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Preparation of Nonaqueous Dispersion of Colloidal Silver by Phase Transfer

Hidefumi HIRAI,* Hotaka AIZAWA, and Hyouya SHIOZAKI
Depertment of Industrial Chemistry, Faculty of Engineering,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

Colloidal silver particles dispersed in water are found to be transferred into a nonaqueous liquid by the addition of sodium chloride to an emulsion of the nonaqueous liquid in the aqueous dispersion of colloidal silver with sodium oleate. The colloidal dispersions of silver in cyclohexane, n-hexane and benzene are prepared by phase transfer using sodium oleate and sodium chloride.

Colloidal dispersions of silver in aqueous liquid were prepared by a few method.[1-3] However, a colloidal dispersions of silver in nonaqueous liquid was prepared only by a physical method: the gas flow-cold trap method.[4] The chemical method for preparation of the colloidal dispersion of silver in nonaqueous liquid, except methanol and ethanol,[5] has never been reported to our knowledge. We have found that colloidal silver particles dispersed in water are transferred into a nonaqueous liquid by the addition of sodium chloride (**1**) to an emulsion of the nonaqueous liquid in the aqueous dispersion of colloidal silver with sodium oleate (**2**). This is the first example of the phase transfer of colloidal metal from the aqueous disperse phase to the nonaqueous liquid phase.

The size distribution and the disperse state of silver particles were determined by means of transmission electron microscopy with a Japan Electron Optics Laboratory Model JEM-2010 microscope. The magnification of the electron microscope was 100000. The particle size distribution, the average diameter (d) and the standard deviation (σ) were determined from 250 particles of silver on each of the enlarged photographs which corresponded to a magnification of 400000.

A colloidal dispersion of silver in water was prepared according to the literature[1]: Sodium citrate dihydrate (14 g) and iron(II) sulfate heptahydrate (7.5 g) were dissolved in 60 mL of distilled water at room temperature. Silver nitrate (2.5 g) in 25 mL of distilled water was added. The resulting precipitate was centrifuged and was dispersed in 1000 mL of distilled water. Thus, the colloidal dispersion of silver in water containing Ag atom 14.8 mmol/L was obtained. Figure 1 shows the electron micrograph (a) and the particle size distribution (b) of the colloidal silver dispersed in water. As shown in Fig. 1 (a), the silver particles are well dispersed and the aggregates are very few. As illustrated in Fig. 1 (b), the particles size has a distribution with a sharp single peak: $d = 8.0$ nm, $\sigma = 2.5$ nm

The following procedures for the phase transfer are representative. Cyclohexane (25 mL) and **2** (25 mg) were added to the colloidal dispersion of silver in water (25 mL). The mixture was emulsified by vigorous stirring at room temperature for 4 h. Then, **1** (2.5 g) was added with stirring. On standing for 3 h, the mixture was transformed from an emulsion into two liquid layers : the upper layer was a colloidal dispersion of silver in cyclohexane colored reddish dark brown and the lower layer was a transparent and colorless aqueous solution. The colloidal dispersion of silver in cyclohexane was isolated by using a separatory funnel.

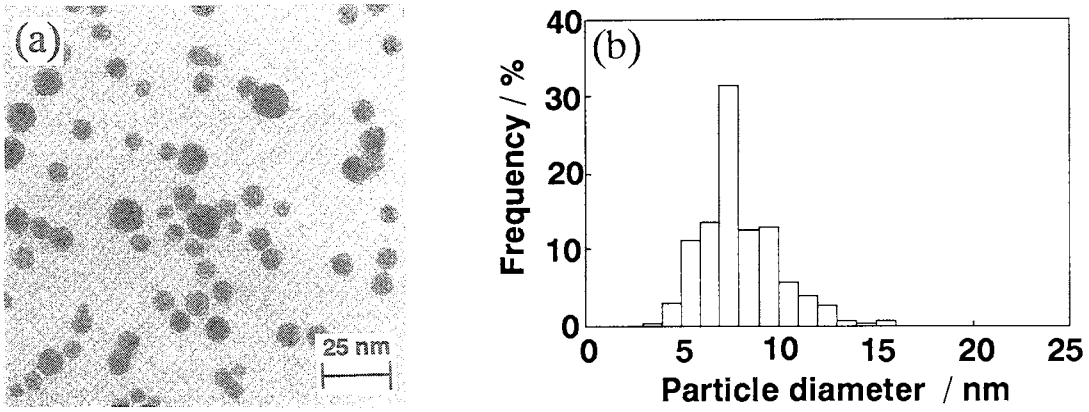

Fig. 1. Electron micrograph (a) and particle size distribution (b) of colloidal silver dispersed in water : d = 8.02 nm, σ = 2.54 nm.

