NOTE

Synthesis of Copper Nanoparticles in Nonionic Water-in-Oil Microemulsions

Synthesis of well-dispersed copper nanoparticles was achieved by reduction of aqueous copper chloride solution using NaBH$_4$ in the nonionic water-in-oil (w/o) microemulsions formed by Triton X-100, *n*-hexanol, cyclohexane, and water. It has been shown that instead of copper oxide produced in aqueous solution, metallic copper particles are formed in w/o microemulsions because of the high local copper concentration in water pools of the microemulsions, indicating the advantage offered by w/o microemulsions over aqueous phases. The absorption spectrum of the colloidal copper particles obtained in microemulsions does not exhibit the plasmon peak characteristic of the Cu surface. It is conceivable that the lack of the plasmon absorption band is attributed to the formation of a CuCl monolayer on the copper particles. © 1997 **Academic Press**

Key Words: copper; nanoparticles; nonionic water/oil microemulsions; copper chloride; plasmon absorption band.

INTRODUCTION

Much attention has been paid to metal nanoparticles, which exhibit novel optical, electronic, magnetic, and chemical properties owing to their extremely small dimensions. Specifically, these small particles are interesting materials for research on catalysts with specific activity and selectivity. On the other hand, for silver, gold, and copper colloids, it is very interesting to investigate their optical properties since they strongly absorb light in the visible region due to surface plasma resonance (1). As a result, many efforts have been directed toward the chemical synthesis of various metal nanoparticles with a narrow size distribution.

Water-in-oil (w/o) microemulsions or reverse micelles are a particularly attractive reaction medium for preparing metal nanoparticles. These microemulsions consist of nanosized water droplets that are dispersed in a continuous oil medium and stabilized by surfactant molecules accumulated at the oil/water interface. The highly dispersed water pools have been shown to be ideal nanostructured reaction media, or microreactors, for producing ultrafine and monodisperse nanoparticles (2, 3). Since microemulsions were first used by Boutonnet *et al.* (4) to obtain monodisperse metal nanoparticles of Pt, Pd, Rh, and Ir by reducing corresponding salts in water pools of w/o microemulsions, the microemulsion-mediated synthesis of nanoparticles has been reported for a wide variety of materials. In particular, metal nanoparticles of Ag (5–7) and Au (5) have been produced by reduction of the corresponding metal salts in w/o microemulsions using sodium borohydride or hydrazine, the optical properties of which have also been investigated.

Recently, copper nanoparticles have been synthesized in Aerosol OT (AOT) reverse micelles by using a functionalized surfactant, copper bis(2-ethylhexyl)sulfosuccinate [Cu(AOT)$_2$] as reactant (8, 9). In contrast to the two noble metals, Ag and Au, the light transition metal Cu usually cannot be obtained by reduction of simple copper ion salts such as copper chloride in aqueous solution unless other reagents like protective polymers

(10) carrying functional groups that can form complexes with copper ions are present. Instead, the reduction tends to stop at the Cu$_2$O stage due to the presence of a large number of water molecules; however, since the microenvironment of the water pools in w/o microemulsions is significantly different from that of bulk aqueous solution, it is worthwhile to explore the possibility of synthesis of copper nanoparticles by reduction of simple copper ion salts in microemulsions. To avoid the poor solubility of copper ion salts and NaBH$_4$ in AOT reverse micelles, a nonionic w/o microemulsion system formed by Triton X-100 (TX-100), *n*-hexanol, cyclohexane, and water, which we previously used to prepare BaSO$_4$ nanoparticles (11), was used for this study.

In this paper we present our preliminary results obtained for the synthesis of copper nanoparticles by reduction of CuCl$_2$ in nonionic w/o microemulsions using sodium borohydride. The optical absorption properties of the obtained copper colloids are also investigated.

MATERIALS AND METHODS

The nonionic surfactant TX-100 [*p-tert*-C$_8$H$_{17}$C$_6$H$_4$(OC$_2$H$_4$)$_{9.5}$OH] was obtained from Rohm & Haas and the cosurfactant *n*-hexanol was a CP grade Fluka product. Cyclohexane (AR grade), CuCl$_2$·2H$_2$O (AR grade), and NaBH$_4$ (CP grade) were locally available reagents. All the preceding reagents were used without further purification. The water used in this work was deionized and distilled.

