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Elongated Copper Nanoparticles Coated with a Zwitterionic Surfactant

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Received: March 8, 1999; In Final Form: August 16, 1999

A sonochemical approach to the preparation of elongated copper nanoparticles coated with a zwitterionic surfactant, cetyltrimethylammonium *p*-toluene sulfonate (CTAPTS) is reported. A shape transition of the copper nanoparticles is found to occur due to the presence of an organized medium, consisting of a cylindrical, interconnected network of threadlike micelles. Transmission electron micrographs (TEM) show the presence of elongated copper nanoparticles coated with the surfactant. UV−visible spectroscopic studies point to the elongation of the copper nanoparticles and to the adsorption of the CTAPTS on the surface of the copper nanoparticles, which is corroborated by IR and NMR spectral studies. A monolayer coating of the surfactant is formed on the surface of the elongated copper nanoparticles. This is confirmed by comparing the weight loss obtained in thermogravimetric analysis with that obtained theoretically.

1. Introduction

Nanotechnology has been receiving increased attention in the past decade due to its tremendous applications in the field of catalysis, sensor technology, and in the fabrication of ultra-modern electronic devices.[1] There are diverse approaches to the preparation of the nanoscale materials. Among those which have been reported in the literature,[2−5] can be found controlled chemical reduction,[2] electrochemical reduction,[3] and metal vaporization[4] techniques. Recently, sonochemical processing has proved to be a useful technique for generating novel materials with unusual properties.[5] The chemical effects of ultrasound arise from acoustic cavitation, which produces unusual chemical and physical environments. The extreme conditions thus attained have been exploited to prepare nanoscale metals,[6] metal oxides,[7] and nanocomposites.[8]

Increasingly, chemists are contributing to the synthesis of advanced materials with enhanced or novel properties by using colloidal systems as templates. These offer an unique way to tailor the shape and size of metallic nanoparticles, using a rich array of liquid crystalline and amphiphilic self-assembled systems. Numerous methods have been used for the preparation of elongated metal nanoparticles. The use of colloidal assemblies as templates,[9] the use of microemulsion media for the synthesis of the nanosized particles[10] using reverse micelles as microre-actors,[11] electron beam lithography,[12] the sol−gel method,[13] and use of a plasma polymer matrix[14] are among the several reported techniques for the formation of elongated metal nanoparticles.

Recently, Dhas et al.[15] have described a sonochemical procedure for the preparation of nanocrystalline particles of copper. Increased focus[16,18] on the preparation of nanoparticles through a surfactant-mediated process led us to devise a new method, wherein elongated copper nanoparticles can be prepared in the presence of a surfactant cetyltrimethylammonium *p*-toluene sulfonate (CTAPTS), $C_{16}H_{33}N^+(CH_3)_3H_3C-C_6H_4-$

SO_3^{-}-*p*. This surfactant in water shows the presence of elongated threadlike micelles.[17] The presence of organized assemblies during the preparation of nanomaterial has been shown to have an effect on the shape of the nanoparticles formed.[18] It is also believed that the interparticle collisions which happen at very high speed during high-intensity ultrasound radiation ultimately lead to agglomeration, changing the morphology of the particles.[19]

The objective of the present work is to use the sonochemical method for the preparation of elongated copper nanoparticles coated with the surfactant CTAPTS, using an interconnected network of threadlike micelles as a template. The threadlike micelles formed in this system are not affected by sonication, as observed from the highly viscous character of an aqueous solution of CTAPTS after sonication. The formation of an interconnected network of elongated threadlike micelles favors the uniaxial growth of the copper nanoparticles within the assembly, leading to the formation of elongated nanoneedles of copper.

2. Experimental Section

Preparation of the Elongated Copper Nanoparticles. The copper hydrazine carboxylate (CHC) precursor was prepared as reported in the literature.[15] In an aqueous solution containing the surfactant CTAPTS (99% Sigma), 500 mg of CHC was reduced ultrasonically in an argon−hydrogen atmosphere, at room temperature, to a reddish brown powder. The presence of the surfactant should have an effect on the shape and morphol-ogy of the metallic copper nanoparticles. The presence of the surfactant on the surface of the copper nanoparticles was proved using several techniques such as transmission electron micros-copy, UV−visible, FT-IR, and FT-NMR spectroscopy, and thermogravimetric analyses. The template of the interconnected cylinders is undisturbed by sonication, as was observed from

Figure 1. Transmission electron micrograph of the elongated copper nanoparticles coated with CTAPTS.

the unaltered viscoelastic character of a solution of CTAPTS after sonication for 1 h. The synthesis was carried out under controlled conditions of temperature to ascertain that there was no change in the phase behavior during the sonication.

