ordered Two-Dimensional Self-Assembly of Au Nanoparticles from Stable Hydrosol

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A novel hydrosol of alkanethiol-modified Au nanoparticles was reported for constructing large-scale ordered two-dimensional (2D) self-assembly for the first time. The degree of long-range order is displayed by both the low-angle transmission electron diffraction and fast Fourier transform pattern of the electron microscope image. We discuss the preparation of stable hydrosol of Au nanoparticles coated with octanethiol and the role of ethanol and octanethiol in the preparation as well as the 2D self-assembly of Au nanoparticles from the hydrosol in reference to the nanoparticle without stabilizers.

Introduction

Recently, the assembly of nanoparticles into well-defined two- and three-dimensional (2D and 3D) superlattices has attracted much attention, because the novel properties of the superlattices and the potential applications are expected in optical gratings, optical filters, data storage, and microelectronic devices.^{1–3} The development of a general method for the fabrication of such quantum crystals is a major challenge for future research. Several approaches, such as self-assembly,^{4–12} Langmuir–Blodgett (LB) techniques,¹³ and the electrophoretic deposition method^{14–16} have been used in order to obtain 2D and 3D structures.

The self-assembly of nanoparticles requires hard sphere repulsion, a controlled size distribution, and an inherent van der Waals attraction between the particles and the dispersion forces. Polydispersion in the particle size prevents the construction of such well-defined 2D and 3D structures, and an appropriate surface passivation is required. The limitation of this method is that when the

colloidal sols are allowed to dry on the substrate, solvent evaporation tends to create circular voids, from which the particles are excluded. Another problem is that a large number of water-soluble colloids tend to aggregate instead of forming ordered 2D structures after the solvent evaporates. So in most of the published studies about nanoparticle self-assembly, the sols used are organosols.^{4–12} Monodisperse Ag and Ag₂S nanoparticles were synthesized from AOT reverse micelles,⁴ the nanoparticles passivated with alkanethiols are able to self-organize in 2D and 3D superlattices from their hexane (for Ag) and heptane (for Ag₂S) dispersions. Au, Pt, and Pd nanoparticles were formed using a nonionic inverse micelle technique;^{5,6} these nanoparticles capped with thiol can also form 2D and 3D superlattices from their alkane dispersions. Apart from the alkane, toluene, and chloroform are the organic solvents in common use. The preparation of 3D hexagonal close-packed superlattice of dodecanethiol passivated Ag nanoparticles from toluene dispersion⁷ and the organization into 2D and 3D structures of thiol-stabilized Au nanoparticles in toluene dispersion⁸ were reported. The toluene dispersions of Au, Ag, and Pt nanoparticles were also prepared by the phase-transfer technique, and the 2D self-assembled monolayers were obtained.⁹ With chloroform or dichloromethane as solvent, the self-assembled 2D ordered superlattice of Ag nanoparticles capped with 1-nonenethiol¹⁰ and the self-assembled 2D and 3D superlattice of amine-stabilized Au nanoparticles¹¹ were reported. Particularly, mesitylene was used as a solvent¹² to self-assemble a 2D superlattice of Au nanoparticle synthesized by a gas-phase technique and stabilized by dodecanethiol. There is no report on the stable gold hydrosol that can be used for ordered 2D or 3D self-assembly by evaporating solvent. So the challenge is whether hydrosol can be used for ordered 2D and 3D self-assembly. In our lab, recently, through adjusting the pH value of hydrosol of mercaptosuccinic acid (MSA) coated Au nanoparticle to acid state by HCl^{17–19} or adding 4-pyridinecarboxylic acid to the hydrosol,²⁰ ordered 2D and 3D superlattices resulting from gradually changing of hydrophilicity of Au nanoparticle to hydrophobicity were

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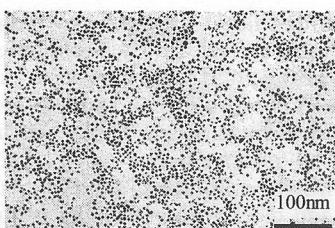


Figure 1. TEM micrograph of the Au particles obtained when a drop of Au hydrosol without octanethiol was placed on a carbon-coated copper grid and the solvent was allowed to evaporate.

obtained at the air/water interface. In this report, we show the large-scale ordered 2D self-assembly of Au nanoparticles from stable hydrosol with alkanethiol by just placing a drop of the Au hydrosol on a carbon-coated copper grid and allowing the solvent to evaporate in air. To the best of our knowledge, this is the first example of large-scale ordered 2D self-assembly of Au nanoparticles by the evaporation technique from stable hydrosol.

