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Production of Ultrafine Gold and Silver Particles by means of a Gas Evaporation and Solvent Trap Technique

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Abstract

Gold (Au) and Silver (Ag) colloids were produced in ethanol by a gas evaporation technique combined with a solvent trap method. Both the clusters in the solution and those collected before entering the solution were examined by transmission electron microscopy. The size of colloids in ethanol was 30 ~ 100 Å for Au and 50 ~ 200 Å for Ag. In contrast, the clusters collected before the solution trap had a dimension of 10 to 60 Å, which is smaller than those trapped in ethanol. This size increase was brought about by coalescent growth in the solution, which took place when the solution temperature was raised from dry ice/acetone temperature to room temperature.

Introduction

There is a growing interest in physical and chemical properties of ultrafine metal particles less than *ca.* 50 Å in diameter. In this size range, a large fraction of metal atoms are on the surface. As a result, these metal clusters form a new realm of matter; an intermediate range of matter between two limiting forms, *i.e.* molecules/atoms on the one hand, and infinite solids on the other. For several metals, the atomic arrangement as well as the interatomic distances are reported [1–4] to be different from those in the corresponding bulk materials. A softening of lattice vibrations and a decrease in melting point [5] are also found for many metals. In such a small dimension, the translational symmetry and continuum conduction bands characteristic for the infinite bulk system are not yet formed. Furthermore, the dimensions of the clusters are smaller than some intrinsic lengths, such as the wavelength of light, the electron mean free path, the London penetration depth of a superconductor, and the coherence length of the superconducting state. Therefore, it is expected that these clusters exhibit interesting optical properties, magnetism, and superconductivity [6].

To obtain useful experimental data for the physical properties of metal clusters, it is important to select a technique that allows one to prepare clean and well separated clusters with a narrow size distribution. In addition, if one wishes to conduct chemical reaction studies on metal clusters, it is convenient to have them suspended in a solvent. It is well known [7] that metal clusters with one size and one shape can be synthesized by chemical means. However, the size is limited up to ~15 Å. Physical methods such as vacuum evaporation and gas evaporation, on the other hand, are routinely used to produce metal particles larger than 50 Å. It is conceivable that one way to obtain metal clusters in the size range of 10–50 Å in diameter is to combine the gas evaporation (physical) and the solvent trap (chemical) techniques in order to produce a stable colloidal solution of ultrafine metal particles. In this combined technique, fine metal particles produced by the gas evaporation technique (*i.e.* evaporation and condensation of a material in an atmosphere of a low pressure inactive gas [2, 3, 8]) are transfered with a flow of gas into the solvent.*

In this paper we wish to report our attempts to obtain ultrafine Au and Ag clusters in ethanol using the combined gas evaporation and solution trap technique. Transmission Electron Microscopy (TEM) was used to characterize these ultrafine metal particles before and after entering the solution. We find that

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*A similar technique was employed by Kimura and Bandow [9a] to produce gold and silver particles of 50–200 Å in diameter. Yet another technique known as VEROS (Vacuum Deposition on Running Oil Substrate) can also be used to produce fine (20 ~ 50 Å) metal clusters suspended in low vapor pressure oil, e.g. vacuum oil used for diffusion pump. However, the oil suspension technique is not suitable for the subsequent chemical reaction studies [9b].

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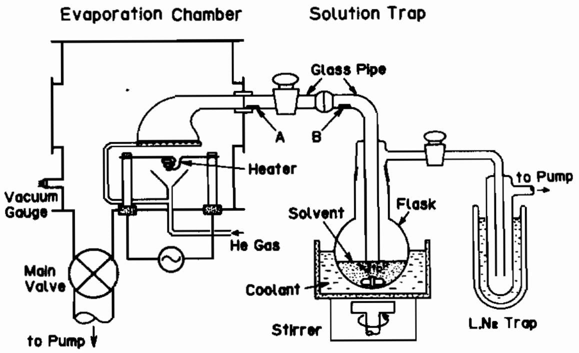


Fig. 1. Apparatus for the preparation of ultrafine colloidal metal particles by the gas evaporation solvent trap technique.

clusters collected before the solution trap are much smaller than those found in the ethanol solution (10–60 *versus* 30–100 Å for Au), indicative of coalescent growth in the solution at room temperature.