Product Characterization. The X-ray diffraction patterns of the copper nanocrystallites were recorded by employing a Rigaku X-ray diffractometer (model 2028, Cu Kα). Absorption spectra were recorded on a Hewlett-Packard 8453 UV−visible spectrophotometer. The transmission electron micrographs (TEM) were obtained by employing JEOL-JEM 100SX microscopes. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, electron microscopy sciences) coated with carbon film and were allowed to dry in air. TEM-EDAX measurements were carried out on a JEOL 2000FX TEM/STEM microscope. FT-IR spectra were recorded on a Nicolet (Impact 410) infrared spectrophotometer. FT-NMR spectra were recorded on a Bruker 300 MHz instrument. The sample for NMR was prepared by dispersing the substrate in D_2O, heating the deuterated solution, and then cooling again for equilibration. The thermogravimetric analysis was done using a Mettler Toledo TGA/SDTA851, in the temperature range 30−600 °C, at the rate of 10 °C per minute, in an argon atmosphere.

3. Results and Discussion

Figure 1 shows the transmission electron micrographs of the elongated copper nanoparticles coated with the surfactant, CTAPTS. The presence of the surfactant during the preparation
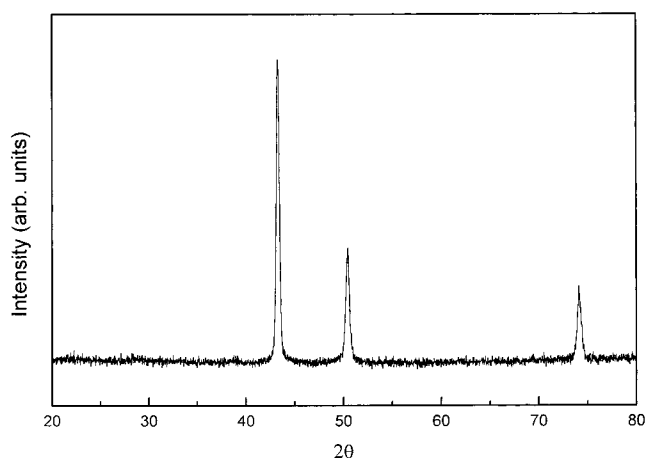

Figure 2. X-ray diffraction pattern of the elongated copper nanoparticles coated with CTAPTS.

TABLE 1: Particle Sizes Calculated along Different Planes for the Copper Nanoparticles, with and without CTAPTS, Using the Debye−Scherrer Equation

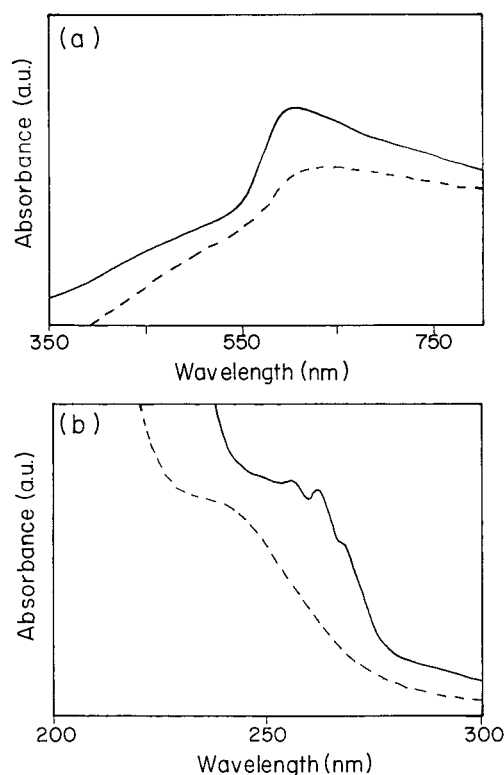|	[111] plane	[200] plane	[220] plane
copper nanoparticles	25	27	62
copper nanoparticles with CTAPTS	36	37	60

Figure 3. Absorption spectra in different regions for copper nanoparticles coated with CTAPTS (solid line) and for the uncoated copper nanoparticles (dashed line): (i) 350−800 nm; (ii) 200−300 nm.