Experimental Section

Au nanoparticles were prepared according to the method of Slot and Geuze.²¹ Typically, (a) 0.1 mL of 5% (w/w) H₄AlCl₄ was added to 40 mL of distilled water, (b) 25 mg of tannic acid, 2 mL of 1% trisodium citrate, and 0.066 mL of 1% Na₂CO₃ were added to distilled water to produce a final volume of 10 mL. Both solutions were heated to 60 °C, and solution b was rapidly added with stirring to solution a. After the development of a red color, the colloid was heated to boiling for 10 min. The special conductivity of the obtained Au sols was decreased to less than 5 μ s cm⁻¹ by dialysis using a collodion bag. Then 0.3 mL of 15.8 mmol dm⁻³ ethanol solution of octanethiol was added to 10 mL of the Au sol. The Au sol so prepared was used for the formation of 2D superlattices of Au nanoparticles on carbon film. Transmission electron microscopy (TEM) experiments and corresponding electron diffraction were carried out on a Hitachi-8100 transmission electron microscope operated at 200 kV.

Results and Discussion

Before protection with thiol, the Au nanoparticle hydrosol cannot be used to assemble 2D ordered superlattice. Figure 1 shows a TEM micrograph of the Au particles obtained when a drop of Au hydrosol without octanethiol was placed on a copper grid coated with about a 30 nm thickness amorphous carbon film and the solvent was allowed to evaporate in air. From this picture clear spherical nanoparticles can be observed; however, some of the particles are aggregated. This is agreeable with the result of Slot and Geuze.²¹ As aqueous colloids are largely charge stabilized, it is difficult to fabricate “close-packed monolayers” of charged nanoparticles.¹² So the preparation of steric-stabilized water solvable nanoparticles is required.

Generally, alkanethiol-stabilized Au nanoparticles are unstable in water phase.¹⁴ To obtain the alkanethiol-stabilized Au nanoparticles in water, 0.3 mL (15.8 mmol dm⁻³) of ethanol solution of octanethiol was added to 10 mL of Au sol. When a drop of the Au hydrosol with octanethiol was placed on a carbon-coated copper grid and the solvent was allowed to evaporate, large-scale ordered 2D self-assembly of Au nanoparticles formed on the carbon film, and the largest area can achieve 100 μ m². Shown in Figure 2 is a typical TEM micrograph of the Au particles monolayer. On comparison with Figure 1, it is observed that by coating with octanethiol, the arrangement of Au nanoparticles become homogeneous, with neither void nor

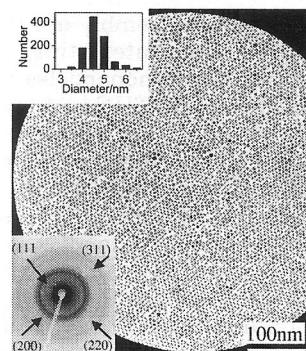


Figure 2. TEM micrograph of the Au particles obtained when a drop of Au hydrosol with octanethiol was placed on a carbon-coated copper grid and the solvent was allowed to evaporate. ED pattern and the size distribution are in the inset. The mean diameter is 4.6 nm, and the size deviation is 11%.

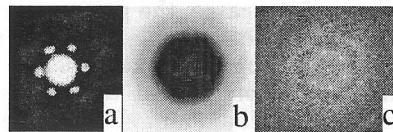


Figure 3. Low-angle TED dark field (a) and bright field image (b) of the whole area in Figure 2 and FFT pattern (c) of selected area in Figure 2.

aggregate in the monolayer. The self-assembled monolayer was formed by many ordered domains, and particles in the domains were orderly packed and were of densely packed structures. A high-angle transmission electron diffraction (ED) pattern of nanoparticles in Figure 2 is shown in the lower insert of Figure 2. It reveals dense ring patterns with d spacings of 2.33, 2.07, 1.45, and 1.23 Å, which match the standard body centered cubic gold lines (JCPDS card, no.04-0784). The dense ring patterns indicate that the Au nanoparticles are randomly oriented with respect to each other. The size distributions of the particles were measured from enlarged photographs of the TEM images. The mean diameter of the Au particles is 4.6 nm, and the size deviation is 11%. The narrow size distribution may result from the self-correcting processes occurring in the formation of the monolayer.¹⁹ The histogram of the size distribution is shown in the upper insert of Figure 2.