Experimental

Figure 1 shows a schematic drawing of the experimental apparatus. The apparatus consists of an evaporation chamber, for producing clusters, and a solvent trap, for collecting the clusters. The evaporation chamber and the solvent trap are connected by 1/2 in. glass pipe. The evaporation chamber was evacuated using an oil diffusion pump equipped with a liquid nitrogen trap. When the pressure reached $\sim 1 \times 10^{-6}$ Torr, the main valve was closed. Helium (He) gas was then introduced into the chamber through two outlet systems: one through the bottom of the lower funnel and the other through small holes (1 mm in diameter) equally spaced around the ring pipe which is located at the edge of the upper (inverted) funnel. Since the solvent trap is evacuated by a mechanical pump, the gas flows from the chamber to the trap. The gas flow carries the particles formed in the evaporation chamber to the solvent trap, in which ethanol was used as a solvent. To lower the vapor pressure of the ethanol, the ethanol in the trap was cooled to dry ice/acetone temperature. The solvent was continuously stirred during collection to insure the uniform mixing of the trapped particles.

Metal clusters of Au and Ag were produced by evaporating the metal in an atmosphere of flowing He gas. The evaporation was carried out using a tungsten basket in which ~100 mg of the metal was charged. The basket was heated at various temperatures between 1400 and 1700 ℃ for Au, and between 1200 and 1500 ℃ for Ag. The gas pressure in the evaporation chamber was varied from 1 to 10 Torr. The cluster size can be controlled by the evaporation temperature, the evaporation rate, and the gas pressure; the lower the temperature and gas pressure, the smaller the clusters become [10]. The He gas and the metals (Au and Ag) were commercial materials of 99.99% purity. The ethanol used was also a commercially available, high grade material, and neither special purification nor dehydration were carried out.

Specimens for electron microscopy were obtained by dropping the sample solution on copper grids covered with a thin (~200 Å) carbon film. The clusters collected before entering the solution trap were also examined. These samples were obtained by depositing clusters directly onto carbon-coated copper grids, which were placed on the inner wall of the glass pipe at locations A (upstream) and B (downstream), as shown in Fig. 1. TEM micrographs were obtained using a Philips 420T electron microscope operated at 120 KV.

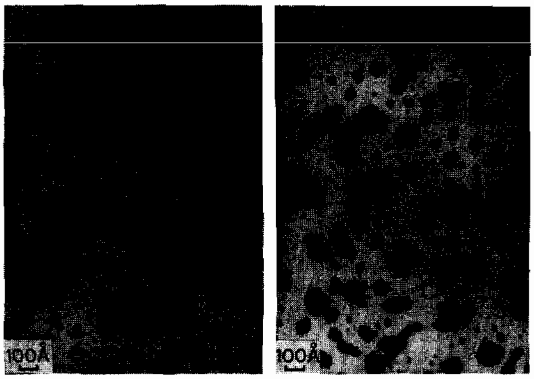
Results and Discussion

Some colloids obtained by us were stable at room temperature (RT) for weeks. Others agglomerated rapidly within minutes after the temperature was raised to RT. Yet they are quite stable at dry ice/acetone temperature. At present, it is not clear what determines the stability of the colloids. However, there was a general tendency for the colloids to be more stable when the size of the metal particles was smaller. The stable colloids were often obtained when the He pressure was lower than 7 Torr and the evaporation temperature was lower than 1600 ℃ for Au and 1400 ℃ for Ag.

Gold

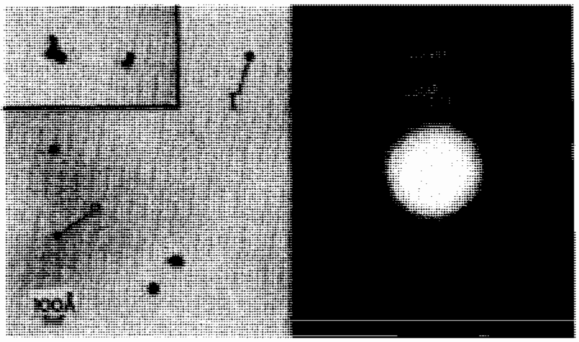
Freshly prepared gold colloids in ethanol initially showed a reddish purple color at dry ice/acetone temperature. The color changed to purple when the temperature was raised to RT. As will be discussed later, this color change is due to the increase of cluster size occurring in ethanol solution.