Microemulsions were prepared by solubilizing aqueous CuCl$_2$ or NaBH$_4$ solution into a TX-100/*n*-hexanol/cyclohexane solution, which has a TX-100 and *n*-hexanol weight ratio of 4:1 and a TX-100 concentration of 0.126 *M*. The preparation of copper particles was achieved by mixing rapidly the same volume of two w/o microemulsion solutions, with CuCl$_2$ solubilized in one solution and NaBH$_4$ as the reduction agent in the other solution. In both microemulsion solutions the water-to-surfactant molar ratio (*w*) was selected to be 7 because preliminary experiments had shown that suitable Cu^{2+} ion concentration and Cu particle size could be attained at this water content. The salt concentrations in the aqueous phase were 0.2 *M* in CuCl$_2$ and 0.4 *M* in NaBH$_4$, respectively. After mixing, the final Cu^{2+} ion concentration in the total microemulsion solution was 1.6×10^{-3} *M*. All the experiments were done at room temperature without removing the oxygen.

The absorption spectrum of colloidal copper particles was recorded 10 min after mixing with a Shimadzu UV-250 spectrophotometer. At the same time, a drop of the colloidal solution was dropped onto a Formvar-covered copper grid placed on filter paper and evaporated in air at ambient temperature. Electron micrographs were taken with a JEM-200CX transmission electron microscope operating at 200 kV.

RESULTS AND DISCUSSION

Figure 1A is a typical transmission electron micrograph of the copper nanoparticles obtained by reduction of CuCl$_2$ in microemulsions using NaBH$_4$, which shows that the particles formed within the water droplets are well dispersed, with most particles in the size range 5 to 15 nm. The corresponding electron diffraction pattern (Fig. 1B) reveals that the observed seven fringe patterns with plane distances of 2.10, 1.79, 1.27, 1.09,
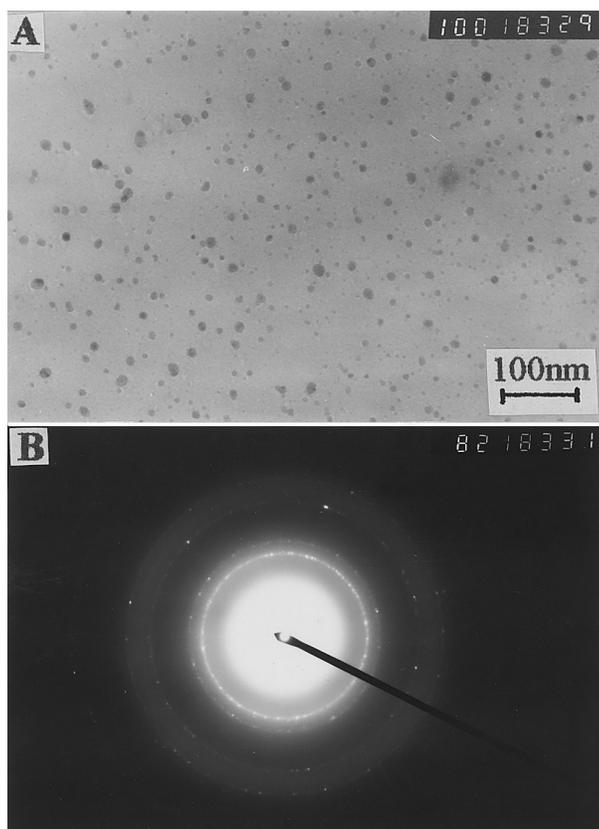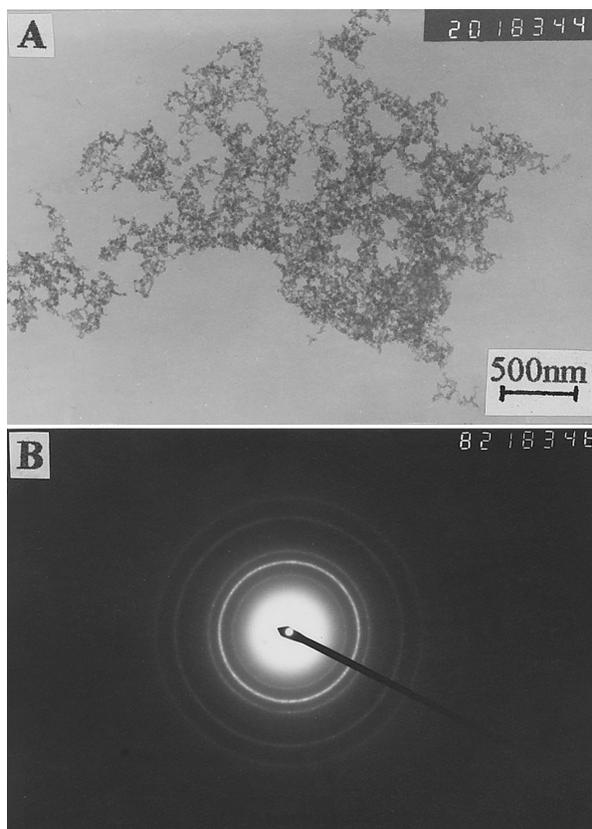
FIG. 1. Transmission electron micrograph (A) and electron diffraction pattern (B) of copper particles synthesized in nonionic water-in-oil microemulsions. $[CuCl_2] = 1.6 \times 10^{-3}$ M; $[NaBH_4] = 3.2 \times 10^{-3}$ M.

