Preparation of a Gold Organosol in Chloroform and its Discolouration by Photoirradiation

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A gold organosol in chloroform prepared from a cetylpyridinium chloride-stabilized gold hydrosol was discoloured by photoirradiation owing to the dissolution of colloidal gold particles.

Organosols of noble metals such as gold, silver and platinum are prepared by somewhat complicated procedures including the reduction of noble metal salts in water pools of microemulsions,[1] thermal decomposition,[2] and phase transfer of colloidal particles to an organic layer.[3] Recently, we have reported that hydrosols of several noble metals including gold were prepared by reducing the corresponding noble metal salts with sodium borohydride ($NaBH_4$) in aqueous solutions in the presence of a cationic, anionic, or nonionic surfactant as a stabilizer.[4] In this report, we describe the conversion of a gold hydrosol stabilized by a cationic surfactant, cetylpyridinium chloride (CPC), to a gold organosol and its discolouration by photoirradiation.

A gold hydrosol (200 ml) containing 0.1 mg atoms of gold and 0.4 mmol of CPC was prepared at 30 °C by the successive addition of separate aqueous solutions of $NaBH_4$ and $HAuCl_4 \cdot 4H_2O$ to a solution of CPC at an interval of less than 5 s in a similar manner to that previously reported[4] except for the order of addition. 200 ml of a 1 mol dm^{-3} aqueous solution of NaBr was poured into the gold hydrosol with vigorous agitation. Colloidal gold in the sol was converted to an aggregate within a few minutes. Then, 200 ml of ethanol-free chloroform previously washed with water was added to the mixture. This led to the redispersion of the aggregate from the aqueous layer to the chloroform layer. The chloroform layer was then separated and dried over anhydrous Na_2SO_4 to give a gold organosol in chloroform. The organosol like the starting hydrosol was dark reddish brown with the colour gradually changing to red on standing in the dark at room temperature for a period of about 10 days. After that time the sol showed no further change and was used for photoirradiation experiments.

The gold organosol was irradiated with visible light at 30–35 °C using a 500 W high pressure mercury lamp through a water layer and a Pyrex glass wall. The red organosol faded gradually, became colourless after 1 min, and changed to light yellow upon further photoirradiation. The VIS spectra of the organosol during the course of photoirradiation are shown in Fig. 1. In the first stage up to 1 min, a peak at 530 nm assigned to the surface prasmon absorption of colloidal gold[5] was reduced in intensity and the diameter of the colloidal gold as observed by TEM decreased as shown in Fig. 2. These indicate that the colloidal gold particles dissolved in chloroform. A peak at 395 nm which increased in the next stage was in accord with the formation of an ion pair, $[CP]^+[AuBr_4]^-$ ($[CP]^+$ = cetylpyridinium ion), which has been synthesised by the dissolution of gold in a bromine–cetylpyridinium bromide–benzene system.[6]

The organosols before and after photoirradiation were separatedly evaporated to dryness and the Cl/Br contents of the resulting residues were determined by elemental analysis. The starting organosol was found to contain Br exclusively, which suggested that Cl^- in CPC had been completely replaced by Br^-. This suggests that the aggregation of colloidal gold in the hydrosol was caused by the decrease in solubility of the cetylpyridinium salt owing to anion replacement.[7] The Cl contents in the residues were increased with increasing photoirradiation time. Such additional Cl is presumed to derive from chloroform. The FIR spectra of the residues from the solutions irradiated for 1 or 5 min indicated a main peak at 256 or 254 cm^{-1}, respectively, which could be assigned to the vibrational frequencies of $[AuBr_2]^-$ and $[AuBr_4]^-$.[8]

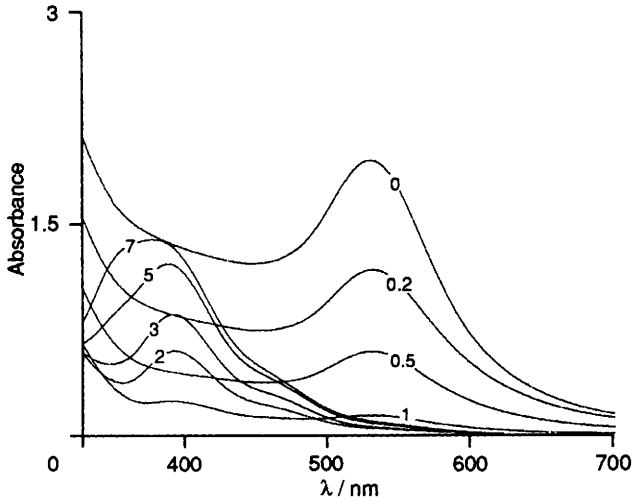

Fig. 1 VIS spectra of gold organosols (pathlength = 1 cm; numbers indicate photoirradiation time in min)