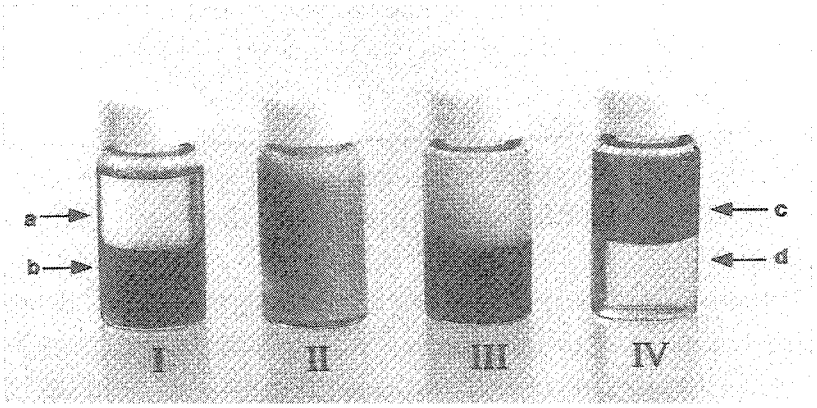

Fig. 2. Photograph of phase transfer of colloidal silver from water to cyclohexane.
(I) Before addition of sodium oleate, (II) Addition of sodium oleate with stirring, (III) Standing for 3 h without sodium chloride, (IV) Standing for 3 h after the addition of sodium chloride; (a) Cyclohexane, (b) Colloidal dispersion of silver in water, (c) Colloidal dispersion of silver in cyclohexane, (d) Water

Figure 2 shows a photograph of each of the steps of the phase transfer. The addition of cyclohexane to the colloidal dispersion of silver in water forms two liquid layers : The upper layer is the transparent and colorless cyclohexane and the lower layer is the colloidal dispersion of silver in reddish dark brown, as shown in Fig. 2 (I). Figure 2 (II) shows the formation of the emulsion of cyclohexane in the aqueous dispersion of colloidal silver after the addition of **2** with vigorous stirring : the emulsion is colored yellow ocher. On standing for 3 h, the emulsion is transformed into the original two liquid layers : the upper layer is the transparent and colorless cyclohexane and the lower layer is the aqueous dispersion of colloidal silver as shown in Fig. 2

(III). There occurs no phase transfer of colloidal silver. The addition of **1** to the emulsion at the step of Fig. 2 (II) transforms the emulsion into two liquid layers on standing for 3 h, in contrast to the case without addition of **1**. The upper layer is the colloidal dispersion of silver in cyclohexane colored brown and the lower layer is the transparent and colorless aqueous solution, as shown in Fig. 2 (IV). Thus, almost all the colloidal silver particles are transferred from the water phase to the cyclohexane phase. Figure 3 shows an electron micrograph and a size distribution of the colloidal silver particles dispersed in cyclohexane : d = 7.9 nm, σ = 3.2 nm.

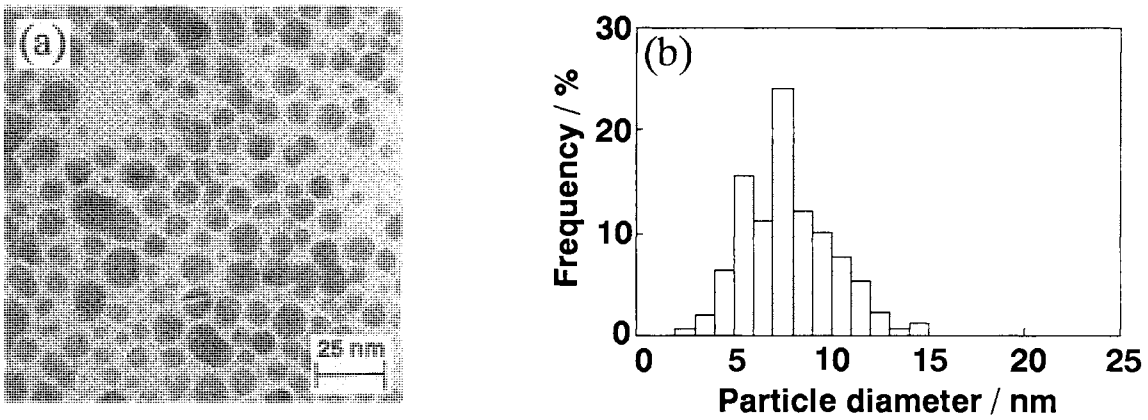

Fig. 3. Electron micrograph (a) and particle size distribution (b) of colloidal silver dispersed in cyclohexane : d = 7.91 nm, σ = 3.18 nm

By comparing Fig. 3 with Fig. 1, it is clear that the colloidal silver particles are transferred from the water phase to the cyclohexane phase with no change in the size distribution of silver particles, keeping the well- dispersed state. The colloidal dispersion of silver in cyclohexane was stable on standing at room temperature over two months. The colloidal dispersion of silver in n-hexane was prepared by the phase transfer using n-hexane in the place of cyclohexane. The electron micrograph (Fig. 4 (a)) shows the well-dispersed state of silver particles. As shown in Fig. 4(b), the size distribution of silver particles (d = 7.9 nm, σ = 3.1 nm) is almost the same with the original aqueous dispersion of silver (Fig. 1(b)). The colloidal dispersion of silver in n-hexane was stable on standing at room temperature over one months.