1.04, 0.83, and 0.80 Å are consistent with the fcc metal Cu (111), (200), (220), (311), (222), (331), and (420) plane distances of 2.088, 1.808, 1.278, 1.090, 1.044, 0.829, and 0.809 Å, indicating the formation of pure metallic particles. It is also noted that faint rings due to nantokite structure CuCl are evident in the diffraction patterns of some selected regions of the transmission electron microscopy sample; however, no copper oxide (Cu_2O) rings can be seen in all the selected area electron diffraction patterns. It is noteworthy that in aqueous solution, reduction of copper ions salt such as copper chloride induces the formation of bulk copper oxide, Cu_2O. Figure 2A is a representative transmission electron micrograph of the particles produced by reduction of $CuCl_2$ in aqueous solution using $NaBH_4$. It can be seen that the particles obtained in aqueous solution associate to form large aggregates in contrast to the well-dispersed particles formed in microemulsions as shown in Fig. 1A. The corresponding electron diffraction pattern (Fig. 2B) shows sharp rings with plane distances of 2.99, 2.47, 2.12, 1.51, and 1.28 Å, which match with the d spacing for cubic copper oxide, indicating the formation of pure Cu_2O. Further experiments also show that when the preparation of Cu particles in aqueous solution is carried out in the presence of the surfactant TX-100, the situation is similar to that without surfactants and no significant improvement in the dispersion state of particles can be attained. These results suggest that in the preparation of metal nanoparticles, w/o microemulsion media offer a significant advantage over aqueous phases in controlling the oxidation state of the particles in addition to controlling the size and the dispersion state of the particles.

The results presented above suggest that the presence of water droplets in microemulsions favors the formation of pure copper metallic particles. It is interesting to note that the explanation for these results is analogous to that for the results obtained from the copper nanoparticle synthesis per-

formed by reduction of copper dodecyl sulfate, $Cu(SD)_2$, in aqueous solution using $NaBH_4$ (12). It has been suggested that nuclei, obtained by reduction, can react either with water molecules to form copper oxide or with other nuclei to give pure copper metallic particles. In aqueous $Cu(SD)_2$ solution below the critical micellar concentration (CMC), reduction of copper ions that are totally dissociated like $CuCl_2$ results in the formation of pure copper oxide. At the CMC, a strong increase in the local copper concentration at the interface is induced; hence the high local concentration of copper nuclei, formed by chemical reduction, favors the formation of relatively large copper metallic particles having a local environment that prevents particle oxidation. In w/o microemulsions, the copper concentration in water droplets is rather high; moreover, in the TX-100 microemulsions with a w value of 7, the presence of a high proportion of bound water, which is tightly bound to the oxyethylene groups of the polar chain of the surfactant (11), may lead to a much higher local copper concentration in water pools of w/o microemulsions. Thus, the formation of pure copper metallic particles, instead of copper oxide, is favored.