stage also dictates the shape of the ultrasonically formed copper nanoparticles. The size of the elongated copper nanoparticles was approximately 500 nm in length and 50 nm in width. On the other hand, the copper nanoparticles prepared without using surfactant were spherical in shape, with a diameter of approximately 50 nm.[15] The TEM-EDAX measurements have revealed that the same concentration of copper can be found along the acicular particle and the periphery. The presence of sulfur atoms was also detected in both areas equally. This
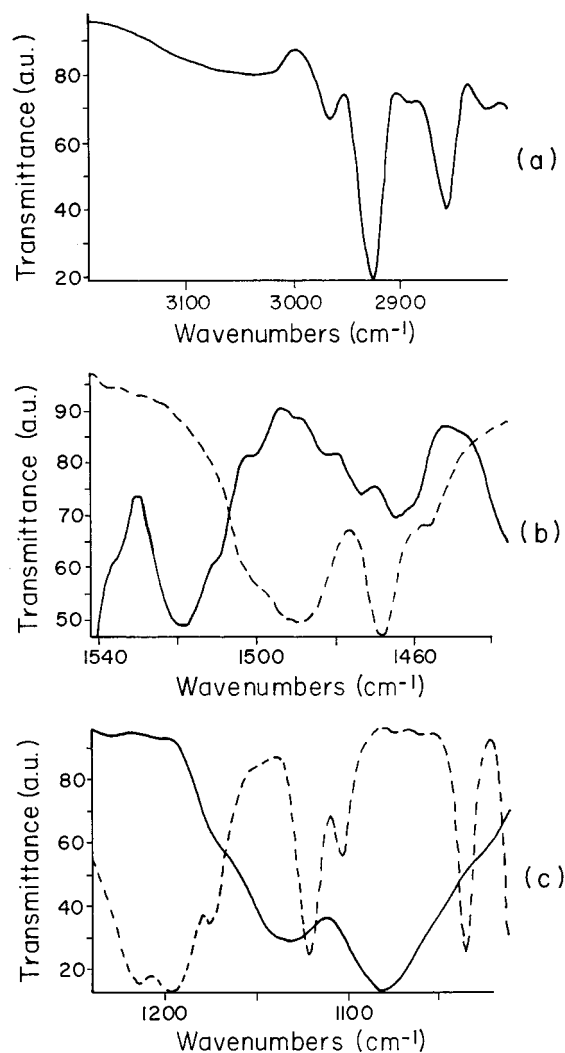
Surfactant-Coated Copper Nanoparticles

J. Phys. Chem. B, Vol. 104, No. 5, 2000 **895**

Figure 4. FT-IR spectrum in different regions for the copper nanoparticles coated with CTAPTS (solid line) and for pure CTAPTS (dashed line): (a) 3100−2800 cm^{-1}; (b) 1540−1440 cm^{-1}; (c) 1200−1090 cm^{-1}.

suggests the presence of the surfactant in assembling the observed solid structure.

Figure 2 displays the XRD pattern of the elongated copper nanoparticles. The peak positions observed are consistent with those reported earlier for metallic copper.[15] Comparison of the XRD pattern with that obtained for the copper nanoparticles prepared without using the surfactant revealed an elongation to
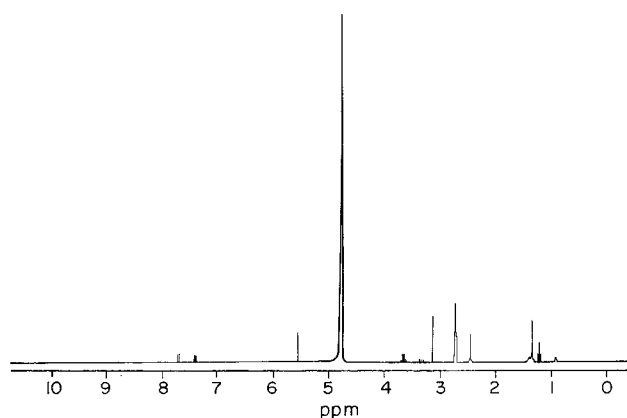

Figure 5. FT-NMR spectrum of the surfactant, CTAPTS (in D$_2$O), on the surface of the elongated copper nanoparticles.

be taking place along the [111] and [200] planes of the copper nanocrystals. The comparison was done taking into account the line widths at half height for each of the peaks obtained in the XRD patterns. Using the Debye−Scherrer equation, the particle sizes were calculated along these planes (Table 1). The elongation does not occur along the [220] plane due to adsorption of the surfactant molecule along this plane. This prevents any side interconnections with more copper ions, thus inhibiting further growth. The calculations, however, are approximate and were limited by the fact that the peaks due to the copper nanoparticles appear at very high angles in the XRD measurements.

