Growth of rodlike Au/Pt particles in cationic micelles by UV irradiation

Kunio Esumi,* Megumi Nawa, Nariaki Aihara and Kiyoshi Usui

Department of Applied Chemistry and Institute of Colloid and Interface Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Colloidal Au/Pt particles were prepared by irradiation of $HAuCl_4$ and H_2PtCl_6 mixed solutions with 253.7 nm light in the presence of rodlike micelles of hexadecyltrimethylammonium chloride. Lengths of fibrous particles formed were considerably longer compared to those formed from $HAuCl_4$ alone. This result suggests that H_2PtCl_6 accelerates growth of fibrous Au/Pt particles during irradiation.

Many ultrafine noble metal particles have been prepared by various methods.[1] For silver, gold and copper, in particular, it is very interesting to study their optical properties since they strongly absorb light in the visible region due to the surface plasma resonance. Recently, we have prepared rodlike gold particles,[2] whose formation depends on the concentration of Au ions and UV irradiation time, using cationic micelles as a soft template. Longer irradiation times also provide fibrous gold particles. Similarly, copper rodlike particles have been prepared using a reverse micellar solution with lamellar phases.[3] Thus, a soft template using surfactants is useful for formation of anisotropic particles in the surfactant aggregates. Anisotropic gold particles have also been prepared using hard templates[4,5] such as porous anodizing alumina.

When a preliminary study of the preparation of anisotropic bimetallic particles of gold and platinum from mixtures of two metal salts was carried out using a soft template, an elongation of rodlike particles was observed.

The objectives of this study were to elucidate the formation of anisotropic bimetallic particles of gold and platinum using a cationic micelle template by UV irradiation.

Experimental

$HAuCl_4$ and H_2PtCl_6 were kindly supplied by Tanaka Kikinzoku Kogyo. Hexadecyltrimethylammonium chloride (HTAC) was obtained from Kokusan Kagaku Kogyo and was recrystallized from acetone. A 3 cm^3 portion of mixed aqueous solutions of HTAC, $HAuCl_4$ and H_2PtCl_6 was transferred to a quartz cell. UV irradiation was carried out with a 200 W low-pressure mercury lamp ($\lambda_{max} = 253.7$ nm). Here, the concentration of HTAC used was 30 wt% in which rodlike micelles of HTAC were formed.[2] UV/VIS spectra of the colloidal solutions were measured with a Hewlett–Packard 8452A diode array spectrophotometer. Electron micrographs of the metal colloids were taken with a Hitachi H-800 transmission electron microscope, operating at 200 kV.

Results and Discussion

It has been reported[2,6] that rodlike gold particles are formed in the rodlike micelles of HTAC by reduction of $HAuCl_4$ through UV irradiation and their elongation considerably depends on both UV irradiation time and UV power intensity. According to Kurihara *et al.*,[7] photolysis of $AuCl_4^-$ gives rise to gold atoms by formation and dissociation of divalent gold complexes and through disproportionation; these atoms then coagulate to form colloidal gold and bulk gold.

When the mixtures of $HAuCl_4$ and H_2PtCl_6 in the rodlike micelles of HTAC were irradiated by UV, the particle sizes and shapes obtained were appreciably dependent on the mixed salt ratio. To demonstrate clearly the change of shape and length of particles obtained, only a few particles are shown in Fig. 1(a)–(c). With $HAuCl_4$ alone in the rodlike micelles of HTAC fibrous gold was obtained, while the reduction of H_2PtCl_6 alone by UV provided large aggregates consisting of small platinum particles. In the $HAuCl_4 : H_2PtCl_6$ (4 : 1 mole ratio) mixture, the length of the fibrous particles obtained was about 60 μm and was quite a lot longer than that of fibrous gold after 2 h UV irradiation time. This suggests that H_2PtCl_6 plays an important role in

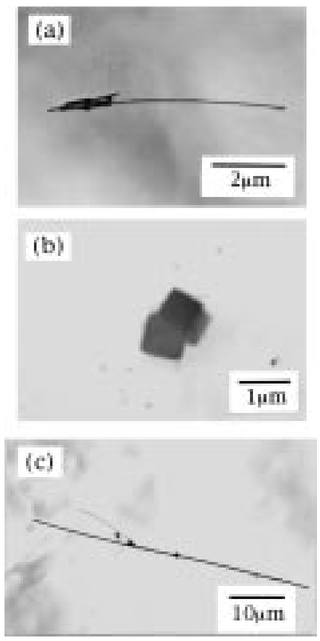

Fig. 1 TEM micrographs of particles obtained from metal ions in 30 wt% of HTAC with 2 h UV irradiation: (a) $HAuCl_4$, 40 mmol dm^{-3}; (b) H_2PtCl_6, 40 mmol dm^{-3}; (c) $HAuCl_4$, 40 mmol dm^{-3} plus H_2PtCl_6, 10 mmol dm^{-3}

