Influence of Organic Vapors on the Self-assembly of Gold Nanoparticles at Solution-gas Interfaces

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The self-assembly of gold nanoparticles at gas/suspension interface was strongly affected by the presence of organic vapor in the gas phase. Nonpolar organic molecules in the gas phase induced spherical assembly of gold nanoparticles, while polar organic molecules favored the formation of irregular aggregates at the gas/suspension interfaces.

The fabrication of nanoparticle assemblies with controllable dimensions has recently attracted a great deal of attention because of their potential applications in sensors, microelectronics, biology, and so forth.[1–8] The preparation of three-dimensional gold nanoparticle self-assemblies with quality crystal features was reported previously and the crystal structure of the gold nanoparticle superlattice has been determined.[8,9] We have also studied the solid substrate dependence in the growth of gold nanoparticle self-assemblies in aqueous suspensions.[9] It is also important and interesting to investigate the effect of the nature of gas phase molecules on the self-assembly because many self-assemblies of nanoparticles occur at suspension surfaces. We report herein the influence of organic vapor on the self-assembly of gold nanoparticles at the gas/suspension interface, and the investigation results in a novel method for preparing selectively spherical aggregates of gold nanoparticles having possible applications in multifunctional materials, macroscopic devices, and photonic devices.[6]

Sodium mercaptosuccinate (MSA)-coated 3.5-nm gold nanoparticles were prepared using a procedure as described in a previous work.[10] The percentage of coverage was estimated to be nearly 100% and the schematic surface structure of the nanoparticles is shown in Figure 2. To make gold nanoparticle self-assemblies, 4.0 mg of as-prepared gold nanoparticles was dispersed in 2.0 mL of 0.25 M HCl aqueous suspension in a closed glass vial (5.0 mL in volume). The other volumes in the vial were filled with air or the mixture of air and saturated organic vapor at room temperature. The total pressure in the sealed vial was kept 1 atmosphere. After 4 days at room temperature, self-assemblies of gold nanoparticles formed on the suspension surfaces. Then the self-assemblies were transferred to silicon substrates for further characterization by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). It was found that the introduction of organic vapor into the gas phases greatly affected the morphologies of the self-assembly of gold nanoparticles which were dependent on the components of the gas phases. The results are summarized in Table 1 and are illustrated in Figure 1.

Clearly, gold colloidal crystals possessing hexagonal, or triangular, or diamond-like shapes grew at the gas/suspension interfaces (Figure 1a) when the gas phase consisted of air, or pure nitrogen, or pure oxygen. EDX spectrum (inset in Figure 1a) recorded from these individual gold colloidal crystals shows that the elemental composition of these regular self-assemblies is mainly gold accompanied with carbon, oxygen, and sulfur, which are attributed to the coating organic layers of MSA. When organic vapor was introduced into the gas phase; however, no gold colloidal crystal with sharp facets was observed at the gas/suspension interfaces. Spherical assemblies of gold nanoparticles with several micrometers in diameters formed when the gas phase contained nonpolar organic molecules such as pentane, hexane, octane, or cyclohexane. This is clearly shown in Figure 1b. The EDX spectrum apparently suggests that these assembly spheres are made of MSA-coated gold nanoparticles. However, when the gas phase contained polar organic vapors such as acetonitrile or chloroform, irregular shaped aggregates of gold nanoparticles formed (Figure 1c). These irregular shaped aggregates are made of MSA-coated gold nanoparticles as shown by the EDX spectrum (Figure 1c inset). The results indicate that the introduction of nonpolar organic vapor into the gas phase provides a novel method for preparing spherical assembly of gold nanoparticles at suspension surface. Therefore, an assembly of gold nanoparticles with controllable dimension at the gas/suspension interfaces could be achieved by controlling the components of the gas phases.

Small angle X-ray diffraction was adopted to demonstrate the arrangement of MSA-coated gold nanoparticles in assemblies with varying shapes. X-ray diffraction patterns A, B, and C in Figure 2 were recorded from the gold nanoparticle self-assemblies with crystal features, spherical shapes, and irregular morphologies, respectively. Pattern A clearly suggests nanometer-scaled periodicity in the gold colloidal crystals. The MSA-coated gold nanoparticles within the colloidal crystals were stacked in a hexagonal close-packed structure as determined in previous works.[9,11] Compared with those in gold colloidal crystals, the MSA-coated gold nanoparticles in the spherical assemblies and the irregular shaped aggregates should be

Table 1. Dependence of the self-assembly morphologies on the gas phase components

Self-assembly morphology	Hexagonal, trigonal,etc	Spherical	Irregular shaped
Gas Phase components	Air Nitrogen Oxygen	Air + hexane Air + cyclohexane Air + pentane	Air + acetonitrile Air + chloroform

