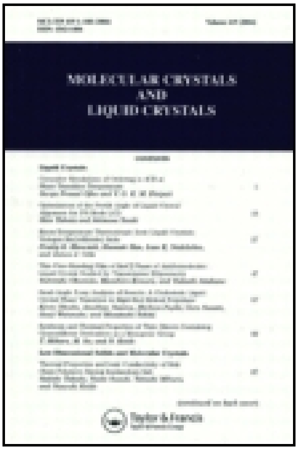

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Two-dimensional Arrangement of Silver Nanoparticles on Water Surface

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Version of record first published: 24 Sep 2006

To cite this article: Koji Abe, Takeshi Hanada, Tomohiko Yamaguchi, Hiroshi Takiguchi, Hiroshi Nagasawa, Masami Nakamotod & Kiyoshi Yase (1998): Two-dimensional Arrangement of Silver Nanoparticles on Water Surface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 322:1, 173-178

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 173–178
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Two-dimensional Arrangement of Silver Nanoparticles on Water Surface

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Received 6 April 1998; accepted 26 April 1998

ABSTRACT Silver nanoparticles passivated with alkylate were formed via thermal decomposition of silver alkylates. The nanoparticles prepared from silver *n*-tetradecanoate were spread on the water surface, where they may move easily and thus expected to be arranged regular two-dimensional array. The properties and preparation conditions of the nanoparticle film were investigated by surface pressure – area isotherm and Brewster microscopic observation. The transmission electron micrographs of transferred film of the nanoparticles suggested that the nanoparticles distribute in the film regularly. Control of surface pressure enable us to form the C14-AgNP film with less defects on water surface.

Keywords: Silver nanoparticle; Surface pressure – area isotherm; Area compressibility; Brewster angle microscopy; Transmission electron microscopy

INTRODUCTION

Thermal decomposition of silver salts of fatty acids in an atmosphere of nitrogen produces fine silver nanoparticles passivated with alkylate. The nanoparticles, prepared via this easy and low-cost procedure, have an advantage of high stability due to the passivation. Regular arrangement of such nanoparticles is expected to bear unique photo-electric and magnetic properties, due to the nanometer size metal particles[1-3].

To arrange the nanoparticles in two dimensional space, the nanoparticles were spread on water surface, where they may move easily and expected to be arranged regularly. Compressing the film, i.e. applying surface pressure, it would bear less defects and/or closer packing of nanoparticles. To optimize the preparation conditions for regular arrangement of the nanoparticles, we examined the nanoparticle films on water surface (surface pressure – area isotherm, area compressibility and Brewster angle microscopic observation) and those transferred from water surface (transmission electron microscopy).

EXPERIMENTAL

The silver nanoparticles were prepared via thermal decomposition of silver salts of fatty acid at 250 °C under nitrogen atmosphere as shown in Fig. 1[4,5]. The nanoparticles prepared from silver *n*-tetradecanoate (C14-AgNP) were dispersed in toluene and spread on water surface. After spreading C14-AgNPs, the film on water was left for 30 min to evaporate toluene. The rate for successive compression of the film was 5 mm/min. Surface pressure was determined by the Wilhelmy plate method[6] using a filter paper plate with a moving wall trough (Nippon Laser & Electronics Lab., NL-LB240S-MWC) at 22 °C. Simultaneously, morphologies of C14-AgNP film were visualized with Brewster angle microscope (Nippon Laser & Electronics Lab., NL-EMM633). The C14-AgNP films were transferred from onto carbon

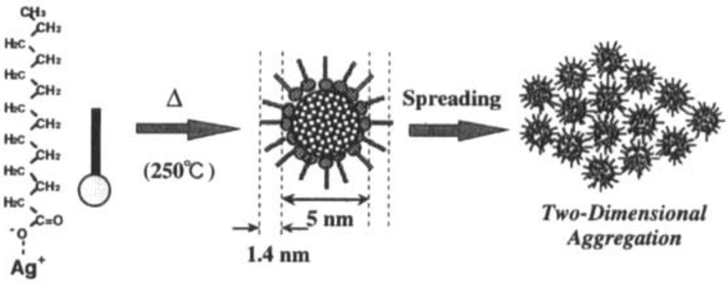

FIGURE 1 Schematic drawing of silver nanoparticle preparation via thermal decomposition of silver *n*-tetradecanoate.

supporting film at 10 mN m^{-1} by a horizontal transfer method. The distribution of the C14-AgNP in the transferred film was observed by transmission electron microscope (Carl Zeiss CEM-902).

