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The sonochemical preparation of amorphous silver nanoparticles

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Amorphous silver nanoparticles of *ca.* 20 nm size have been prepared by the sonochemical reduction of an aqueous silver nitrate solution in an atmosphere of argon–hydrogen. The silver nanoparticles have been characterized by TEM, X-ray diffraction, absorption spectroscopy, differential scanning calorimetry and EPR spectroscopy. The mechanism of the sonochemical reduction has been discussed, and occurs through the generation of hydrogen radicals during the sonication process.

Today, nanoparticles have become the focus of intensive research, owing to their numerous applications in diverse fields such as catalyst production, ultramodern electronic and electrooptical devices, supermagnets, photographic suspensions, *etc.*[1,2]

Nanoparticles have a large surface-to-volume ratio, and consequently exhibit an increased surface activity as compared to bulk material. This enables their use in catalysis, the large surface area being an important factor in increasing the efficiency of the catalysis of certain organic reactions.[3]

A variety of methods can be used for the formation of nanoparticles, such as molecular beam epitaxy,[4] chemical vapor deposition,[5] reduction by ionizing radiation,[6] thermal decomposition in organic solvents,[7] chemical reduction or photoreduction in reverse micelles,[8] and chemical reduction with[9] or without[10] stabilizing polymers. From all this work, it has been assessed that the colloidal stability (for colloidal solutions), particle size, and the properties of nanoparticles depend strongly on the specific method of preparation and the experimental conditions applied. The sonochemical method has been used extensively to generate novel materials with unusual properties,[11] since they form particles of a much smaller size and higher surface area than those reported by other methods. The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth, and implosive collapse of bubbles in liquid. The implosive collapse of the bubble generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hotspots have been experimentally determined, with transient temperatures of *ca.* 5000 K, pressures of 1800 atm, and cooling rates in excess of 10^{10} K s^{-1}. These extreme conditions attained during bubble collapse have been exploited to decompose the metal–carbonyl bonds and generate metals,[11b–e] metal carbides,[11f] and metal oxides.[11g,h]

Nagata *et al.*[12] formed stable colloidal dispersions of silver prepared by ultrasonic irradiation of aqueous $AgClO_4$ or $AgNO_3$ solutions in the presence of surfactants. In their proposed mechanism the surfactant is active as a reducing agent.

In the present paper, we report a sonochemical method for the preparation of silver nanoparticles. Silver nanoparticles are widely used due to their role in the photographic process[13] and as substrates for surface-enhanced Raman spectroscopy (SERS).[14,15] Silver has also been extensively used as a catalyst for various oxidation reactions.[16]

The silver nanoparticles were prepared by the ultrasonic irradiation of an aqueous solution of silver nitrate under an argon–hydrogen atmosphere. These nanoparticles are *ca.* 20 nm in size, as seen using a transmission electron microscope (TEM). The silver nanoparticles are also characterized using powder X-ray diffraction (XRD), plasmon spectroscopy, differential scanning calorimetry (DSC), and EPR spectroscopy.

Experimental

Materials

$AgNO_3$ (99+%) was purchased from Riedel-de-Haen. Double distilled water was used. Absolute ethanol used was from Pharmco products.

Instruments

Absorption spectra were recorded on a Hewlett Packard 8453 UV-visible spectrophotometer. The size of the nanoparticles was determined using a JEOL-JEM 100SX transmission electron microscope (TEM). Powder X-ray diffraction patterns were recorded using a Rigaku 2028 Cu-Kα X-ray diffractometer ($\lambda = 1.5418$ Å). Nickel was used as the filter. The differential scanning calorimetric (DSC) spectrum was recorded using a Mettler Toledo (DSC 25) Instrument. The heating rate was 2 °C min^{-1}. EPR spectra were recorded on a Bruker EMX Instrument. Ultrasonic irradiation was performed with a high intensity piezolectric ultrasonic probe (Misonix, XL sonifier, 1 cm diameter Ti horn, 20 kHz, 100 W cm^{-2}).

Preparation of silver nanoparticles

Silver nitrate (1 g) was dissolved in 100 ml of doubly distilled water and sonicated for 1 h, under an atmosphere of argon–hydrogen, at a temperature of 10 °C. The ratio of argon to hydrogen was 95 : 5. After sonication for 1 h, the solution was carefully transferred to an inert atmosphere glove box (<5 ppm O_2). The solution was centrifuged and washed with water and then with absolute ethanol. All of the manipulations for the silver nanoparticles were performed inside the glove box, to prevent the formation of any traces of silver oxide.

