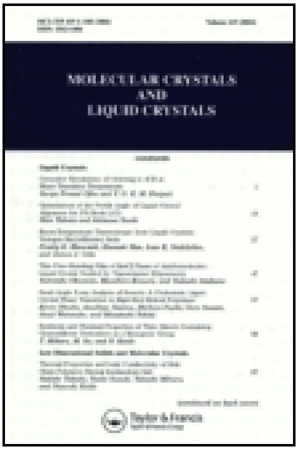

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Optical Properties of Dispersion and Monolayer of Silver Nanoparticles

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Optical Properties of Dispersion and Monolayer of Silver Nanoparticles

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Dispersion of silver nanoparticles was prepared from silver *n*-tetradecanoate via thermal decomposition. The absorption spectrum of the dispersion showed a broad band at ca. 420 nm, characteristic of plasmon in the silver nanoparticles. On the other hand, the nanoparticle monolayers both on water and on quartz had an absorption band at 470 nm, which coincided with the position of the reflection bands. Surface reflectance of the dispersion in toluene also had a broad band with a peak wavelength of 470 nm.

Keywords: silver nanoparticle; dispersion; monolayer; UV-vis absorbance; UV-vis reflectance

INTRODUCTION

Currently, metal nanoparticles are important both for fundamental issues in optical and quantum physics and for practical applications to future optoelectronic devices, because they bear unique optoelectronic and magnetic properties different from bulk metals due to large surface effects and small volume in the metal[1-5]. The problem is that the preparation of such nanoparticles requires complicated and sensitive procedures. To prevent the coagulation of metal nanoparticles, additional process for surface passivation just after the preparation of the nanoparticles is demanded.

Recently, we have developed a low-cost and one-step preparation method of silver nanoparticles including passivation[6-8]. As schematically shown in Fig. 1, silver nanoparticles passivated with alkylates can be prepared via thermal decomposition of silver alkylates at 250 °C in a nitrogen atmosphere. By washing the residue with methanol and dispersing it into toluene, by-products and unreacted reagents are removed. The silver core is surrounded by the alkylates with the alkyl chains protruding outside. The silver nanoparticles are dispersible in nonpolar or little polar liquids, such as hexane, cyclohexane, benzene and toluene, but not in high polar liquids. When the dispersion of the nanoparticles is spread on a water surface, the nanoparticles form a monolayer. In this report, we focus on the optical properties (absorption and reflection) of the dispersions and monolayers of the silver nanoparticles derived from silver *n*-tetradecanoate.

EXPERIMENTAL

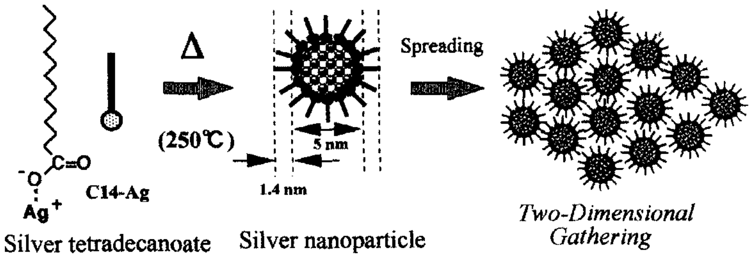

FIGURE 1 Preparation for passivated silver nanoparticles via thermal decomposition of silver alkylates.

Hexane, cyclohexane and toluene (reagent grade) were used as dispersion media without any further purification. The passivated silver nanoparticles were prepared from silver *n*-tetradecanoate as reported previously[6-8]. The silver nanoparticle dispersion in toluene (3 μg/10 ml) was spread onto a clean water surface at room temperature. Before compression, the film of the nanoparticles was left for 30 min to allow for the evaporation of toluene. The monolayer was transferred onto quartz by a horizontal lift method.

UV-vis absorption spectra of the dispersions were measured on a Shimadzu UV3100PC spectrometer. Absorption and reflection spectra of the monolayer on a water surface were measured *in situ* with a set-up schematically depicted in Fig. 2. White light was introduced at an incident angle smaller than Brewster angle of the monolayer. For absorbance (or reflectance) measurements, the reflected light from a submerged mirror (or from the monolayer) was detected. Absorption and reflection spectra of the transferred monolayer on quartz were also measured on the UV3100PC spectrometer.

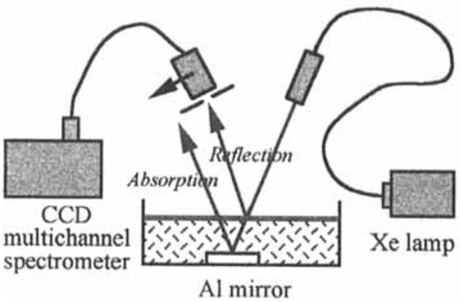

FIGURE 2 Set-up for *in situ* absorbance and reflectance measurements of the silver nanoparticle monolayer on water.

