Structure of Silver Nanoparticle Assemblies Grown at Aqueous Suspension Surfaces by Acid Vapor Diffusion

Seiichi Sato*, Kana Shinogi

Graduate School of Material Science, University of Hyogo, Kamigori-cho, Ako-gun, Hyogo, Japan

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***Corresponding author:** Seiichi Sato, Assistant Professor, Graduate School of Material Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan, Tel/Fax: +81-791-58-0161; E-mail: sato@sci.u-hyogo.ac.jp

Abstract

Silver (Ag) nanocrystals modified with mercaptosuccinic acid (MSA) were slowly assembled at air/water interfaces by dissolving vapors of hydrochloric acid (HCl), formic acid (HCOOH) or acetic acid (CH₃COOH). By introducing HCl, Ag nanoparticle lattices were found in the assemblies. However, the addition of HCOOH resulted in random aggregates of Ag compound crystallites, while exposure to CH₃COOH induced the fusion of the Ag nanocrystals.

Keywords: self-assembly; silver nanocolloid; self-correcting process; superlattices; equilibrium growth

Introduction

Nanoparticle lattices are of considerable scientific interest since adjusting the sizes of the component nanocrystals and the surface modified molecules can tailor the electronic structures of the lattices. Recently, nanoparticle lattices have been successfully produced using spontaneous assembly processes of nanoparticles, the surface of which is modified with oleophilic or hydrophilic molecules [1, 20]. So far, the assembly processes can be roughly categorized into two types: non-equilibrium assemblies of oleophilic nanoparticles dispersed in non-polar suspensions and equilibrium assemblies of hydrophilic nanoparticles dispersed in aqueous suspensions. The oleophilic nanoparticles in non-polar suspensions such as toluene and hexane have been assembled by evaporating the suspensions [3, 14]. This assembly process is usually completed in several minutes, and in such a non-equilibrium process, the quality of the resulting lattice arrangements largely depends on the initial size distribution of the nanoparticles. Conventionally, the standard deviations must be smaller than 15% of the average size to obtain quality lattices [6, 13].

In contrast, hydrophilic nanoparticles in aqueous suspensions can be assembled slowly (e.g. several days or several months) by adjusting the charge of the surface modifiers through pH control by acid. In such an equilibrium process, a narrow size distribution is not an indispensable prerequisite owing to the following self-correcting processes [18, 21]: (1) Non-uniform

particles are repelled towards the boundaries of the lattice if the lattice contains component particles of various sizes, and (2) a nanoparticle trapped inside a metastable site can be released back into suspension and diffuse about the lattice surface until the most stable position is found. These two processes narrow the size distribution within the lattice, remove lattice defects, and improve lattice symmetry. To date, carboxylate-modified gold (Au) nanocrystals have been successfully assembled into high-quality lattice arrangements at air/water interfaces under equilibrium [15, 19].

In the present study, mercaptosuccinic acid (MSA) modified silver (Ag) nanocrystals were slowly assembled (i.e., assembled in equilibrium) at the air/water interface. From a viewpoint of the self-correcting nature, lattice arrangements should emerge without size fractionation of the starting nanoparticles. However, since Ag surface is more reactive than gold, lengthy immersion in aqueous suspensions containing acid may change the Ag nanocrystals into Ag compounds such as silver chloride (AgCl). In addition, surface modifiers may not stably protect the Ag surface, and Ag nanocrystals may be fused into larger crystals. Therefore, it is necessary to examine the reactivity of Ag nanocrystals in various acids as well as the stability of the MSA modification during self-assembly processes. Thus, herein we report structural observations of MSA-modified Ag nanocrystal assemblies grown by vapor diffusion of acids, typically hydrochloric acid (HCl), formic acid (HCOOH) and acetic acid (CH₃COOH).

Methods

MSA-modified Ag nanocrystals were prepared using the same method described in our previous report [22]. First, 150 mg of MSA was dissolved in 100 ml of methanol. Second, 1.7 ml of a silver (I) nitrate (5% w/v) aqueous solution was mixed with the MSA-containing methanol. Third, 25 ml of sodium borohydride in aqueous solution (0.2 M) was added to the solution at a rate of 2 ml/min under vigorous stirring. All of the above preparations were performed at around 0 °C.

