Metal Colloids Produced by Means of Gas Evaporation Technique. V. Colloidal Dispersion of Au Fine Particles to Hexane, Poor Dispersion Medium for Metal Sol

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Metal fine particles are not dispersed at all in pure solvents with a low dielectric constant, such as hexane. The gas flow-cold trap method combined with surfactants was found to be effective in stabilizing ultrafine metal particles in solvents with a low dielectric constant. Ultrafine gold particles can be stably dispersed in hexane in a colloidal state by this method. It was found that the stabilizability of the colloid depends on the ionic types of the surfactant. Thus, a cationic surfactant such as dimethyldioctadecylammonium chloride (DOAC) shows good dispersibility, whereas an anionic surfactant such as 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT) dose not. The optical spectra of colloid solutions suggest a difference in the local colloidal state between two types of surfactants. Colloidal solutions of a gold fine particle/DOAC/hexane system are so stable against heating or drying that the solvents are easily substituted.

In a coagulated metal ultrafine particle (UFP), the wave function of conduction electrons is presumed to diffuse between metal UFP's. The physical characteristics resulting from the electronic state of each metal UFP can be modified through this contact and be changed close to that of bulk materials according to the degree of contact.[1] On the contrary, metal UFP's in dispersions are expected to give physical properties and structural information concerning individual metal UFP more delicately than that in coagulation. We initiated a series of studies[2-5] in order to characterize the features of isolated metal UFP's dispersed into the liquid phase. In general, however, the preparation of stable dispersions of metal UFP in an organic liquid is difficult.

Some approaches to obtain stable dispersions of metal UFP have already been reported by several authors. The vacuum evaporation on running oil substrate (VEROS) method[6] is one of the available approaches for the preparation of dispersions of metal UFP. However, a severe restriction is imposed on the selection of solvents, i.e. oil with a very low vapor pressure must be selected. The chemical reaction method in a liquid phase is also a well-known technique in colloid chemistry for obtaining metal UFP dispersions.[7] However they are restricted to being almost only aqueous dispersions. Furthermore, several kinds of by-product, such as ions, remain in the solutions. The surface of metal UFP in these dispersions cannot be clearly defined because of considerable modifications, such as oxidation or chemisorption of several kinds of compounds. These techniques are, hence, not suitable for our purpose.

The authors have reported on methods for obtaining stable dispersions of UFP in pure organic liquids.[2] These methods were based on the evaporation technique in flow gas combined with matrix isolation techniques using frozen organic solvents (the gas flow-cold trap method) or cooled organic liquids (the gas flow-solution trap method) as a matrix. According to the combination of solvents with a high dielectric constant and metals with a high electron affinity, stable colloidal dispersions can be obtained by this method.[8] However, it is difficult to prepare stable dispersions for solvents with a low dielectric constant. We report here a method for obtaining stable colloidal dispersions of metal UFP in organic solvents with a low dielectric constant, employing the gas flow-cold trap method with the cationic surfactant of dimethyldioctadecylammonium chloride (DOAC). We tested the validity of this method with gold fine particles and hexane as the dispersed phase and dispersion medium, respectively. The surfaces of gold fine particles are considered to be free from oxidation, and hexane is one of the most poor solvents with respect to the formation of stable colloidal dispersions of metal UFP.[8] The colloidal solutions obtained by this method were found to be quite stable against such thermal processing as increasing temperature or freezing. Further, it was found that stable colloidal solutions are readily reproduced by exchanging the dispersion media after the drying process.

