Original Paper

J. Jpn. Soc. Colour Mater. (SHIKIZAI), 67 [11], 695-699 (1994)

Preparation of Ultrafine Metal Particles in Ethanol Using a Photoinitiator

Tetsuyuki ITAKURA*, Kanjiro TORIGOE* and Kunio ESUMI*

Abstract

Ultrafine metal particles (Ag and Cu) were prepared by UV irradiation of their salts dissolved in ethanol. The reaction was greatly accelerated by using benzoin as a photoinitiator. This method was applied to obtain Ag/Cu composite particles: The observed optical spectra of Ag/Cu composite were in good agreement with the calculated spectra using the Mie theory.

Key-words : Metal particles, photoinitiator, UV irradiation, Ag/Cu composite, Mie theory

1. Introduction

Ultrafine metal particles have many properties different from bulk metals in optical property, magnetic property, and catalytic activity. In particular, Ag, Au, and Cu colloids strongly absorb light in the visible region due to surface plasmon resonance^{1~3}. Their peak wavelengths depend on the size, shape, and dispersion state of the particles. Therefore, it is very interesting to investigate their optical property.

Until now, many colloidal particles have been prepared by a variety of methods, such as photochemical methods^{4~7}) and reduction by reductant such as NaBH₄⁸), N₂H₄, and alcohols^{9~11}). In the photochemical methods, hydrated electrons or free organic radicals formed by the irradiation of γ -ray or UV light reduce metal ions. On the other hand, the photoinitiator absorbs light at UV-vis region and forms reactive intermediates such as free radicals. Benzoin derivatives represent the most important classes of initiators for photopolymerization and undergoes primarily α -cleavage to produce benzoyl and benzyl radicals^{12~14}). It appears to be possible for benzoin and benzyl radicals to reduce metal ions to metals.

In this study, we report the formation of ultrafine metal particles (Ag, Cu, and their composite) using benzoin as a photoinitiator.

2. Experimental

2.1 Materials

Silver perchlorate (AgClO₄) of high purity was kindly supplied by Tanaka Kikinzoku Kogyo. Copper perchlorate (Cu(ClO₄)₂) was obtained from Aldrich. Polyvinylpyrrolid-

Received Aug. 4, 1994

* Department of Applied Chemistry and Institute of Colloid and Interface Science, Science University of Tokyo, 1-3, Kagurazaka, Shinjuku-ku, Tokyo 162

done (PVP, $M_w=40000$) as a stabilizer was obtained from Tokyo Kasei. They were used without further purification. Benzoin obtained from Tokyo Kasei was used after recrystallized from methanol twice.

2.2 Preparation of the Metal Colloids

Ethanol solution of metal salts (0.1 mmol dm^{-3}) containing PVP (100 mmol dm^{-3}) and benzoin ($0\sim 2 \text{ mmol dm}^{-3}$) was deaerated by bubbling with nitrogen for 2 h. A 3-cm^3 portion of the solution was transferred to a rectangular quartz vessel in a glovebox under nitrogen atmosphere. The UV irradiation was carried out with a 200-W low-pressure mercury lamp SUV 200—GL (Sen Tokushu Kogen) equipped with a power supply UVB-200 L-1. The samples were irradiated in a dark box with two motor fans which drove ozone out and kept the system at ambient temperature.

2.3 Characterization of the Metal Colloids

Absorption spectra of the colloidal solution were measured with a Hewlett Packard 8452 A Diode Array Spectrophotometer at 1 cm of path length. Theoretical spectra using the Mie theory¹⁾ were calculated from optical constants of the pure metals. We calculated them by using the equations in the analytical form reported by Sato et al¹⁵. Electron micrographs were taken with a Hitachi H-800 transmission electron microscopy, operating at 200 kV. Their particle sizes were determined from maximum length of the particles. The size distributions were determined by counting about 200 particles.

3. Results and Discussion

Firstly we discuss the photoreaction of benzoin in ethanol solution. (Figure 1 shows the spectral change of benzoin in ethanol with UV-irradiation time. A distinct absorption peak at about 315 nm decreased gradually with the irradiation time. This spectral change is due to the α -cleavage of benzoin to produce benzoyl and benzyl radicals^{12~14}).

