Formation of Gold Sols using Ultrasound

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The formation of colloidal gold particles of diameter less than 10 nm has been achieved by the irradiation of aqueous $\mathrm{HAuCl_4}$ solutions with 20 kHz ultrasound; the particle size and efficiency of particle formation is highly dependent on the presence of alcohol, its type and concentration, in the solutions.

The observed chemical effects associated with the absorption of ultrasound by water are attributed to the action of cavitation, which is the formation and violent collapse of microbubbles or gas cavities, in the liquid being irradiated.[1] Suslick, Henglein and their coworkers[2,3] have concluded that the temperature inside collapsing gas bubbles can be in excess of 4000 K. Under such high temperature conditions water molecules dissociate into the primary $\mathrm{H^\bullet}$ and $\mathrm{OH^\bullet}$ radicals in the cavitation bubble. In the absence of dissolved oxygen the radicals can recombine to form $\mathrm{H_2O}$, $\mathrm{H_2}$ and $\mathrm{H_2O_2}$. Henglein has estimated that 80% of the primary radicals recombine to form water.[3] However, in the presence of other chemical species in solution the primary radicals can be scavenged to yield secondary radicals and, as a consequence of this, other chemical reactions may ensue.[3,4] This article describes how colloidal gold particles may be generated from aqueous solutions containing $\mathrm{AuCl_4^-}$ that are exposed to ultrasound.

Based on the tactics commonly used in radiation chemistry[5,6] to capture $\mathrm{H^\bullet}$ and $\mathrm{OH^\bullet}$ radicals, propan-2-ol was added to a solution of $\mathrm{HAuCl_4}$, purged with nitrogen to eliminate oxygen in solution, and sonicated with a conventional 20 kHz (23–47 W $\mathrm{cm^{-3}}$) horn sonifier. The expected sequence of reactions that would lead to the formation of colloidal gold are shown is eqns. (1)–(4).

$$\mathrm{H_2O}\quad \text{sonication}\,)))))) \quad \mathrm{H^\bullet + OH^\bullet} \qquad (1)$$

$$\mathrm{H^\bullet(OH^\bullet) + Me_2CHOH \rightarrow Me_2COH + H_2(H_2O)} \qquad (2)$$

$$\mathrm{3Me_2COH + AuCl_4^- \rightarrow Au + 3Me_2CO + 4Cl^- + 3H^+} \qquad (3)$$

$$n\mathrm{Au} \rightarrow (\mathrm{Au})_n \qquad (4)$$

However, the only evidence for the formation of gold particles under these conditions was a small amount of a dark precipitate. In an attempt to stabilize the primary particles, which we assumed were initially formed before precipitation occurred, polyvinylpyrrolidone (PVP) (0.1 wt%, M_w = 40 000) was added and sonication repeated with the results shown in Fig. 1.

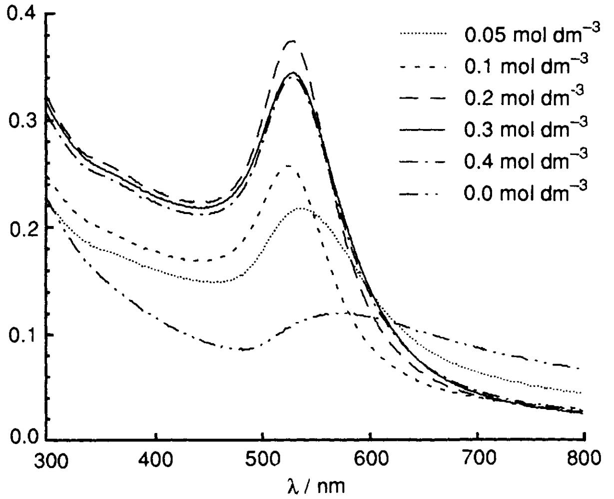

Fig. 1 Absorption spectra of gold sols from solutions containing 1 × 10^{-4} mol $\mathrm{dm^{-3}}$ $\mathrm{AuCl_4^-}$, 0.1 wt% PVP, and various concentrations of propan-2-ol following sonication. Total power absorbed by the solution was 24.2 kJ.

In the absence of propan-2-ol the solution appeared bluish in colour and the spectrum resembled that typical of gold sols where agglomeration of sol particles had occurred.[7] In the presence of alcohol the solution was pinkish in colour and the absorption spectrum was similar to gold sols in which the particle size was less than about 20 nm in diameter.[7] These spectral interpretations were essentially borne out in electron micrographs of the particles in the different solutions. The bluish coloured sols showed clusters of somewhat elongated

Table 1 Average particle diameters of colloidal gold particles obtained in the different alcohol systems

Alcohol	<Diameter>/nm[a]
Methanol	7 ± 2
Propan-2-ol	6 ± 4
n-Pentanol	5 ± 3

[a] <Diameter> number average diameter from Fig. 2 histograms.