Experimental

Materials. Pure (99.99%) pieces of gold were purchased from Tanaka Kikinzoku Kougyou company. The dispersibility of the fine particles was examined for different types of surfactants, i.e. DOAC as a cationic surfactant and AOT (Aerosol OT, sodium 1,2-bis(2-ethylhexyloxycarbonyl)-ethanesulfonate) as an anionic surfactant. Both surfactants were of guaranteed grade and purchased from Tokyo Kasei Ltd. AOT was purified by a method reported by Kunieda et al.[9] A benzene solution of 15% AOT was washed three times with distilled water to remove water-soluble impurities. After evaporating benzene, AOT was dissolved into a 25% aqueous methanol solution and washed three times with petroleum ether to remove oil-soluble impurities. The solvents were removed by evaporation for 12

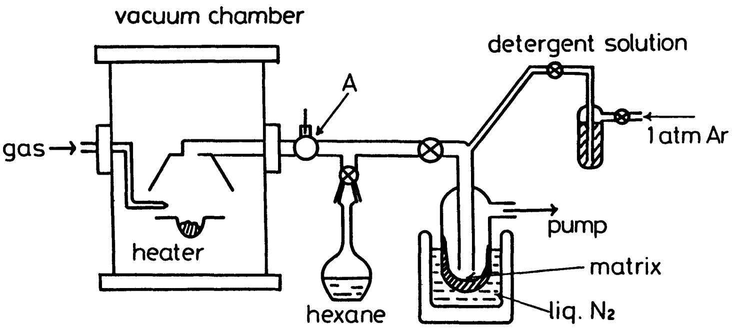
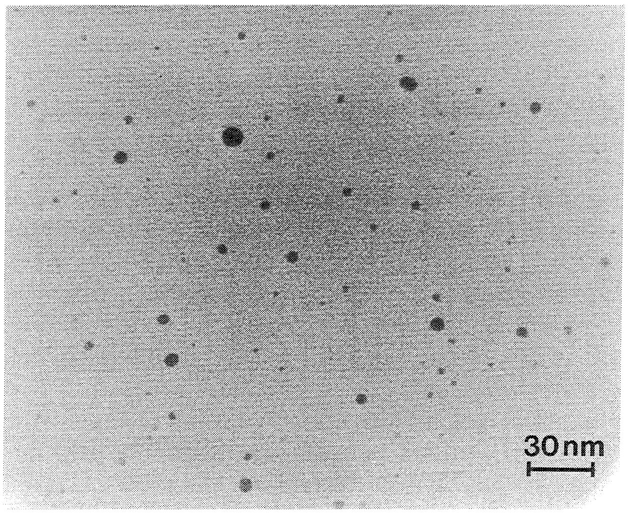


Fig. 1. The apparatus for the gas flow-cold trap method. Gas phase sampling of fine particles was performed at the point A by exposing Cu mesh with evaporated carbon film to the flow of carrier gas.

hours. AOT was then dissolved into methanol and shaken with hexane. Finally, AOT in the hexane phase was extracted and evacuated again for 12 hours. DOAC was recrystallized three times from dehydrated acetone and evacuated to dryness for 12 hours. Hexane solutions of both 0.1 wt% AOT and 0.01 wt% DOAC were prepared for the experiments. Since DOAC was hardly soluble in hexane, a cationic surfactant of (2-dodecylhexadecyl)trimethylammonium chloride (g-C28TAC)[10] was used for concentrated samples after the same purification process as DOAC. The solubility of g-C28TAC is sufficiently high due to a branched alkyl chain in this compound. g-C28TAC was kindly supplied by Mr. Kazuyuki Yahagi of Tokyo research laboratories, Kao corporation.

Preparation of Au UFP/Hexane Colloidal Solution. Au fine particles were formed and collected by the gas flow-cold trap method.[2] Figure 1 shows a schematic diagram of this method. The chamber was evacuated to 5.0×10^{-6} Torr prior to the introduction of inert gases (1 Torr≈133.322 Pa). The constant flow of He as a surrounding gas and Ar as a carrier gas were supplied around the heater. The particles in the gas stream were led to the trap which was cooled by liquid N_2. The partial pressures of He and Ar were 8 and 2 Torr, respectively. Purified and degassed hexane was vaporized into the gas stream from the chamber to the trap. Under an atmosphere of constant-flow inert gases, pieces of gold were heated in a tungsten wire heater and the UFP's produced were led to a frozen hexane matrix in the trap. After the accumulation of a sufficient amount of gold fine particles, liquid N_2 was removed. As soon as the matrix surface began to melt, a detergent solution was introduced on the matrix surface and the trap was filled with Ar gas at atmospheric pressure. Then, the trap was irradiated by ultrasonic waves. This ultrasonic wave treatment was continued for more than 5 minutes after a full melting of the matrix.