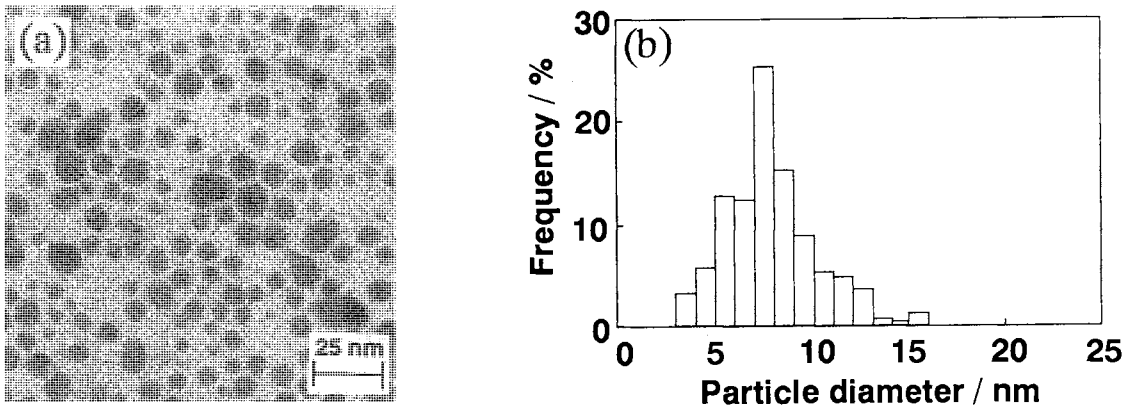

Fig. 4. Electoron micrograph (a) and particle size distribution (b) of colloidal silver dispersed in n-hexane : d = 7.93 nm, σ = 3.07 nm

The colloidal dispersion of silver in benzene was obtained by the phase transfer using benzene instead of cyclohexane. The electron micrograph (Fig. 5(a)) shows the well-dispersed state of silver particles. As shown in Fig. 5(b), the silver particles smaller than 8 nm in diameter decrease in frequency and the particles larger than 8 nm in diameter increase in frequency (d = 10.4 nm, σ = 3.4 nm), compared with those of the original aqueous dispersion of silver (Fig. 1(b)). The growth of the silver particles may be attributed to the weak interaction of benzene with the silver atoms on the particle surface.

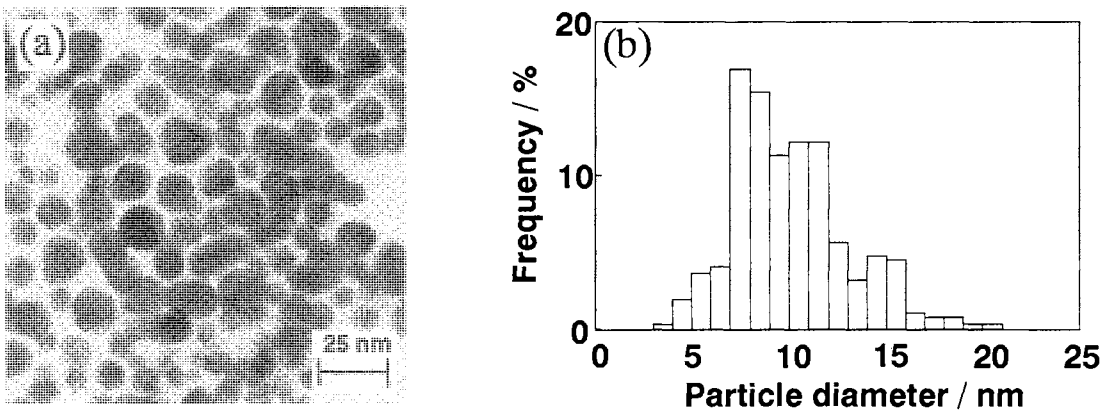

Fig. 5. Electron micrograph (a) and particle size distribution (b) of colloidal silver dispersed in benzene : d = 10.4 nm, σ = 3.39 nm

The role of **1** may be ascribed to dehydration of **2** and silver particles. The dehydration of **2** was observed as the condensation of **2** on the interface of the water layer with the cyclohexane layer. When **1** was added to the mixture of the aqueous dispersion of colloidal and nonaqueous liquid, in the absence of **2**, the silver particles aggregated to deposite a precipitate in water and no phase transfer was observed. Sodium oleate acts as an emulsifier of nonaqueous liquid in the aqueous dispersion of colloidal silver and also has a protective action of the colloidal particles of silver on the phase transfer. Thus, the hydrophilicity of the silver particles protected with **2** probably is decreased by the addition of **1** , resulting in the phase transfer of the silver particles from water to nonaqueous liquid.

Further extensions of this study and elucidation of the precise mechanism are underway.

References

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