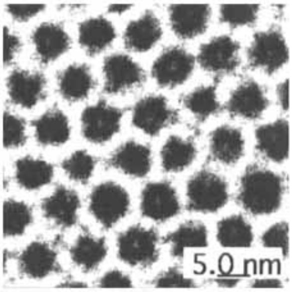

FIGURE 3 Two-dimensional array of the passivated silver nanoparticles.

RESULTS AND DISCUSSION

The equilibrium spreading pressure of the silver nanoparticles, the driving force for the spreading of the particles on a water surface, was negligibly small: the nanoparticles hardly form a monolayer by themselves. For the homogeneous film preparation, therefore, a dispersion medium, which is also a spreading solvent, plays an important role. The criteria of the dispersion medium as a spreading solvent are (1) moderate volatility (e.g., hexane is too volatile), and (2) a positive spreading pressure (i.e., the dispersion medium should easily spread on water surface). In this respect, toluene is the most suitable spreading solvent for the silver nanoparticle monolayer preparation. In fact, the nanoparticles form a monolayer that resembles an insoluble surfactant monolayer on a water surface[6-7]. Figure 3 shows a transmission electron micrograph of a transferred monolayer. Dark and bright regions correspond to silver cores and alkyl moieties, respectively. It is clear that the nanoparticles are hexagonally packed in the monolayer.

The monolayer of the silver nanoparticles on water surface reflected and absorbed visible light quite strongly. The absorption spectrum of the nanoparticle monolayer on water is shown in Fig. 4, together with that of the dispersion in toluene. The dispersion exhibited a broad band with a peak wavelength of ca. 420 nm due to plasmon in the silver nanoparticles[9]. The peak wavelength slightly depended upon the dispersion medium; the peak wavelength of the dispersion in toluene (422 nm) was a few nanometers longer than those in hexane and cyclohexane (420 nm). On the other hand, the peak wavelength in absorbance of the monolayer was ca. 470 nm, which coincided with that in the reflection spectrum (data not shown).

The monolayer transferred on quartz also exhibits similar absorption and reflection spectra with a peak wavelength of ca. 470 nm (Fig. 5). It is noteworthy that the peak wavelength in absorbance of the monolayer was also shifted by ca. 50 nm compared with that of the dispersion. Those red-shifts would be attributed to the gathering of silver nanoparticles both at the water and at the quartz surfaces[4].

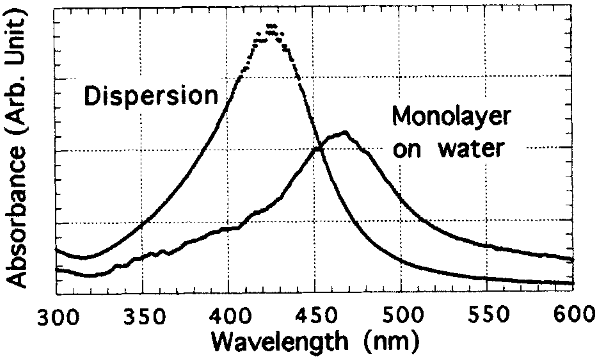

FIGURE 4 Absorption spectra of the passivated silver nanoparticles in toluene and in a monolayer on water.

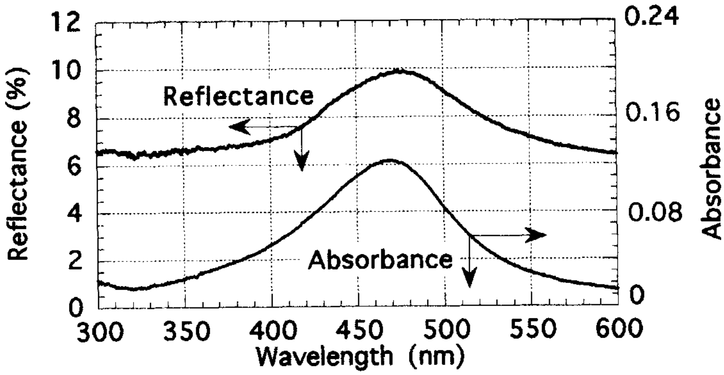

FIGURE 5 Absorption and reflection spectra of the monolayer of the silver nanoparticles on quartz.

In addition, we observed reflection at the air/liquid interface of the dispersion in toluene, which is absent in the cases of hexane and cyclohexane. The peak wavelength of the reflection spectrum (ca. 470 nm) was also ca. 50 nm longer than that of absorption spectrum of the dispersion. This reflection spectrum resembles those of monolayers on water and quartz. A tentative explanation is as follows: the silver nanoparticles should adsorb at the surface of toluene dispersion since the passivated silver nanoparticles should be expelled from toluene due to their somewhat lower affinity with toluene having certain polarity and π electrons. Gathering the nanoparticles at the toluene surface, as well as in the monolayers on water and quartz, would change the environments of the nanoparticles and cause the red-shifts.

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