To induce the self-assembly of the nanoparticles, HCl, HCOOH

or CH_3COOH was dissolved by the following vapor diffusion method [23]. First, 6.0 mg of MSA-modified Ag nanocrystals was dissolved in 3 ml of distilled water in a glass vial A, which was 4.0 cm high and had an internal diameter (ID) at the opening of 1.3 cm. In a glass vial B, which was 4.5 cm high with an ID at the opening of 1.5 cm, 5 ml of 6 M HCl, 6 M HCOOH or 6 M CH_3COOH aqueous solution was prepared. Then, the vial A and a set of two vials B were stored in a shielded vessel, which measured 10 cm high with an ID of 5 cm, in a dark room. After three weeks, assemblies appeared at the air/suspension interface. The assemblies were scooped with a Cu grid covered with an amorphous carbon film for transmission electron microscope (TEM) observations.

Surface modification of the nanocrystals was evaluated with a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer in transmission mode. TEM images and corresponding selected area electron diffraction patterns were obtained using a HITACHI H-8100 TEM operated at 200 kV acceleration voltages. The nanocrystal size and crystallinity were evaluated using a RIGAKU RINT 2000 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 20 mA.

Results and Discussion

Figure 1 shows the structural properties of the starting Ag nanoparticles. The FTIR result (Figure 1a) suggested the following three characteristics. First, the peak at 2550 cm^{-1} , which corresponds to the S-H stretching mode [24], disappeared in the spectrum of the Ag nanoparticles. This indicates that the Ag nanocrystal surface is modified with MSA through the S atom. Second, the MSA on the nanocrystals formed carboxylate salts: The counter cations of the CO_2^- are probably Na^+ because NaBH_4 was used in the reduction of AgNO_3 . Third, the Ag-O peak, which is usually observed as a strong peak at $540\text{--}550 \text{ cm}^{-1}$ [24], was not seen. This shows that the Ag nanocrystals are successfully modified with MSA. The average diameters of the Ag nanocrystals obtained from the TEM image (Figure 1b) and X-ray diffraction (XRD) pattern (Figure 1c) were 2.8 nm and 2.2 nm, respectively. The slight difference between these sizes may be due to the fusion of the nanocrystals by electron beam irradiation during TEM observation.

Figure 2 shows the TEM images of the assemblies obtained by three types of vapor diffusion. In the HCl vapor, lattice arrangements were grown ubiquitously. Figure 2(a) shows a typical assembly. The diffraction rings are fully explained by assuming a bulk Ag crystal structure (fcc with $a = 0.409 \text{ nm}$). It should be noted that AgCl was not found, which was sometimes observed when HCl solution was directly mixed with the Ag nanoparticle suspensions [25]. However, the use of HCOOH vapor did not result in the lattice formation, but instead produced random aggregates (Figure 2b). The diffraction pattern of the aggregates cannot be explained by assuming Ag or Ag oxide crystals. Considering the chemical species contained in the suspension, the crystals are presumably Ag formates. The diffraction pattern consists of numerous rings at close distances, indicating that the assemblies are low symmetric crystals such as rhombic structures, which metal formates usually form. We

will continue to evaluate the crystal structure, and the results will be published elsewhere. Our preliminary conclusion at this stage is that the addition of HCOOH induces the formation of Ag compounds, and that HCOOH is an inappropriate acid for producing Ag nanoparticle lattices. When CH_3COOH vapor is introduced, Ag crystals, which ranged from 30 to 200 nm emerged (Figure 2c). The diffraction pattern is explained by assuming Ag twin crystals, implying that the Ag crystals were grown owing to the fusion of the Ag nanocrystals. These observations show that the stability of surface-modified Ag nanocrystals depends on interaction between surface-modifier molecules and acid ions as well as the reactivity with internal Ag nanocrystals with the ions.

Summary

MSA-modified Ag nanocrystals were self-assembled at aqueous suspension surfaces by dissolving HCl, HCOOH or CH_3COOH vapors into the suspensions. All three types of acid addition induced the formation of assemblies after at least three weeks, but the structures of the assemblies differed. By introducing HCl vapor, lattice arrangements of Ag nanocrystals

Figure 1: Structural properties of the as-prepared Ag nanoparticles: (a) FTIR spectra of (i) pure MSA and (ii) MSA-modified Ag nanocrystals, (b) TEM image and the size distribution of the Ag nanocrystals, and (c) XRD pattern.

Figure 2: TEM images and diffraction patterns of the assemblies grown at suspension surfaces by exposure to vapors of (a) HCl, (b) HCOOH and (c) CH₃COOH. In image (a), magnification of the outlined part is shown in the bottom-right corner.

were found, and no AgCl formation was found in the assemblies. However, exposure to HCOOH vapor resulted in the formation of random aggregates consisting of Ag compounds. Moreover, when CH₃COOH vapor was used, the Ag nanocrystals grew 30–200 nm with twin structures, indicating that the MSA modification was unstable in the presence of CH₃COOH.

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