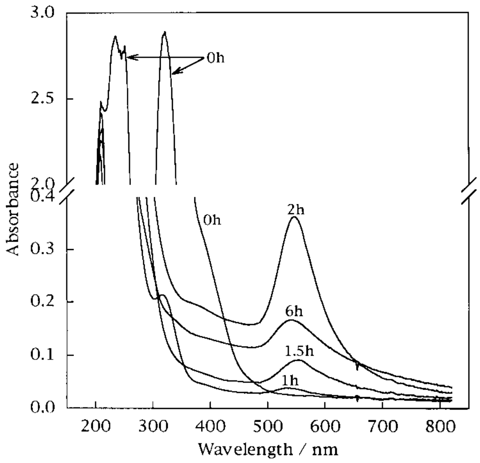

Fig. 2 Change in the UV/VIS spectra of an $HAuCl_4$ (40 mmol dm^{-3}) plus H_2PtCl_6 (10 mmol dm^{-3}) aqueous solution in the presence of HTAC (30 wt%) as a function of UV irradiation time

growing fibrous particles. Also, after 2 h UV irradiation, spherical particles were obtained in both Fig. 1(a) and (c), so that at the present time, a homogeneous dispersion of fibrous particles alone could not be obtained.

In order to study how the fibrous particles are formed by UV irradiation, the change in the UV/VIS spectra of HTAC aqueous solutions containing 40 mmol dm^{-3} $HAuCl_4$ plus 10 mmol dm^{-3} H_2PtCl_6 with UV irradiation time was measured, as well as the change in particle size and shape. Fig. 2 shows that an absorption band at 320 nm, which is assigned to $AuCl_4^-$, disappears and a plasmon band at around 526–530 nm appears with UV irradiation. Its intensity increases with UV irradiation time, but after 6 h of UV irradiation the intensity of the band decreases, due to precipitation of the particles to some extent. Furthermore, after 2 h UV irradiation the intensity of the band above 600 nm increases, probably due to formation of fibrous particles. The plasma absorption bands of spherical particles are known to shift to longer wavelengths as the aspect ratios increase.[8] From Fig. 3, it is seen that at 1 h UV irradiation, tiny particles are formed and then an elongation of spherical particles proceeds with further UV irradiation, in which spherical particles are present to some extent.

When an aqueous solution of $HAuCl_4$ and H_2PtCl_6 is added to an aqueous solution of HTAC, anionic species such as $AuCl_4^-$ and $PtCl_6^{2-}$ bind to the surface of the positively charged HTAC rodlike micelles and the rest of the species are present freely in aqueous solution. It seems likely that free $AuCl_4^-$ and $PtCl_6^{2-}$ are easily reduced at short UV irradiation times, compared to the $AuCl_4^-$ and $PtCl_6^{2-}$ bound to the micellar surface, resulting in the formation of spherical particles at short UV irradiation times. Further UV irradiation will reduce the anionic metal species bound and near to the micellar surface to provide fibrous particles. Interestingly, in the growing of fibrous particles, the diameter of the fibrous particles was almost unchanged with UV irradiation time. In the case of low metal ion concentration, only spherical particles were formed by UV irradiation.

Thus, it is found that the elongation of gold particles is markedly enhanced with addition of H_2PtCl_6 through UV irradiation. A further detailed study is required to understand the mechanism of formation of fibrous noble metal particles.

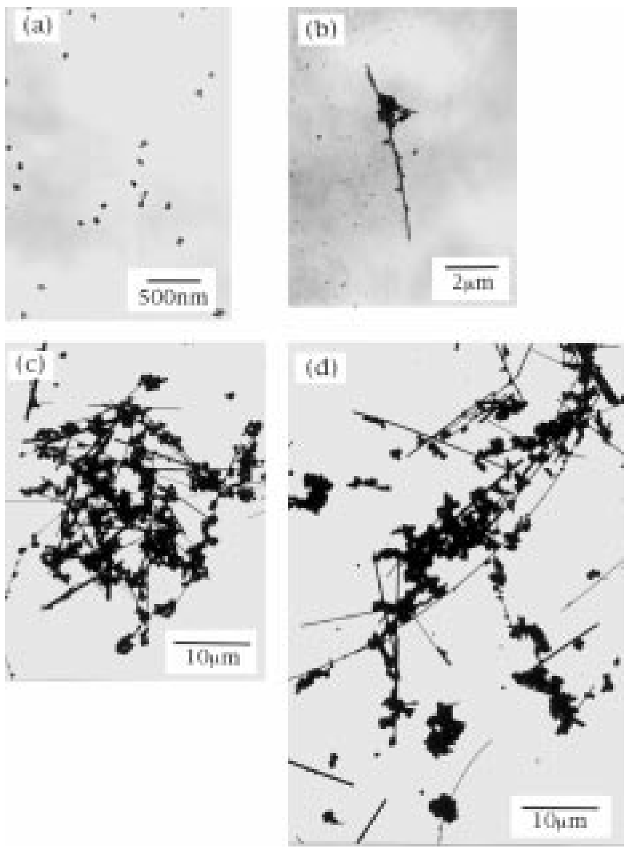

Fig. 3 TEM micrographs of particles obtained from an $HAuCl_4$ (40 mmol dm^{-3}) plus H_2PtCl_6 (10 mmol dm^{-3}) aqueous solution in the presence of HTAC (30 wt%). UV irradiation time: (a) 1 h; (b) 1.5 h; (c) 2 h; (d) 6 h

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