Characterization of Colloidal Solutions. The size distributions and the states of contact of UFP's were determined by a Hitachi H-500H type transmission electron microscope (TEM) of the laboratory of electron microscopy, the National Institute for Physiological Sciences at Okazaki. Specimens for TEM were obtained by dropping sample solutions on Cu grids coated by carbon film of 8 nm thickness. In order to obtain the size distribution of Au fine particles in the gas phase, Au fine particles were sampled at point A in Fig. 1, the location of which was the midpoint of the vacuum chamber and the solvent pool. A sample mesh for the electron microscope was exposed to the flow of the fine particles for about 1 second. The size distributions of Au fine particles were determined by TEM photographs using an Image analyzer (Kontron IBAS-1 of the Center for Analytical Instrument, the National Institute for Basic Biology at Okazaki).



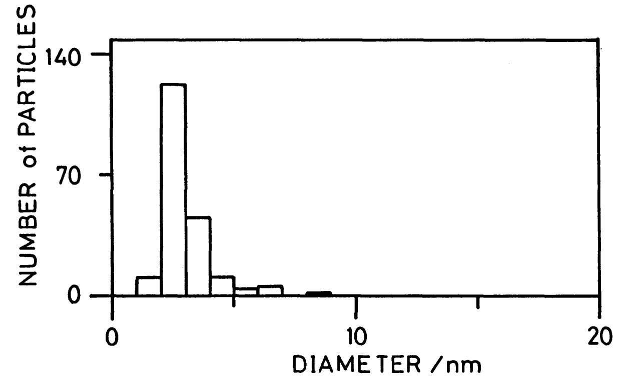


Fig. 2. (a) TEM micrograph of Au UFP's sampled in gas phase. The exposure time was about 1 second. (b) Size distribution of picture (a).

Optical measurements were carried out using a Varian Cary 2300 spectrophotometer. The absorption spectra were

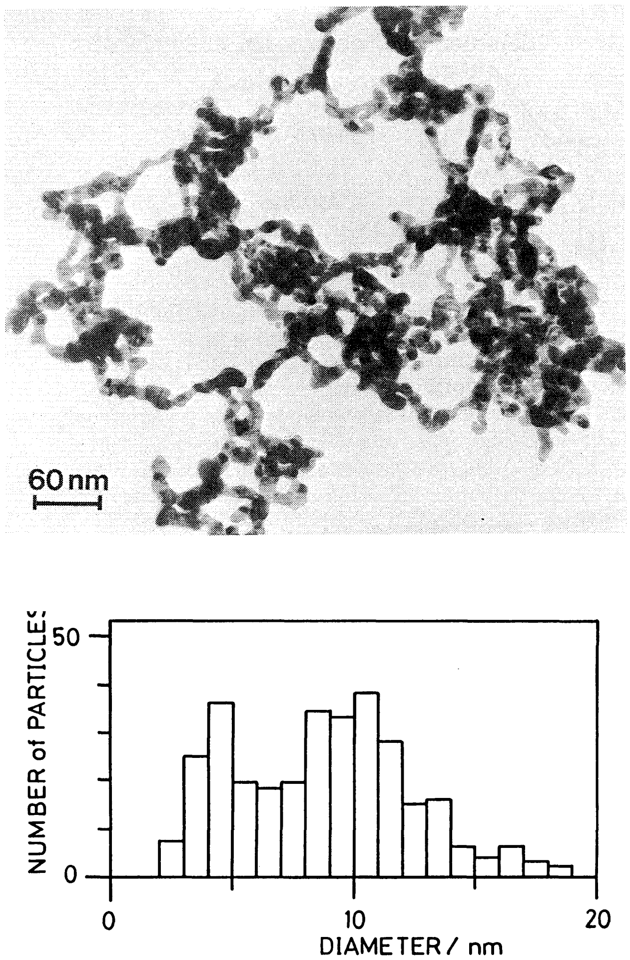


Fig. 3. (a) TEM micrograph of precipitates of Au UFP's deposited from hexane. (b) Size distribution of picture (a).