Results and discussion

TEM observations for the as-prepared, amorphous silver nanoparticles showed that the nanoparticles of silver are *ca.* 20 nm in size (Fig. 1). X-Ray powder diffraction patterns of the as-prepared silver nanoparticles showed that they were amorphous [Fig. 2(a)]. The amorphous-to-crystalline transition of the silver nanoparticles occurred at 340 °C, as indicated by an exotherm in the DSC spectrum (Fig. 3). The crystallized silver nanoparticles showed an X-ray diffraction pattern which could be ascribed to metallic silver [Fig. 2(b)]. The peak

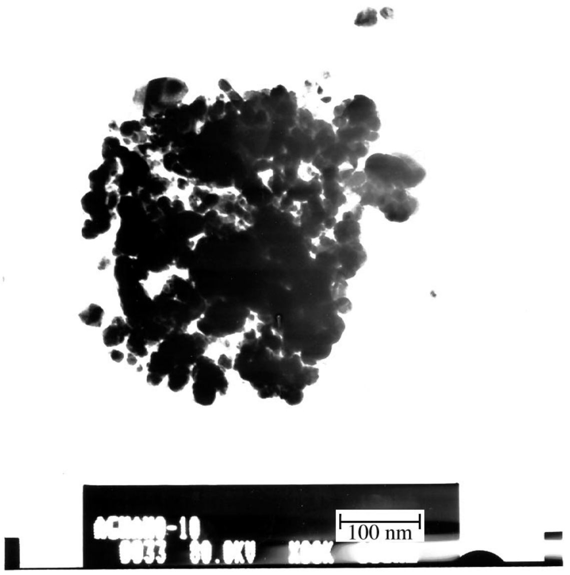

Fig. 1 Transmission electron micrograph of the amorphous silver nanoparticles.

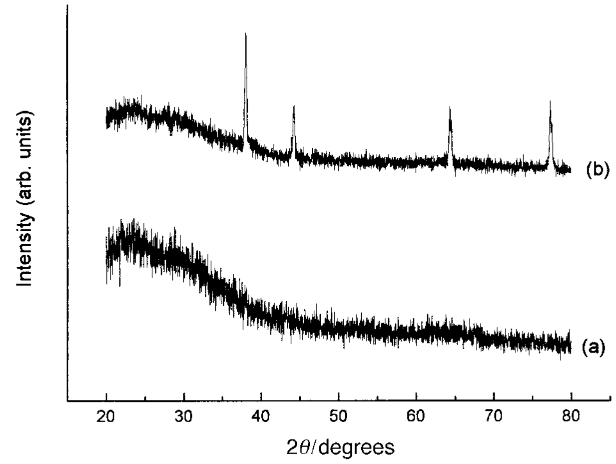

Fig. 2 X-Ray diffraction pattern of as-prepared silver nanoparticles, and silver nanoparticles crystallized at 340 °C.

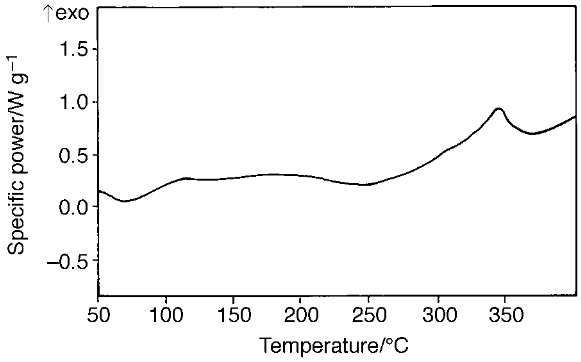

Fig. 3 DSC spectrum of the amorphous silver nanoparticles. The crystallization temperature is indicated by a sharp exotherm at 340 °C.

positions observed are consistent with those reported for metallic silver (JCPDS card no. 4–783). The particle size calculated for the crystalline nanoparticles using the Debye–Scherrer equation is 39.8 nm.

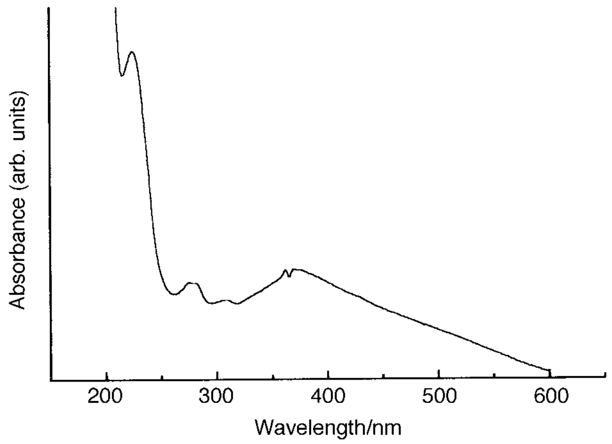

Fig. 4 Absorption spectrum of an aqueous solution containing silver nanoparticles.

The UV–VIS absorption spectra (Fig. 4) of an aqueous solution containing silver nanoparticles showed a sharp and symmetric absorption peak at *ca.* 370 nm. This well defined plasmon peak is indicative of relatively large, spherical silver clusters.