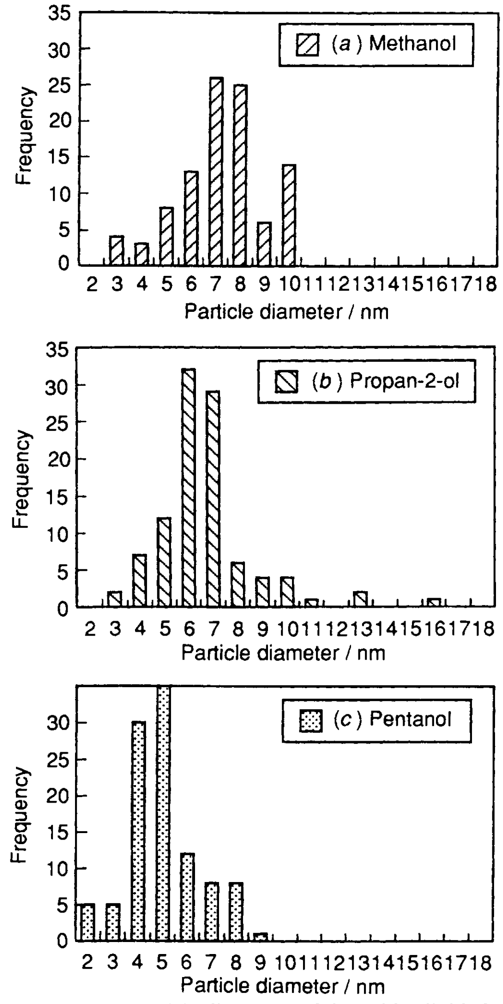

Fig. 2 Histograms of particle diameters of the gold colloids formed in different alcohol containing solutions. Particle diameters were measured in solutions in which all the $\mathrm{AuCl_4^-}$ had reacted. Total power absorbed by the solutions was 23.5 kJ.

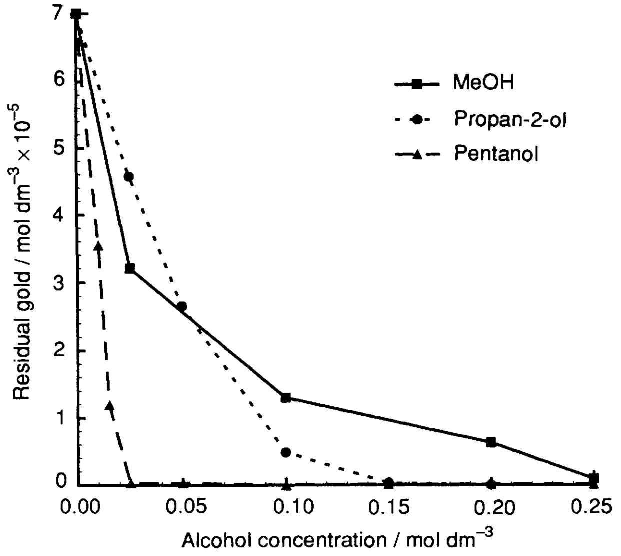

Fig. 3 Concentration of $AuCl_4^-$ remaining following sonication of solutions containing 1×10^{-4} mol dm^{-3} $AuCl_4^-$ and different concentrations of alcohol (no PVP in solution). The average ultrasound power deposited in each solution was 20.6 kJ.

particles (suggestive of particle–particle fusion) of diameter of about 20 to 30 nm. In contrast the pinkish coloured sols showed well dispersed particles with diameters as shown in Table 1 and size distribution as seen in Fig. 2. Evidence for particle–particle fusion in the alcohol containing solutions was seen although at a low occurrence, much like that observed when chemical methods are used to make gold sols.[7] This is quite an interesting result because Suslick[2] has shown that metal particle–particle fusion under sonication does occur. The implication is that the presence of the alcohol, presumably by adsorption onto the particles, provides quite effective protection against fusion whereas PVP alone, only provides partial protection.

We observed also that the efficiency of gold particle formation was dependent on the alcohol type used. This can be readily seen in Fig. 3, which shows the loss of $AuCl_4^-$ as a function of alcohol concentration and type, at a constant amount of power absorbed by the solution. The order of effectiveness of $AuCl_4^-$ reduction by the alcohols, n-pentanol> propan-2-ol> methanol, is in order of their air/water surface activity. This suggests that the scavenging of the primary radicals occurs at the cavitation bubble liquid interface. Scavenging in the bubble itself can be ruled out because this would be expected to be dependent on the partial vapour pressure of the alcohol, which is in the opposite order to their reduction efficiency. Nor is scavenging of the primary radicals in regions away from the interface likely to be important since at a particular amount of reduced $AuCl_4^-$ the concentration of the alcohol in the bulk is lower for the more efficient compound. These observations and conclusions are in line with work of Henglein[3] who found that the more hydrophobic the solute the smaller the yield of H_2O_2, again due to the ability of the solute to scavenge the primary OH radicals at the bubble liquid interface.

One final observation to comment on is the mean diameter of the particles formed with the different alcohols. It is clear from Table 1 that the more hydrophobic the alcohol the smaller the mean diameter of the particles produced. It is tempting to ascribe the order of particle size due to the stabilization of primary 'seed' nuclei by adsorbed alcohol. It can be argued that the more hydrophobic the alcohol the more will be adsorbed onto the particles and hence the greater stability to growth of the seed nuclei. Indeed, it has been suggested that in the chemical formation of gold particles in the presence of surfactants, particle growth is inhibited by surfactant adsorption onto the particles.[8] However, kinetic effects owing to the particular spatial distribution of secondary radicals formed by sonolysis cannot be ruled out as a contributing factor in the final size of the particles formed.

We are currently engaged in examining the formation of other metal particles by sonolysis of aqueous metal ion solutions in the presence of a broader range of solute radical scavengers. Our intention is to gain a better understanding of the initial scavenging process and the subsequent spread of the radicals away from the cavity interface into bulk solution.

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