Figure 3 is the absorption spectrum of the colloidal copper particles obtained in microemulsions; it shows a smoothly increasing absorbance through the wavelength region 700 to 400 nm. It is noteworthy that the this spectrum of copper colloids is relatively featureless and does not exhibit an absorption peak near 570 nm due to the plasma oscillation characteristic of the Cu surface. The absorption spectra of colloidal copper particles of various sizes have been described and simulated (8, 9). It has been shown that progressive appearance of the 570-nm plasmon peak occurs on an increase in the size of the copper clusters, and the copper particles with a diameter below 4 nm exhibit a strong broadening of the plasmon band. Since the copper particles obtained in this work have an average particle

FIG. 2. Transmission electron micrograph (A) and electron diffraction pattern (B) of copper oxide particles produced in aqueous solution. $[CuCl_2] = 1.6 \times 10^{-3}$ M; $[NaBH_4] = 3.2 \times 10^{-3}$ M.
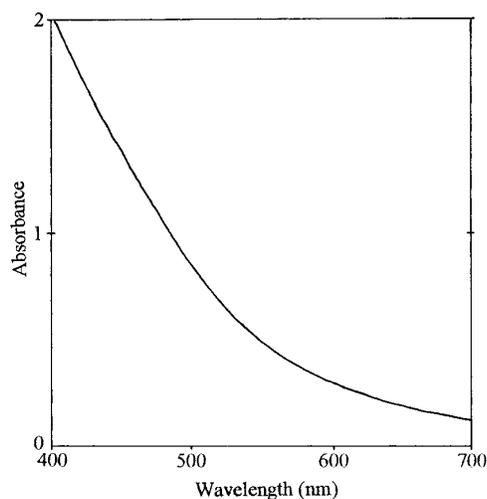
FIG. 3. Absorption spectrum of copper particles synthesized in nonionic water-in-oil microemulsions. $[CuCl_2] = 1.6 \times 10^{-3}$ M; $[NaBH_4] = 3.2 \times 10^{-3}$ M.

size much larger than 4 nm, the lack of the plasmon peak could not result from the broadening of the band due to the size effect. On the other hand, it has been demonstrated that the plasmon absorption band of metals such as Ag is very strongly influenced by chemical modification of the surface (13). In particular, anions that readily form complexes (or insoluble salts) with Ag^+ ions are strongly adsorbed on silver particles, leading to a decrease in the band intensity and broadening of the band. By analogy, in the case of metal Cu, Cl^- anions that can form the insoluble salt CuCl with Cu^+ may be strongly adsorbed on Cu particles to form a monolayer of CuCl, resulting in strong damping of the plasmon band. Although the typical diffraction pattern indicates the formation of pure copper particles, it should be noted that the electron diffraction is not sensitive enough to exclude the formation of a CuCl monolayer. Furthermore, the results obtained from electron diffraction have revealed the presence of some CuCl particles as well as Cu particles which are the main products of reduction in microemulsions, implying the fact that Cl^- anions can readily form insoluble CuCl with Cu^+ in w/o microemulsion media. Therefore, it is conceivable that the formation of a CuCl monolayer on the Cu particles brings about the lack of the plasmon peak in the absorption spectrum of the copper particles obtained in this work; however, a detailed investigation is needed to confirm this possible mechanism.

CONCLUSIONS

Metallic copper nanoparticles have been prepared by reduction of the simple copper ion salt $CuCl_2$ in TX-100/n-hexanol/cyclohexane/water w/o microemulsions using $NaBH_4$ as reduction agent. The prepared copper particles were characterized by transmission electron microscopy and absorption spectroscopy. It has been shown that well-dispersed metallic copper particles are formed in w/o microemulsions, whereas only associated copper oxide particles are obtained when the reaction is performed in aqueous solution. This result could be explained in terms of the high local copper concentration in water pools of the microemulsions. The absorption spectrum of the copper particles synthesized in microemulsions shows the lack of the plasmon band characteristic of the Cu surface, which could result from the formation of a CuCl monolayer on the copper particles.

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