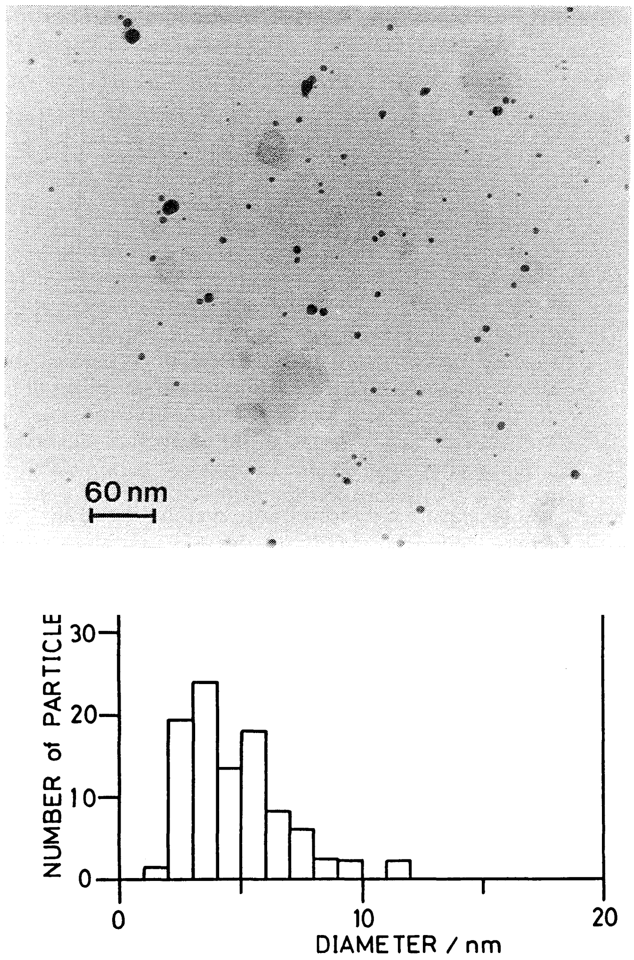


Fig. 4. (a) TEM micrograph of Au UFP's deposited from colloid solution of Au UFP's/DOAC/hexane system. (b) Size distribution of picture (a).

recorded at room temperature just after the preparation of a colloidal solution. A conventional quartz cell was used.

Results

Figure 2(a) shows an electron micrograph of the particles sampled in the gas phase. A number of particles of about 2.5 nm in diameter can be seen in the photograph. The smallest particles are less than 1.0 nm. Figure 2(b) shows the size distribution determined from this picture. It can be seen that the evaporation method with a flow gas provides a size distribution with a sharp single peak. The maximum of this distribution curve was 2.5 nm. As reported in Ref. 5, almost all kinds of metallic fine particles, including Au, do not disperse in hexane at all without surfactants. Au fine particles coagulated as soon as the melting of a matrix and precipitated and were deposited within a few minutes. Figure 3(a) shows a TEM picture of these precipitates just after an ultrasonic treatment. Fine particles come into contact with each other to form larger aggregates. The boundaries of constituent particles become indistinct. It seems that particles coalesce to each other to some extent. A typical size-distribution curve of the system of Au UFP/hexane is shown in Fig. 3(b). Compared with a size histogram of these particles with those in the gas phase, it is easy to realize that further growth by coalescence proceeded in complex ways.