The degree of long-range order is displayed more statistically by both the low-angle transmission electron diffraction (TED) and the fast Fourier transform (FFT) pattern (Figure 3). The low-angle electron diffraction dark field image and bright field image of the whole area in Figure 2 is shown in panels a and b of Figure 3, respectively. The 6-fold symmetry of the structure is apparent. This indicates that the Au nanoparticles crystallize into a hexagonal close-packed lattice. The lattice constant can be calculated to be 5.7 nm, based on the formula $d = L\lambda/r$, and therefore the average interparticle separation (core–core) $a = 2d/(\sqrt{3}) = 6.6$ nm. On comparison with a mean diameter of 4.6 nm from TEM, the interparticle spacing is about 2.0 nm, which is similar to that of Mulvaney et al.’s result.¹⁴ Apart from the well-resolved first-order hexagonal diffraction pattern, even the second-order diffraction patterns can be observed (Figure 3b). This means that the coherent single domain is large. Figure 3c shows the FFT pattern of selected area in Figure 2. The first- and second-order reflexes are observed, showing the 6-fold symmetry of the 2D superlattice.

The role of ethanol and octanethiol in the preparation of stable hydrosol of Au nanoparticles coated with oc-

tanethiol and the 2D self-assembly of Au nanoparticles from the hydrosol is very interesting. To obtain the alkanethiol-stabilized Au nanoparticles in water, Mulvaney et al.¹⁴ added 6 mL of THF to 4 mL Au hydrosol, and then the alkanethiol in THF was added to the THF–water mixture. But the sol so prepared was only stable for several hours. In our paper, only 0.3 mL of 15.8 mmol dm⁻³ ethanol solution of octanethiol was added to 10 mL of Au hydrosol, the amount of ethanol is so small that the dispersion of Au nanoparticles can still be considered as hydrosol and no phase separation was observed. This octanethiol-stabilized hydrosol was stable and can be used to self-assemble a 2D superlattice in 1 month at least after preparation. To examine the role of ethanol, two controlled experiments were carried out: in the first 0.03 mL of 15.8 mmol dm⁻³ ethanol solution of octanethiol was added to 10 mL of Au hydrosol, in the second 0.3 mL of ethanol without octanethiol was added to 10 mL of Au hydrosol. In both of the cases, the prepared mixtures of Au nanoparticle dispersion is stable, only in the first case, some little drops of oil appear on the surface of the liquid phase, which can be contributed to the insoluble octanethiol as a very small amount of ethanol was added. As expected, ordered 2D self-assembly of Au nanoparticles cannot be obtained with either of the two hydrosols. This indicated that stable hydrosol of Au nanoparticles coated with octanethiol and the ordered 2D self-assembly result from the cooperation of ethanol and octanethiol. Recently, water-dispersible Au nanoparticles were formed using a technique based on surface-bound interdigitated bilayers consisting of a dodecylamine primary monolayer directly coordinated to the Au particle surface and a secondary monolayer of CTAB, this secondary monolayer providing sufficient hydrophilicity.²² In our case, the octanethiol molecule directly coordinated to the Au particle surface through the sulfur atom in the mercapto group, leaving the hydrocarbon tails turned out. An interdigitated structure may be formed between the hydrocarbon tails

of octanethiol and ethanol, although the length of ethanol hydrocarbon chain is short. The hydrophobic interactions between the interdigitated hydrocarbon chains is expected to be energetically favorable in an aqueous environment,²³ and the ethanol derivatization of the Au nanoparticles provides the Au nanoparticles good stability in the hydrosol. The bilayer-stabilized Au nanoparticles avoided the disadvantage of charge-stabilized aqueous colloids tending to aggregate instead of forming ordered 2D structures after the solvent evaporates. Particularly, a short hydrocarbon chain permits ethanol molecular evaporation from the surface of a octanethiol monolayer on a Au particle surface after the evaporation of water, as the hydrophobic interactions are not very strong. Evaporation of ethanol molecules made the hydrophilic Au particle become hydrophobic, so they can self-assemble into ordered 2D superlattice like organosols in the literature.^{4–12}

Conclusion

A simple and efficient route was reported for the 2D self-assembly of Au nanoparticles from hydrosol with alkanethiol. The degree of long-range order is displayed by both the low-angle transmission electron diffraction and FFT pattern. The preparation of stable hydrosol of Au nanoparticles coated with octanethiol is a critical factor. This method may be applied to self-assembly of other nanoparticles, such as Ag, Ag₂S, Pt, Fe₃O₄, and so on.

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