RESULTS AND DISCUSSION

The dispersibilities of C14-AgNP were examined. The C14-AgNP did not disperse at all in solvents with high polarity, such as water, methanol, ethanol and acetone. They were dispersible in non-polar solvents, such as benzene, toluene, cyclohexane and hexane. In chloroform and tetrahydrofuran, they were dispersible but most of them precipitated a few weeks later. These dispersing tendency attributes to alkyl chains surrounding silver core. In this study, therefore, toluene was employed as a spreading solvent.

In figure 2, surface pressure π of the C14-AgNP film is plotted against the occupied area A of C14-AgNP on water surface, estimated from calculation of C14-AgNP weight on the assumption that the C14-AgNP have an uniform size as illustrated in Fig. 1. The area of C14-AgNP in the film is much larger than those of common surfactants, cf. *n*-tetradecanoate at 10 mN m^{-1}, pH 2 and 25 ℃, $A = 0.35$ nm^2. This difference comes from the size difference

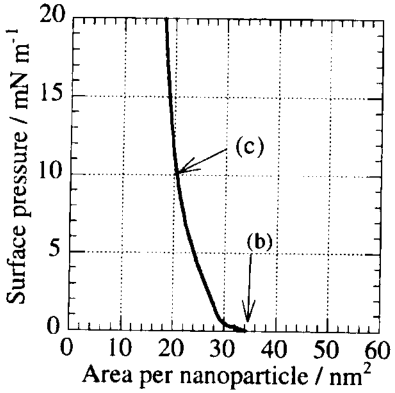

FIGURE 2 π–A Isotherm of C14-AgNP film

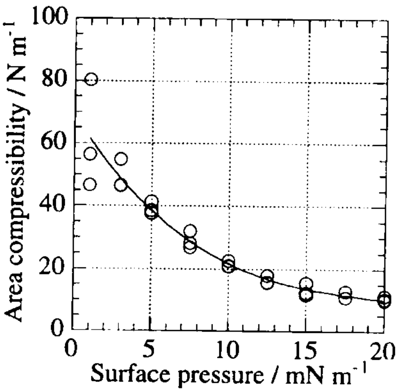

FIGURE 3 Area compressibility of C14-AgNP film

between C14-AgNP and molecule of common surfactant. Unfortunately, however, the estimated area of C14-AgNP in the film was not exact, because of a little precipitate in the C14-AgNP dispersion and uncertainty in the assumption. To avoid these uncertainties, the area compressibility κ_A of the film was estimated (Fig. 3)[6]. The κ_A value decreased hyperbolically. At high surface pressure, the κ_A of C14-AgNP approaches to that of common surfactants (ex. arachidic acid) forming condensed phase[6], which bear closed packing.

Morphologies of the C14-AgNP film correlated with the π-A isotherm as follows. At low surface density, the domains of C14-AgNP (bright area) moved around quickly (Fig. 4(a)). The domains were not circle, i.e., fluidity of C14-AgNP in the domain is small due to strong interaction between C14-AgNPs on water surface. At the lift-off point of the π-A isotherm, indicated as point (b) in Fig. 2, the domains contacted each other and were not mobile (Fig. 4(b)). The coverage factor of C14-AgNP domains increased with an increase in surface pressure. The area decrease accompanying with surface

