Formation of Colloidal Silver in Water by Ultrasonic Irradiation

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Stable colloidal dispersions of silver were prepared by ultrasonic irradiations of aqueous $AgClO_4$ or $AgNO_3$ solutions in the presence of surfactants.

Colloidal dispersions of noble metals have attracted remarkable attention in various fields of chemistry because of their interesting physicochemical properties. The methods of preparation such as a photoreduction, chemical and electrochemical reduction have been reported.[1]

We report that colloidal silver can be prepared from an aqueous solution of $AgClO_4$ or $AgNO_3$ by ultrasonic irradiation. Although the chemical effects of ultrasound have been extensively studied, there is only a brief report on colloidal metal formation by a sonochemical method.[2]

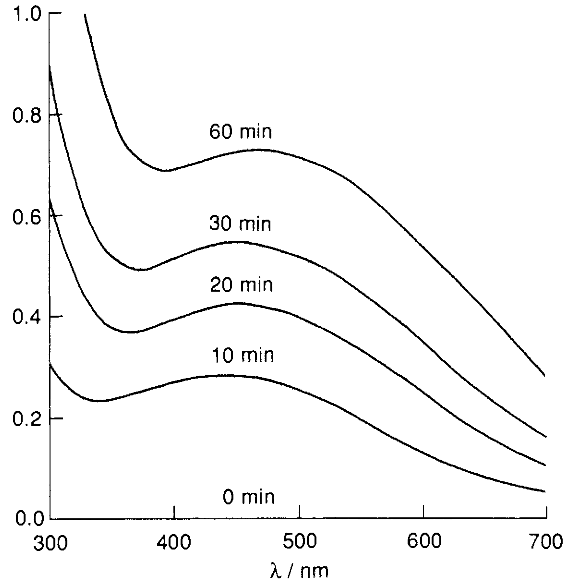

Fig. 1 Absorption spectra of irradiated $AgClO_4$–ADS solution in argon (run 5)

A ceramic oscillator (65 mm) was used for ultrasonic irradiation which was operated at 200 KHz with an input intensity of 200 W. The irradiation was carried out in a water bath with circulating tap water. An argon or air saturated aqueous solution (25 ml) of 1–10 mmol dm^{-3} of $AgClO_4$ or $AgNO_3$ was sonicated in a 115 ml cylindrical glass vessel. The vessel had a side arm equipped with a quartz cell to measure the optical absorbance without exposing the solution to air, and also had an arm with a silicone rubber septum for gas bubbling or sample extracting without opening the vessel. The bottom of the vessel was planar and 1 mm in thickness. The vessel was fitted at a constant position (3.75 mm *viz.* $\lambda/2$ from the oscillator) and was closed during the sonication. Under these conditions, the rate of hydrogen formation was 12.5 μmol dm^{-3} min^{-1} by the sonication of pure water under argon.

Sodium dodecylsulfate (SDS), polyoxyethylene(40)-monostearate (PEG40) and polyoxyethylene(20)sorbitan monolaurate (Tween20) were used as surfactants. The amount of reduced silver was determined from the absorbance at 440 nm and/or concentration of $C(NO_2)_3^-$ ($\varepsilon = 1.4 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 350 nm) arising from the reaction[3] [eqn. (1)]. A colourless clear solution turned to yellowish-brown by

$$Ag^0 + C(NO_2)_4 \rightarrow Ag^+ + C(NO_2)_3^- + NO_2 \qquad (1)$$

irradiation indicating the formation of fine silver particles, which was also confirmed by scattering light from a He–Ne laser.

Fig. 1 shows the change of absorption spectra of a $AgClO_4$–SDS solution during irradiation in argon. The absorption band around 440 mm owing to colloidal silver emerged. The absorption band was small and ambiguous when the same solution was irradiated in air. The rate of formation of colloidal silver (= reduction of Ag^+), was estimated as 7.4 μmol dm^{-3} min^{-1} in argon and 0.71 μmol dm^{-3} min^{-1} in air. Similar results were obtained by sonication of Ag^+–PEG40 and Ag^+–Tween20 solutions, though the absorption band was broader to some extent compared with Ag^+–SDS solutions.