Figure 1 Change in optical spectra of benzoin in ethanol with irradiation time

Figure 2 Change in optical spectra of 0.1 mmol dm^{-3} $\text{Cu}(\text{ClO}_4)_2$ ethanol solution with various benzoin concentrations; Irradiation time is 60 min

Figure 3 Transmission electron micrographs of colloidal particles formed by UV irradiation; (a) Concentration of $\text{Cu}(\text{ClO}_4)_2 = 0.1 \text{ mmol dm}^{-3}$, benzoin = 0.5 mmol dm^{-3} , PVP = 100 mmol dm^{-3} ; Irradiation time is 60-min.; (b) Concentration of $\text{AgClO}_4 = 0.1 \text{ mmol dm}^{-3}$, benzoin = 0 mmol dm^{-3} , PVP = 100 mmol dm^{-3} ; Irradiation time is 30-min.; (c) Concentration of $\text{AgClO}_4 = 0.1 \text{ mmol dm}^{-3}$, benzoin = 0.1 mmol dm^{-3} , PVP = 100 mmol dm^{-3} ; Irradiation time is 30-min.; (d) Concentration of $\text{AgClO}_4 = 0.1 \text{ mmol dm}^{-3}$, benzoin = 0.5 mmol dm^{-3} , PVP = 100 mmol dm^{-3} ; Irradiation time is 30-min.; (e) Concentration of $\text{AgClO}_4 = 0.1 \text{ mmol dm}^{-3}$, benzoin = 1.0 mmol dm^{-3} , PVP = 100 mmol dm^{-3} ; Irradiation time is 30-min

In order to investigate whether these radicals can reduce metal ions, we have studied spectral change of metal ions through photoreduction by these radicals. **Figure 2** shows the spectral change of 0.1 mmol dm^{-3} $\text{Cu}(\text{ClO}_4)_2$ containing $0 \sim 1 \text{ mmol dm}^{-3}$ benzoin after 60-min irradiation. In the absence of benzoin, any spectral change was not observed, whereas a distinct peak of Cu colloid near 570 nm developed with increasing benzoin concentration. The reduction from Cu^{2+} to Cu^0 did not occur in the presence of benzoin in the dark room. Accordingly the above results imply that benzoin works for promoting the photoreduction of Cu^{2+} ions via photolytically produced benzoyl and/or benzyl radicals. From a TEM micrograph (**Figure 3 (a)**), highly dispersed particles with a mean particle size of 3 nm without any aggregation were observed.

Similarly, Ag system was also studied. **Figure 4** shows the optical spectra of 0.1 mmol dm^{-3} AgClO_4 ethanol solution containing 1.0 mmol dm^{-3} benzoin with the UV-irradiation time. The plasmon band of Ag shifted from 410 to 404 nm and increased in the absorbance with the irradiation time. At 60-min irradiation, the Ag particles were readily aggregated as represented by a small broad band peaking at 420 nm.

A remarkable shift in the absorption band of Ag was observed, depending on the concentration of benzoin (**Figure 5**). In the absence of benzoin, the band was very broad and located at 420 nm which was due to the formation of aggregation of Ag particles. With increasing benzoin concentration, the band gradually shifted to shorter wavelength

Figure 4 Change in optical spectra of 0.1 mmol dm^{-3} AgClO_4 ethanol solution containing benzoin (1.0 mmol dm^{-3}) with irradiation time

Figure 5 Change in optical spectra of 0.1 mmol dm^{-3} AgClO_4 ethanol solution with various benzoin concentrations; Irradiation time is 30-min

Figure 6 (a) Observed absorption spectra of various Ag-Cu composite colloids (molar ratios) in ethanol; Concentration of metals = 0.1 mmol dm^{-3} , PVP = 100 mmol dm^{-3} and benzoin = 1 mmol dm^{-3} ; Irradiation time is 60-min

Figure 6 (b) Calculated absorption spectra of various Ag-Cu alloy colloids (molar ratios) in ethanol; Diameter = 10 nm

from 420 to 400 nm accompanying band sharpening. This blue shift suggests that benzoyl and benzyl radicals inject electrons into Ag particles and peptization of the aggregates occurs. The TEM micrographs (**Figures 3 (b)~(e)**) show that the aggregates of Ag become small with increasing concentration of benzoin.

Finally, the preparation of Ag/Cu composite particles by photoreduction was carried out, since the composite particles were expected to show optical spectra with absorption maximum at different wavelengths. They were prepared by the UV irradiation of

mixtures of Ag ClO_4 and $\text{Cu}(\text{ClO}_4)_2$ in ethanol in the presence of benzoin. The observed (**Figure 6(a)**) and the calculated spectra (**Figure 6 (b)**) based on the Mie scattering theory were in good agreement with each other. These results strongly suggest the formation of the Ag/Cu composites.

The other measurements are in progress to confirm the formation of Ag/Cu composites.

Acknowledgements

The authors wish to thank M. Ikeda for helpful discussions.

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