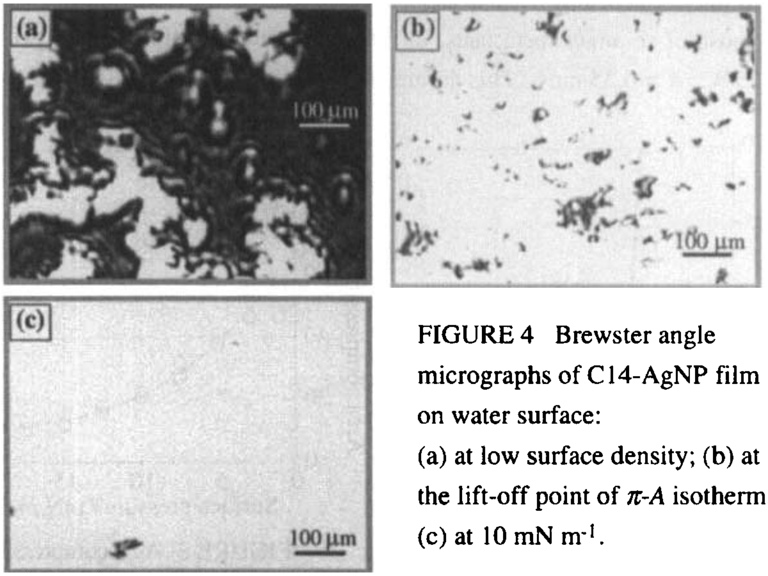

FIGURE 4 Brewster angle micrographs of C14-AgNP film on water surface: (a) at low surface density; (b) at the lift-off point of π-A isotherm; (c) at 10 mN m^{-1}.

tension increase, especially at low surface tension, dominantly owes to the decrease of defect area rather than the decrease of distance between the C14-AgNPs. As shown in Fig. 4c, the film at 10 mN m^{-1} had few defect larger than 10 μm, the resolution in this observation.

Accordingly, observations of a domain in C14-AgNP film transferred at 10 mN m^{-1} were carried out with transmission electron microscope (TEM). Few collapse structure due to the film compression has been observed. One of the TEM images of C14-AgNP film is shown in Fig. 5 together with fast Fourier transformed (FFT) pattern. The C14-AgNPs distribute in the film regularly, though there are several defects smaller than 1 μm. The white ring in the FFT pattern of the image (Fig. 5(a)) suggests the regularity of the C14-AgNPs quantitatively: narrow distribution of distance between the C14-AgNPs faced each other. As shown in Fig. 6(a), locally, C14-AgNPs formed hexagonally packed structure: the FFT pattern of Fig. 6a showed local anisotropic arrangements of C14-AgNPs obviously.

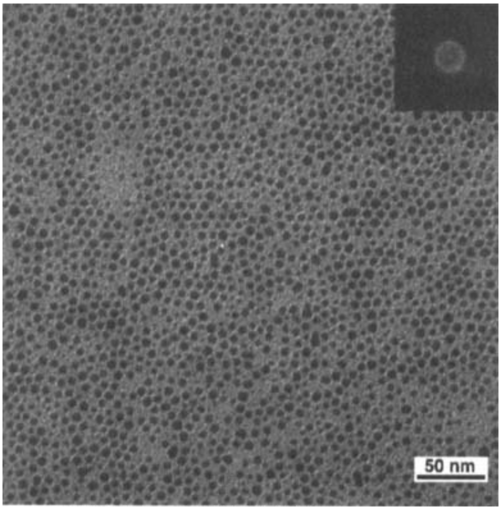

FIGURE 5 Transmission electron micrograph and FFT pattern of transferred C14-AgNP film at 10 mN m^{-1}

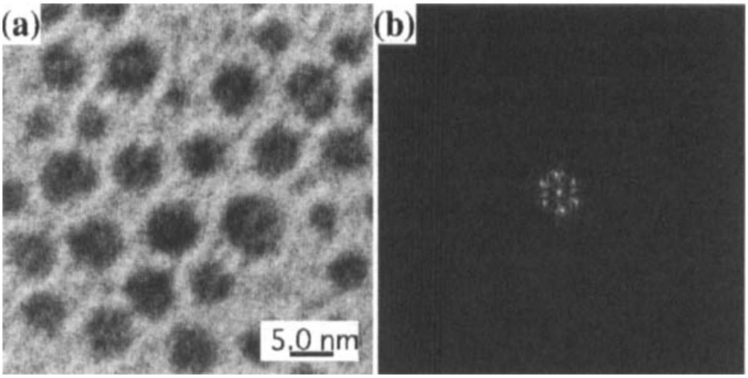

FIGURE 6 (a) Higher magnification TEM image and (b) FFT pattern of Fig. 6(a).

These experimental results indicated that controlling surface pressure enables us to form the C14-AgNP film with less defects on water surface. Furthermore, aging the film at high surface pressure lower than collapse pressure may improve the film.

Acknowledgments

The authors thank Dr. Masahiro Higuchi at NIMC for the use of Brewster angle microscope. And also thank Dr. Fusae Nakanishi at NIMC for valuable comments.

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