The effect of DOAC on the dispersibility of Au UFP is apparent. The colloidal solution prepared by the method described in the experimental section was colored rose-red and transparent, and scattering light through the solution was hardly observable in the visible region. A TEM picture of this solution is shown in Fig. 4(a). Most of the fine particles are observed in isolation in any photogram image. The diameter of the smallest particle observed in this figure is less than 1.0 nm, which is comparable to the size of particles sampled in the gas phase. Figure 4(b) shows a typical size histogram of Au fine particle/DOAC/hexane system. The maximum peak of this histogram is located at nearly the same place as those in the gas phase; however, the width of this histogram is somewhat larger. This fact means that coalescence growth can not be completely avoided, even when

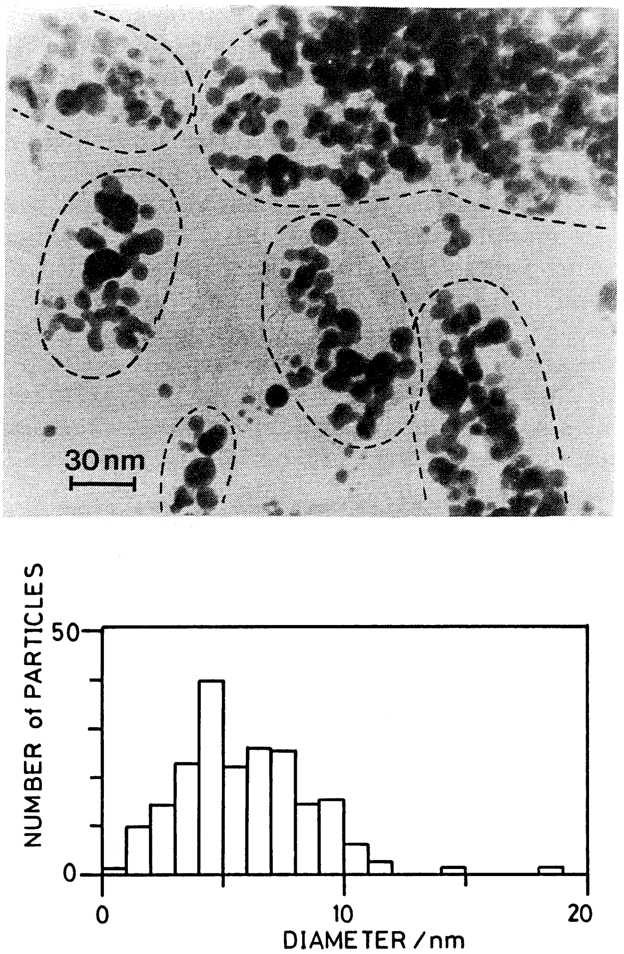


Fig. 5. (a) TEM micrograph of Au fine particles deposited from colloid solution of Au UFP's/AOT/hexane system. The encircled regions by broken lines represent the examples of aggregation unit of densely packed Au UFP's. (see discussion). (b) Size distribution of picture (a).

using the present method.

The effect of surfactants on the dispersibility of Au UFP depends on the ionic types of the hydrophilic part. The solution of the Au fine particle/AOT/hexane system is colored blue and is transparent just after the melting of the matrix. However, the colloidal dispersion of this solution is not stable. The Au UFP/AOT complexes fully precipitate within a few hours. Figure 5(a) shows a TEM picture of this system, sampled just after an ultrasonic treatment. The fine particles in this picture are anisotropic and irregular in shape more than those in Fig. 4(a). As is discussed later, this fact implies that the original Au UFP coalesce in an AOT/hexane system to a greater degree than in a DOAC/hexane system. However, it is worth noting that coalescent growth stopped at some stage. The boundaries of grown Au UFP can clearly be seen. From the size distribution of this colloidal system (Fig. 5(b)), one recognizes that AOT is also effective in preventing the coalescence growth process of fine particles to some extent, though coagulation does takes place.