EPR spectra for the metallic silver nanoparticles were measured. Fig. 5(a) shows a typical EPR spectrum for the silver sample recorded at 300 K and Fig. 5(b) shows the integral of the signal. The resonance lines are quite narrow and exhibit a slight asymmetry. The width of the integral (ΔH) is 1344 G, and the asymmetry parameter (α) is 0.91, as deduced from the ratio of the maximum and the minimum value of the derivative signal. The *g*-value is 2.0709, which is very close to the *g*-value for silver nanoparticles reported.[17]

Proposed mechanism for the sonochemical formation of silver nanoparticles

The chemical reactions driven by intense ultrasonic waves strong enough to produce cavitation are oxidation, reduction, dissolution, and decomposition.[11a,18–21] Other reactions, such as promotion of polymerization, have also been reported to be induced by ultrasound. It is known that three different regions are formed[22] during the aqueous sonochemical process: (a) the inner environment (gas phase) of the collapsing bubble,

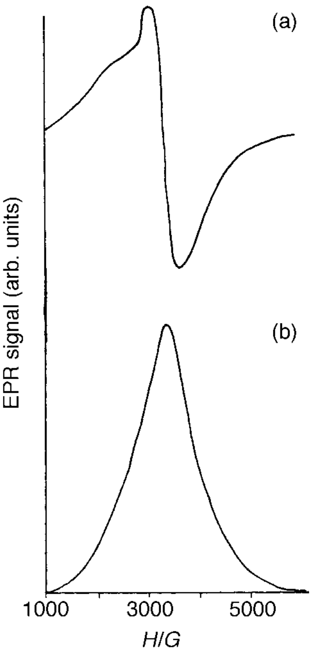

Fig. 5 EPR spectra of the silver nanoparticles first derivative EPR spectrum, and absorption signal, $\Delta H = 1344$ G.

where elevated temperatures (several thousands of degrees) and pressures (hundreds of atmospheres) are produced, causing water to vaporize and further to pyrolyze into H and OH radicals; (b) the interfacial region where the temperature is lower than in the gas-phase region, but still high enough to induce a sonochemical reaction; and (c) the bulk solution, which is at ambient temperatures and which is where the reaction between reactant molecules and OH or H takes place. Among these three regions, it appears that the sonochemical reaction occurs within the interfacial region, yielding amorphous materials, owing to the very high quenching rate experienced by the products.

The mechanism of the formation of silver nanoparticles takes into consideration the radical species generated from water molecules by the absorption of ultrasound [eqn. (1)]

$$H_2O\ )))))\ H^\bullet + OH^\bullet \qquad (1)$$

The pH of the solution was measured before and after the reaction. A decrease in the pH from 6.21 before to 4.32 after the reaction occurred, indicating the generation of H^+ ions during sonication. The $H^\bullet$ radicals formed in eqn. (1) can act as reducing species and trigger the reduction $Ag^+ \rightarrow Ag^0$ [eqn. (2)]

$$Ag^+ + H^\bullet \rightarrow Ag^0 + H^+ \qquad (2)$$

$$nAg^0 \rightarrow Ag_n \text{ (aggregates)} \qquad (3)$$

A possible pathway for the formation of silver oxide, Ag_2O, could be partial oxidation of Ag^0 by secondary species formed by the recombination of $H^\bullet$ and $OH^\bullet$ radicals. In the absence of any additives or scavengers, $H^\bullet$ and $OH^\bullet$ radicals readily recombine to give a variety of products as shown in eqn. (4).[21]

$$2H^\bullet/2OH^\bullet \rightarrow H_2/H_2O_2/H_2O \qquad (4)$$

The oxidant H_2O_2 thus generated can initiate the oxidation of silver metallic clusters into silver oxide [eqn. (5)]

$$Ag^0 + H_2O_2 \rightarrow Ag_2O + H_2O \qquad (5)$$

However, in the presence of an argon and hydrogen atmosphere, the formation of H_2O_2 can be prevented by the scavenging of OH radicals by hydrogen [eqn. (6)],[21] thereby yielding pure silver nanoparticles.

$$OH^\bullet + H_2(g) \rightarrow H_2O + H^\bullet \qquad (6)$$

An argon and hydrogen mixture produces more H radicals than in air, according to eqn. (6), thereby enhancing the reduction of Ag^+ ions under the sonochemical conditions.

The sonochemical reduction process generates high temperatures and pressures for the reduction of silver nitrate to metallic silver. A controlled experiment in which an aqueous solution of $AgNO_3$ was sonicated for 1 h under argon yielded no precipitate. The reduction of an aqueous solution of $AgNO_3$ under the same reaction conditions, however, with fast stirring instead of sonication, did not lead to the formation of silver nanoparticles, even when the reduction was carried out for >2 h. This confirms that the transient high temperatures and fast cooling rates, generated under the sonochemical conditions, are necessary for the reaction to occur.

Conclusion

Silver nanoparticles have been prepared by the sonochemical decomposition of silver nitrate. The advantages of this process are that it is very simple, efficient, and produces nanoparticles which are very small in size (*ca.* 20 nm). These nanoparticles could find use in photographic suspensions, in modern electronics and electrooptical devices and as catalysts for a variety of organic reactions.

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