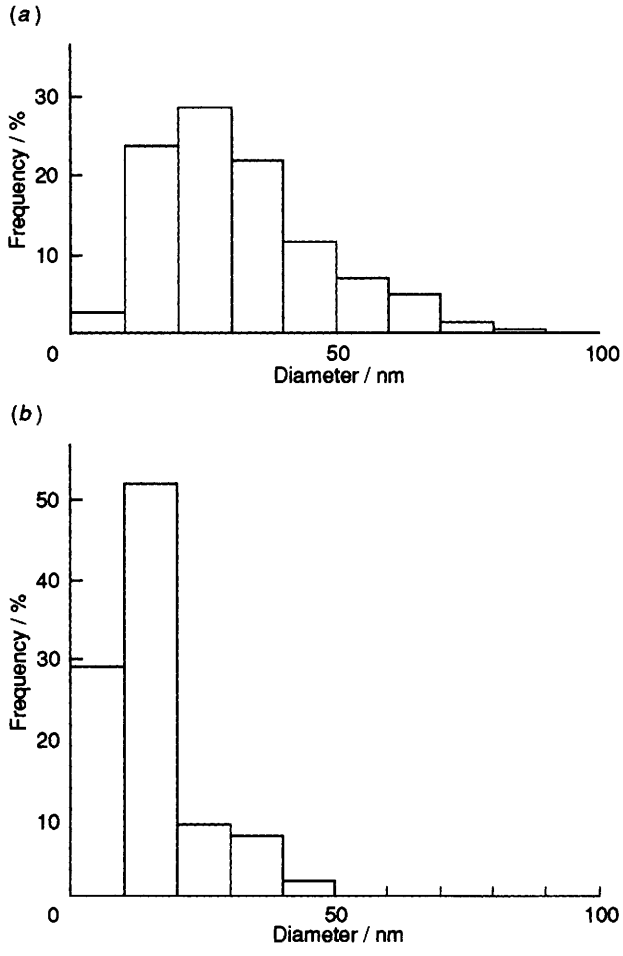

Fig. 2 Diameter histograms of colloidal gold in organosols (*a*) before and (*b*) after 0.5 min photoirradiation

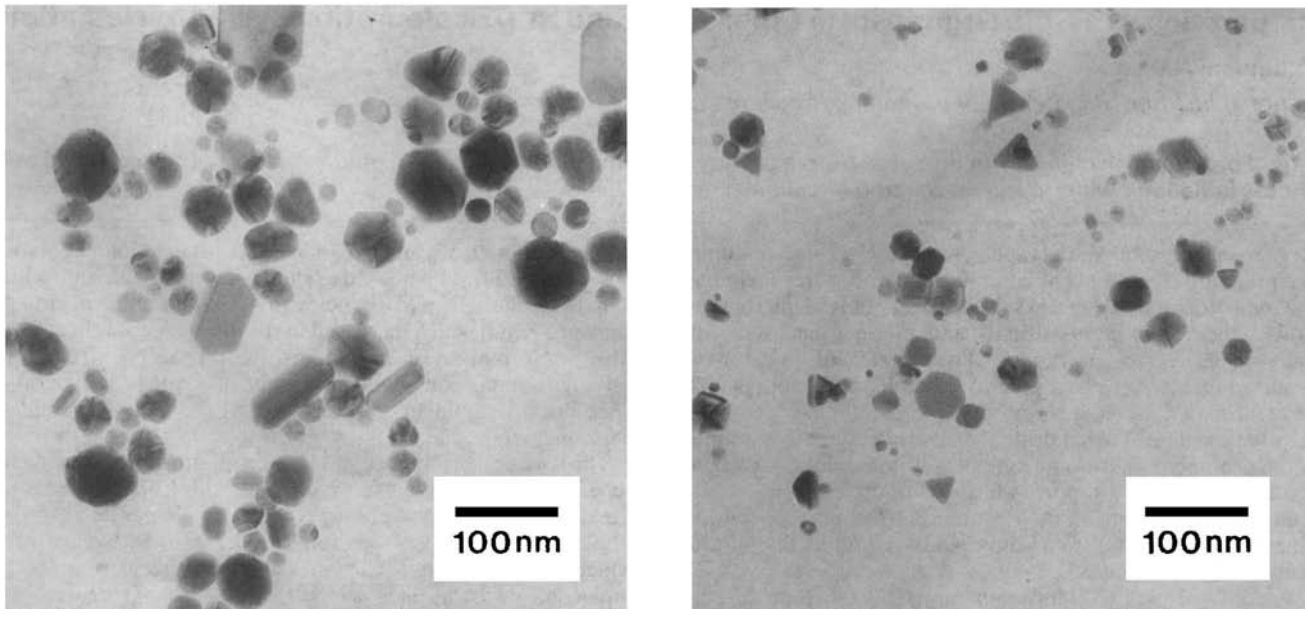

Fig. 3 TEM pictures of colloidal gold in organosols (left) before and (right) after 0.5 min photoirradiation

Use of $NaClO_4$ in the preparation as an aggregating reagent also gave a clear red–gold organosol. This organosol was unaltered by photoirradiation.

The mechanism for the dissolution of colloidal gold may be as follows. It is well known that photoirradiation of chloroform results in the formation of chlorine radicals ($Cl^{\cdot}$).[9] Therefore, the first step must be a photoconversion of chloroform to $Cl^{\cdot}$. The $Cl^{\cdot}$ presumably then generates $Br^{\cdot}$ which oxidizes the colloidal gold. The Au^{I} ion thus formed combines with two Br^{-} to give $[AuBr_2]^{-}$, which dissolves in chloroform by forming a soluble ion pair with the cetylpyridinium ion. The Au^{I} ion is then further oxidized by $Br^{\cdot}$ to Au^{III} giving $[AuBr_4]^{-}$ [eqns. (1)–(4)]

$$CHCl_3 \xrightarrow{h\nu} Cl^{\cdot} \quad (1)$$

$$Cl^{\cdot} + Br^{-} \rightarrow Cl^{-} + Br^{\cdot} \quad (2)$$

$$Au + Br^{\cdot} + [CP]^{+}Br^{-} \rightarrow [CP]^{+}[AuBr_2]^{-} \quad (3)$$

$$[CP]^{+}[AuBr_2]^{-} + 2Br^{\cdot} \rightarrow [CP]^{+}[AuBr_4]^{-} \quad (4)$$

Organosols of palladium (dark brown) and silver (yellow) were successfully prepared in a similar manner and both were also discoloured by photoirradiation.

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