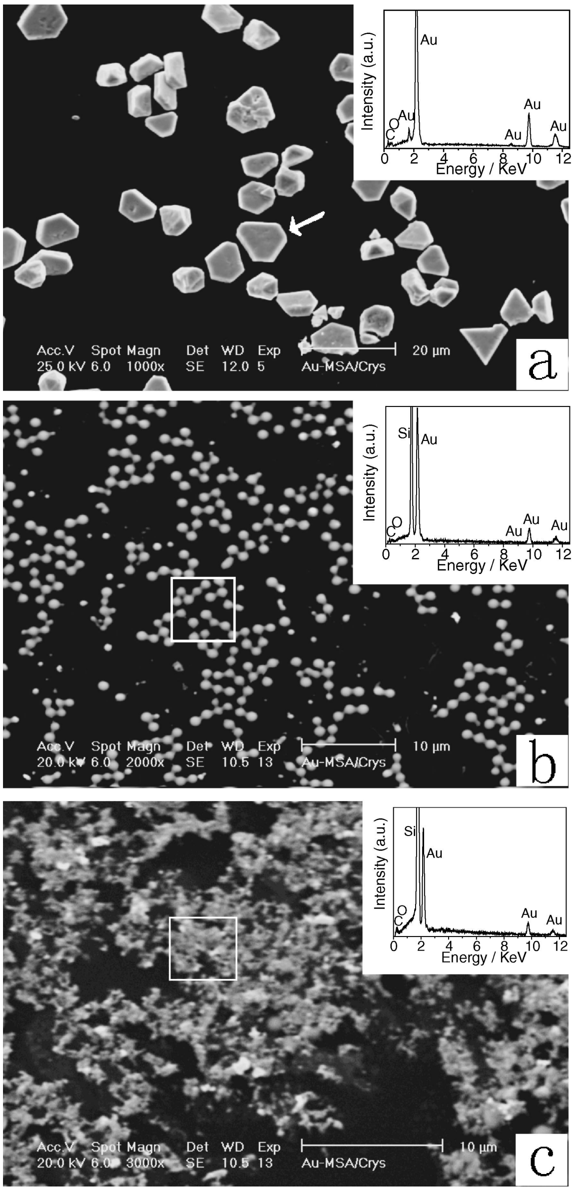

Figure 1. SEM images of self-assemblies of gold nanoparticles prepared under different gas phases. (a) air, (b) air + hexane, (c) air + chloroform. Insets: EDX spectra recorded from the marked colloidal crystal or a squared area. The silicon signals in insets of b and c are attributed to the silicon substrate.

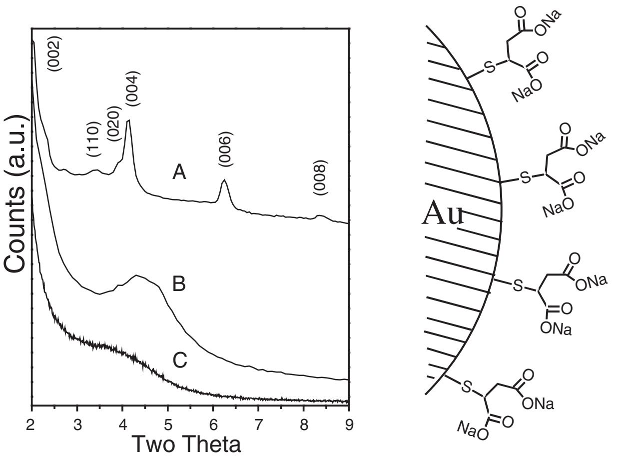

Figure 2. Left: XRD patterns recorded from gold nanoparticle assemblies with (A) quality crystal features, (B) spherical shapes, and (C) irregular shapes. Right: Schematic illustration of the surface structure of as-prepared MSA-coated gold nanoparticles.

randomly arranged, which can be confirmed by small angle XRD patterns B and C recorded from spherical assemblies and irregular aggregate, respectively.

It was reported that the MSA-coated gold nanoparticles nucleated through in-equilibrium conditions at the air/water interface to which chemical homogeneity of the surface is a crucial condition.[12] In the presence of organic vapor the surface of solution becomes inhomogeneous in the molecular level because of adsorption of organic molecules at the surface, which hinders the slow crystallizing process. In the case of polar organic vapor, the organic molecules adsorb randomly at the surface, which interferes with the interactions among gold nanoparticles spontaneously moving toward gas/water interface and consequently induces the formation of amorphous aggregates. On the other hand, nonpolar organic molecules tend to form clusters at the surface of suspension as a nucleation center, resulting in dense spherical aggregate of gold nanoparticles. Although the above statement remains speculation at present and to be clarified, the surface of suspension in this system is an important chemical driving force to control the crystallization of nanophase substances.

In conclusion, MSA-coated gold nanoparticle could self-assemble into colloidal crystals with sharp facets at the air/suspension interfaces. But the introduction of nonpolar organic vapor into the gas phase favored the formation of spherical assemblies and polar organic vapor induced irregular shaped aggregates at the gas/suspension interfaces.

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