Figure 3a exhibits the overlaid absorption spectra (region 350−800 nm) of the copper nanoparticles prepared using the method described previously[15] and the surfactant-mediated sonochemical process. Both spectra display an absorption peak at approximately 570 nm. According to Pileni et al., the appearance of a discrete absorption band at around 570 nm is an indication of a particle size larger than 4 nm.[18] There is, however, a small shift in the absorption toward higher wavelength in the copper nanoparticles prepared using the surfactant-mediated process; that is, a red shift is observed.[16] This red shift of the surfactant-copper spectrum cannot be attributed to the particle size effect since increase of particle size should lead to a blue shift. It is however ascribed to the elongation of the particle when the surfactant-copper is compared with the bare copper particle. Pileni has demonstrated that the elongation should result in a red shift.[18] There is a change in the aspect ratio of the initially spherical copper nanoparticles, which also leads to a strong difference in the particles polarizibility
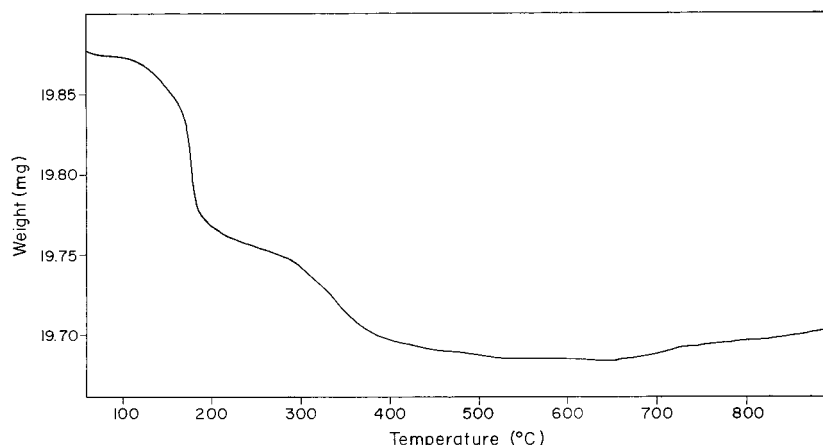

Figure 6. Thermogravimetric spectrum of the elongated copper nanoparticles coated with the surfactant, CTAPTS.

components. The elongated copper nanoparticles of about 0.5 μm size have an aspect ratio of 1:10. It has been reported that one can shift the spectral position of the extinction maximum in a wide range from 480 to 600 nm by variation of the particles' aspect ratio.[12] Figure 3b exhibits the overlaid absorption spectra (region 200−300 nm) of the copper nanoparticles prepared as such and by the surfactant-mediated sonochemical process. The absorption spectra of the elongated copper nanoparticles show a broad band at 255 nm, due to the presence of a conjugated aromatic ring on the surface. This indicates the presence of the surfactant on the surface of the elongated copper nanoparticles.

Figure 4a shows the IR spectrum of the copper coated with CTAPTS in the 3050−2700 cm^{-1} region. The asymmetric stretching mode of the headgroup (N^+)−CH$_3$ is observed at 3034 cm^{-1}. This indicates the adsorption of the CTAPTS on the surface of the copper nanoparticles. The strong bands at 2918 and 2849 cm^{-1} are assigned to the asymmetric and symmetric CH$_2$ stretching modes, respectively. The presence of these bands indicates that the surfactant is adsorbed on the surface of the copper nanoparticles. Figure 4b shows the overlaid spectra of the pure CTAPTS and the copper coated with CTAPTS in the region 1540−1440 cm^{-1}. For pure CTAPTS, there are two broad bands in this region. The first at 1487 cm^{-1} is assigned to the asymmetric mode of the CH$_3$-(N^+) headgroup,[20] and the second at 1472 cm^{-1} is attributed to the CH$_2$ scissoring mode.[21,22] These bands are shifted to lower wavenumbers when the surfactant is coated on the copper, suggesting a less mobile environment, and a strong association of these groups on the surface of the copper. This indicates that the nitrogen of the quaternary ammonium group coordinates to the surface of the copper nanoparticles. Figure 4c shows the overlaid IR spectra of pure CTAPTS and copper nanoparticles coated with CTAPTS in the region 1250−1050 cm^{-1}. The symmetric stretching mode of the S−O is observed as a bimodal broad band around 1230−1150 cm^{-1}. Also, a broad shoulder is observed at 1175 cm^{-1} which is due to the C−H of the aromatic part of the *p*-toluene sulfonate counterion. These bands are also shifted to lower wavenumbers in the sample of the copper nanoparticles coated with surfactant, indicating the relatively lower mobility of these groups in the coated copper samples. The most dramatic effect in this region is the disappearance of the bands due to the aromatic C−H bending vibrations, which appear at about 1100, 1030, and 1000 cm^{-1} in the IR of the pure CTAPTS. We should also mention that the band at 1598 cm^{-1}, the aromatic C−C stretching vibration, is also strongly perturbed. We explain the disappearance of these bands as due to the perpendicular orientation of the aromatic ring of the *p*-toluene sulfonate counterion to the surface of the copper nanoparticles. The perpendicular orientation of the aromatic ring to the surface of the copper nanoparticle results in a significant weakening of the IR bands due to the aromatic ring of the *p*-toluene sulfonate counterion. This is governed by the selection rules which forbid or allow certain transitions to occur, depending upon the relative orientation of the dipole moment of the molecule and the electric field of the probing light.[23]