Table 1 Stability of silver particles formed by sonication

Run/mmol dm^{-3}[a]	Atmosphere Air	 Argon
1 $AgClO_4$(1)–none	Ppt[b]	Ppt
2 $AgClO_4$(1)–Pr^iOH(20)	Ppt	Ppt
3 $AgClO_4$(1)–Tween20(3)	Colloid/ppt[c]	Colloid
4 $AgClO_4$(0.4)–PEG40(0.4)	Colloid[d]	Colloid
5 $AgClO_4$(1)–SDS(8)	Colloid	Colloid
6 $AgClO_4$(10)–SDS(8)	Colloid	Colloid
7 $AgNO_3$(10)–PEG40(0.4)	Colloid	Colloid

[a] Amount used shown in parentheses. [b] Ppt: precipitation after several hours. [c] Colloid/ppt: precipitation after a week. [d] Colloid: stable more than few months.

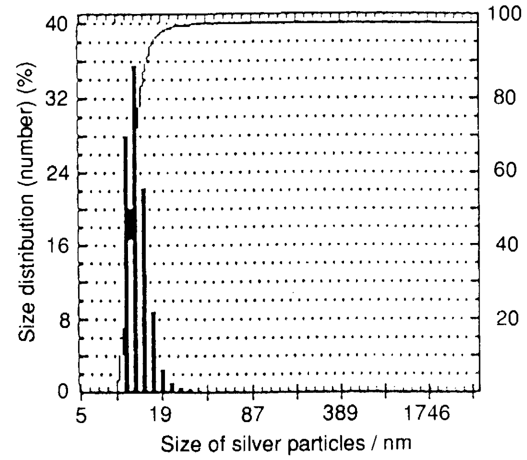

Fig. 2 Size distribution of silver particles from $AgClO_4$–PEG40 solution irradiated for 1 h (run 4)

Table 1 shows the stability of silver particles prepared under various conditions. The rate of reduction of Ag^+ in a pure aqueous solution was very slow and the silver particles were unstable to give precipitation within several hours. When propan-2-ol was added to a Ag^+ solution, the rate of reduction was enhanced but the silver particles were still unstable. The addition of surfactants accelerated the rate and stabilized the colloidal silver for several months.

The mechanism of the colloidal silver formation can be suggested as shown in eqns. (2)–(7) where RH denotes a

$$\begin{array}{lll}
H_2O & \rightarrow H^\bullet + {}^\bullet OH & (2) \\
OH + RH & \rightarrow R^\bullet + H_2O & (3) \\
R^\bullet + Ag^+ & \rightarrow Ag^0 + R' + H^+ & (4) \\
H^\bullet + Ag^+ & \rightarrow Ag^0 + H^+ & (5) \\
Ag^+ + H_2O & \rightarrow Ag^0 + {}^\bullet OH + H^+ & (6) \\
nAg^0 & \rightarrow (Ag^0)_n & (7)
\end{array}$$

surfactant or propan-2-ol. Eqn. (6) refers to the direct reaction of Ag^+ with water in the interfacial region between the cavitation bubbles and the liquid. The rates of colloidal silver formation in air were 1/7–1/15 of those in argon. This may be because (i) the cavitation effect is reduced in air compared with argon and (ii) oxygen in air inhibits the Ag^0 formation by the following reactions [eqns. (8) and (9)].

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \qquad (8)$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad (9)$$

In a Ag^+–propan-2-ol solution, the formation of acetone was confirmed. This lends support to the above mechanism in which the reduction of Ag^+ proceeds *via* reactions (3′) and (4′).

$$Me_2CHOH + {}^{\bullet}OH \rightarrow Me_2COH + H_2O \qquad (3')$$

$$Me_2COH + Ag^+ \rightarrow Ag^0 + Me_2CO + H^+ \qquad (4')$$

The main reaction pathway would be reactions (3) and (4), and the contribution of reactions (5) and (6) may be small because the rate of the formation of silver particles was very slow in the absence of the additives.

Fig. 2 shows the size distribution of the silver particles from the irradiated $AgClO_4$–PEG40 solution (run 4) measured by dynamic light scattering photometry. A fairly narrow distribution with a number average of 13.0 ± 3 nm was observed. It is expected that the colloidal dispersions of silver prepared in this way have various catalytic activities. Further studies of fine particle formation of noble metals by ultrasonic irradiation are now under way.

Received, 22nd July 1992; Com. 2/03899D

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Typeset and printed by Black Bear Press Limited, Cambridge, England