Discussion

The size distributions of UFP strongly depend on the particle growth mechanism. Two growth processes have been proposed, i.e., the absorption and the coalescence growth processes.[5,11] In the absorption process, particle nuclei grow along with the absorption of metal atoms. The size distribution curve in this case is the normal distribution. In the coalescence growth process, however, particles grow by collisions of small clusters and the size distribution is the log-normal distribution. Graphical analyses make it possible to determine which mechanism takes place. Figure 6 shows logarithmic probability analyses of our samples. If the size distribution of particles is a log-normal one, a linear correlation is obtained between the cumulative percentage of particles with a certain size and the logarithm of the size of particles in a logalithmic probability plot. The size distribution of the gas-phase-particles by the gas-flow method is found to follow a log-normal distribution, as shown in Fig. 6. This is a rather surprising fact, since the coalescence growth process was derived by assuming a stationary state, whereas in the gas-flow method particles grow within a turbulent gas stream. The size distribution of a Au UFP/DOAC/hexane system also provides a linear correlation in the log-probability plot. In this case, the original features of the size distribution basically remained unchanged. The size distribution of a Au UFP/AOT/hexane system, how-

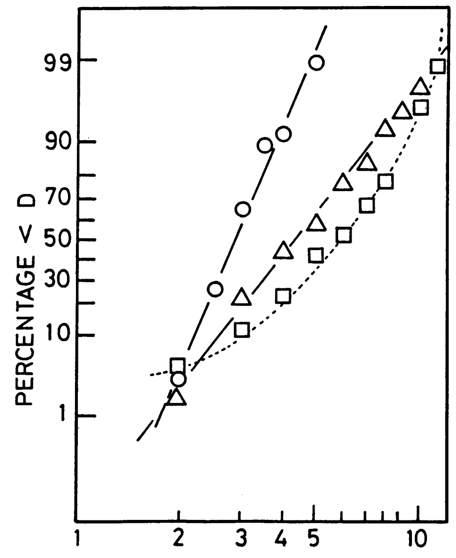


Fig. 6. Logarithmic probability plot of the size distribution of Au UFP's sampled from the gas phase (○), Au UFP/DOAC/hexane solution (△), Au UFP/AOT/hexane solution (□). The ordinate indicates the cumulative percentage of particles with diameters smaller than *D*.

ever, changes slightly from the log-normal distribution. This implies that particles in a Au UFP/AOT/hexane system grew in a more complex manner than in the Au UFP/DOAC/hexane system.