Figure 2a and b show TEM micrographs of Au clusters deposited on the inner wall of the glass pipe at locations A (upstream) and B (downstream), respectively (see Fig. 1). Two kinds of colloidal particles are found; large particles with complex external shapes having 'amoeba-like' appearance and small ones with a spherical shape lying between the large ones. The 'amoeba-like' particles are apparently coalesced particles which have grown on the Cu grids (particles are supported on a carbon thin film covering the grid). The size of the 'amoeba-like' particles decreases as the collection position moves from upstream to downstream (from location A to B in Fig. 1). Since the number density of the clusters is higher at upstream (position A) than that at downstream (position B), the probability of coalescence is



(a) (b)

Fig. 2. Electron micrographs of Au particles deposited on the inner wall of the glass pipe: (a) at the entrance (upstream) and (b) at the exit (downstream) of the pipe. The positions of collection for (a) and (b) are indicated by A and B in Fig. 1, respectively.



(a) (b)

Fig. 3. (a) Electron microgaph and (b) diffraction pattern of colloidal Au particles in ethanol. Clusters P and I show external shapes and contrast characteristics for pentagonal and icosahedral multiply-twinned particles, respectively. The upper insert in (a) shows clusters having a coalesced appearance. Reflection rings observed in the diffraction pattern are indexed as shown in (b).

higher at the upstream. Therefore, the coalesced particles in Fig. 2a are larger than those in Fig. 2b. Moreover, such 'amoeba-like' particles were not found in the suspension.

In Fig. 2, the small particles between the large coalesced ones are believed to be original clusters formed in He gas. The size of these small particles ranges from 10 to 60 Å, and seems to be invariable between Fig. 2a and b, indicating that the growth of the clusters has already been completed prior to entering into the pipe.

Figure 3a shows an electron micrograpn of Au clusters in a stable colloid in ethanol. This micrograph reveals that Au clusters suspended in ethanol were well separated from each other, and that the size ranges from 30 to 100 Å. An electron diffraction pattern indicates that these clusters are normal fcc Au. Multiply-twinned particles (MTPs) [1] are observed and marked with symbols, P and I in Fig. 3a. The MTP is commonly found in fcc metals and is more stable than a single crystal of the corresponding metal when the size of particles becomes less than a few hundred Å in diameter.

Some clusters are apparently recognized as coalesced clusters from their coagulated appearance of the external shape. Such clusters are shown in an insert of Fig. 3a. Although they are coalesced clusters, the size is much smaller than that of the 'amoeba-like' particles found in Fig. 2.

Small clusters less than 30 Å in diameter were observed only among the clusters collected in the pipe and could not be found in the solution. The disappearance of these clusters may be due to the coalescent growth of originally small clusters in the ethanol. The change in color of the colloids from reddish purple at dry ice/acetone temperature to purple at RT further supports an increase in the cluster size. Gold clusters with the size of 10 ~ 60 Å coalesced readily at RT. The occurrence of coalescent growth in ethanol also suggests that the surfaces of the Au clusters are clean.

Silver

Figure 4 is a TEM micrograph showing a stable Ag colloid. The size ranges from 50 to 200 Å, and is larger than that of Au clusters. The large clusters with irregular shapes are obviously coalesced clusters. Like Au colloids, the coalescent growth in ethanol brings about an increase in the cluster size.

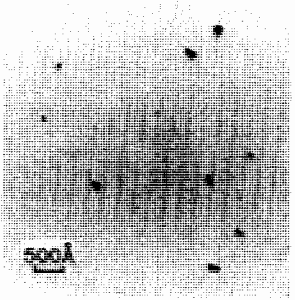


Fig. 4. Electron micrograph of colloidal Ag particles in ethanol.

Concluding Remarks

Ultrafine colloidal gold and silver particles suspended in ethanol can be obtained by means of a gas evaporation technique combined with a solvent trap method. Subsequent coalescent growth was found to take place in ethanol, thus limiting the size of the colloids. For example, the Au metal clusters initially formed by the gas evaporation technique were as small as 10 ~ 60 Å in diameter. In ethanol, the size grew to 30 ~ 100 Å, along with coalesced particles. It is concluded that in order to obtain stable metal colloids with the size of a few tens of Å, it may be necessary to add some reagent to prevent the growth or to change the solvent (work in progress).

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