FT-NMR spectra of the surfactant adsorbed on the surface of the copper nanoparticles is shown in Figure 5. The NMR shows lines characteristic of CTAPTS.[17,24] The doublets due to the aromatic protons of the *p*-toluene sulfonate counterion appear at 7.4 and 7.7 δ respectively, and the methyl group on the *p*-toluene sulfonate appears at 2.7 δ. The protons due to the aliphatic cetyl chain show lines at 1.4 δ, and the protons of the quaternary ammonium group appears at 3.6 δ. Lines due to the aromatic protons, as well as those due to the protons of the aliphatic cetyltrimethylammonium chain are observed in the spectrum, which again point to the existence of the CTAPTS on the surface of the elongated copper nanoparticles.

Figure 6 displays the thermogravimetric spectrum of the elongated copper nanoparticles coated with surfactant, from 30 to 600 °C. The TGA spectrum exhibits two steps, corresponding to the removal of the CTA$^+$ and the PTS$^-$ part of the surfactant molecule from the surface of the copper nanoparticles. The sample also exhibits a small weight loss of about 1% at 200 °C. There are two possible explanations for this small weight loss. One of them is that the CTAPTS must be forming a monolayer on the surface of the elongated copper nanoparticles, and the weight loss is associated with the rupture of the bonds between the copper and the surfactant. The second possibility is that only occluded solvent molecules are coming out of the sample. To confirm the possibility of the coating of the surfactant on the surface of the copper, we carried out a TPD experiment, which revealed a 257 amu peak in the mass spectrometer. The signal peak obtained in the mass spectrometer was obtained at 200 °C, matching the weight loss temperature in the TGA experiments. Although the exact nature of the desorbed molecule is not yet characterized, it is clearly related to the surfactant and not to the solvent.

In addition, we have done some calculations of the amount of surfactant adsorbed on the surface of the copper nanoparticles. If we consider the elongated copper nanoparticle to be a cylinder of typical length 500 nm and width 50 nm (obtained from the TEM measurements) and calculate the ratio of the copper to the surfactant, it is observed that the experimental value obtained is of the same order of magnitude (10^2) as that obtained theoretically, by assuming the density of copper as 8.9 g/cm^3. This lends further support to the concept of monolayer formation on the surface of the elongated copper nanoparticles.

4. Conclusions

A sonochemical approach to the preparation of elongated copper nanoparticles coated with the zwitterionic surfactant CTAPTS is reported. A shape transition of the copper nanoparticles occurs due to the presence of an organized medium. Using interconnected cylinders as a template, elongated copper nanoparticles are produced. The formation of an interconnected network of rodlike micelles favors the uniaxial growth of the copper nanoparticles within the assembly, leading to the formation of elongated nanoneedles of copper. Spectral and electron microscopic evidence points to the adsorption of the CTAPTS on the surface of the elongated copper nanoparticles. These studies are related to the emerging area of biomineralization. They offer a unique way to tailor the shape, size, and magnetization of metallic nanoparticles using a rich array of liquid crystalline and amphiphilic self-assembled systems.

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Surfactant-Coated Copper Nanoparticles

J. Phys. Chem. B, Vol. 104, No. 5, 2000 **897**

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