The optical properties of a colloidal solution sensitively reflect the dispersion state of the colloid, as was fully described by Kreibig.[12] He discussed and analyzed the visible absorption spectra of Au UFP taking into account the topography of the particle assembly, and introduced the fractal dimension as a relevant parameter for characterizing the metal UFP aggregate system.[13] Figure 7 shows the absorption spectra of (a) Au UFP/DOAC/hexane and (b) Au UFP/AOT/hexane solutions (those in Figs. 4 and 5, respectively) measured just after the ultrasonic treatment. The absorption spectra were characterized by a peak at 520 nm for (a) and 600 nm for (b), whereas a shoulder at 270 nm and an abrupt rise below 210 nm for both. The absorption spectrum in the visible region is mainly attributed to the surface plasma absorption of free electrons,[14] which has been well studied and is understood[15,16] in terms of Mie's scattering theory,[17] combined with Drude's free electron model. The ultraviolet spectrum reflects d-s interband transitions, the threshold of which is 2 eV.[14,15,18,19] The theoretical absorption spectra of a Au colloid solution was calculated according to the method of Doremus, in which the homogeneous dispersion was treated[15] within the framework of Mie's theory. Good agreement between the calculated and experimental absorption spectra was obtained in the case of the Au UFP/DOAC/hexane colloidal solution. This implies that DOAC is capable of dispersing Au UFP's ideally in hexane. This is not true for AOT. In the light of the classical free electron model for metal UFP, the maximum wavelength of a plasma absorption peak does not shift with the size of UFP when the size of the particles are sufficiently smaller than the wavelength, while the height and width of the peak are sensitive to the size.[15] Therefore, the differences in the average sizes and or the size distributions between Au UFP's of Au UFP/DOAC/hexane and of Au UFP/AOT/hexane systems could not explain the shift of the peak position from 520 to 600 nm (Fig. 7). A surface plasma peak is known to shift to the longer wavelength and to broaden when a volume fraction of colloid particles increases due to a dipolar interaction.[16,20,21] Since the total volume fraction of Au particles was nearly the same for both samples, the peak shift and broadening of the spectra must be explained in terms of the difference in the local colloidal state of the solutions. Actually, it is reported that a plasma resonance peak shifts to a longer wavelength and broadens when the colloid systems consist of well separated aggregates of densely packed particles.[12] In the TEM images of a Au UFP/AOT/hexane system, most particles are observed in aggregates of several tens or several hundreds of nanometers. An example of these units of aggregate is shown in Fig. 5(a). In the Au UFP/AOT/hexane colloidal system it is reasonably understood from the instability of the colloidal state that Au UFP's tend to form aggregates including AOT, even immediately after the matrix melts. The specificity to the ionic type of surfactants (i.e., the cationic surfactant disperses Au UFP's well, while the anionic surfactant does not) suggests a difference in the affinities of the surfactant to the surfaces of the Au UFP's between a cationic and an anionic surfactant. However, it is not clear at present why Au UFP's prefer DOAC to AOT. Further experiments for understanding the microscopic mechanism of the adsorption of the surfactants to the surfaces of Au UFP's are currently under way.

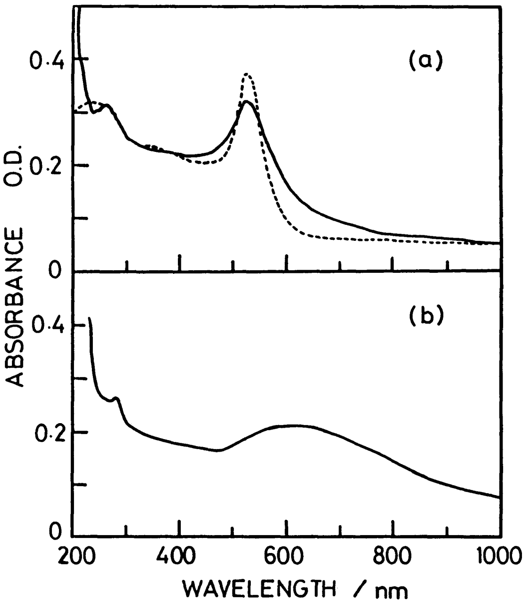


Fig. 7. (a) Optical absorption spectra of calculated (broken line) and Au UFP/DOAC/hexane colloidal solution (solid line). The calculated line was obtained from the first approximation of Mie's theory ($D \ll \lambda$; where D is diameter of UFP, λ, wavelength of light) using complex dielectric constants of Ref. 14.[15] (b) Absorption spectrum of Au UFP/AOT/hexane colloidal solution obtained just after the ultrasonic treatment.

When a Au UFP/DOAC/hexane solution is concentrated by evaporation, a phase separation occurs and Au UFP's precipitate with DOAC. It seems that the maximum concentration of Au UFP's in hexane is determined by the solubility of the surfactant into hexane. g-C28TAC, which has a much higher solubility in hexane than does DOAC due to the branched alkyl chain, is capable of stabilizing Au UFP's with more than a 100-times higher concentration.

The colloidal solutions stabilized by these cationic surfactants are quite stable against the passage of time, thermal processes (to the boiling point of hexane) and drying. In particular, the stability against drying makes it possible to exchange the type of solvent.

Hexane can be substituted for organic solvents with a dielectric constant less than ca. 10. The remarkable features of a colloidal solution of metal UFP's using a cationic surfactant for both the stability and changeability of the solvents are advantageous for future applications.

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