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Size, composition and optical properties of copper nanoparticles prepared by laser ablation in liquids

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ABSTRACT Colloidal copper nanoparticles were prepared by pulsed Nd:YAG laser ablation in water and acetone. Size and optical properties of the nanoparticles were characterized by transmission electron microscopy and UV–visible spectrophotometry, respectively. The copper particles were rather spherical and their mean diameter in water was 30 nm, whereas in acetone much smaller particles were produced with an average diameter of 3 nm. Optical extinction immediately after the ablation showed surface plasmon resonance peaks at 626 and 575 nm for the colloidal copper in water and acetone, respectively. Time evaluation showed a blue shift of the optical extinction maximum, which is related to the change of the particle size distribution. Copper nanoparticles in acetone are yellowish and stable even after 10 months. In water, the color of the blue-green solution was changed to brown-black and the nanoparticles precipitated completely after two weeks, which is assigned to oxidation of copper nanoparticles into copper oxide (II) as was confirmed by the electron diffraction pattern and optical absorption measurements. We conclude that the ablation of bulk copper in water and acetone is a physical and flexible method for synthesis of stable colloidal copper and oxidized copper nanoparticles.

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1 Introduction

Synthesis and optical properties of metal nanoparticles are of primary importance due to unique properties which are different from those of bulk metals. In recent years, copper nanoparticles have attracted great interest due to their potential applications in conductive films, lubrication, nanofluids and catalysis [1–4]. Besides bulk materials, nanoparticles are efficient for catalysis applications because of their large surface to volume ratio. In addition, copper nanoparticles embedded in a dielectric medium such as polymer matrices are useful materials for nonlinear optical devices [5–7].

It is known that the method of synthesis has great influence on size and shape of nanoparticles; hence, many techniques

such as microemulsion, reverse micelles and reduction of copper salts have been developed to prepare copper nanoparticles [3, 8]. Pulsed laser ablation was extensively used for many applications in the synthesis of nanostructured materials, among which nanoparticle formation, alloying, dissociation, fragmentation and size control of the particles are important [9–13].

Recently, pulsed laser ablation was employed for preparation of several metals and semiconductor materials in different media such as vacuum, reactive gas and liquid. Despite the complex mechanism of laser–matter interactions, ablation in liquid provides a simple, flexible and less expensive way for particle formation. In this method both direct ablation of a bulk target and splitting of microparticles or suspended powders under laser exposure are employed [13]. So far, some materials such as gold, silver, palladium, metal oxide and magnetic nanoparticles were synthesized in a liquid carrier medium [9–17].

One of the advantages of the laser ablation in comparison with other conventional techniques is the synthesis of nanoparticles in arbitrary liquids. Preparation of nanoparticles in organic liquids is worthwhile for nanocomposite fabrication and/or embedding in the polymeric matrix.

Physical properties of the ablation liquid environment are important in final properties of the products. Utilizing different liquids, for instance reactive materials, as ablation environment empowers the production of the oxides or capped nanostructured materials. Oxidation of the nanoparticles is an effective and simple method for fabrication of the oxide nanostructure and/or metal core oxide shell materials. It should be mentioned that direct capping of the nanoparticles by adding a surfactant to the liquid carrier medium is a conventional way to increase the stability of the nanoparticles and avoid the agglomeration and sedimentation [18, 19]. It is also vitally important for production of core shell or functionalized nanostructured materials.

The focus of this work is on preparation and characterization of the colloidal copper nanoparticles in liquid by the pulsed laser ablation of a bulk copper target. We focus on size, shape, composition and stability of the colloidal copper nanoparticles. Both organic and inorganic liquids, i.e. acetone and water, were used for the ablation environment. Water is a base medium for many chemical reactions and nanopar-

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ticle formation in acetone is helpful for mixing with other organic polymer solvents to fabricate nanocomposite materials. Additionally, stability studies are performed using optical transmission of the liquids. This work provides a simple and flexible method for the synthesis of stable colloidal copper and oxidized copper nanoparticles in organic and aqueous media, respectively.

2 Experimental

Colloidal copper nanoparticles were prepared by pulsed laser ablation of a bulk copper target. The target with 10-mm thickness and purity of 99.9 was rinsed first with ethanol and then several times with deionized water in an ultrasonic cleaner. The cleaned target was placed on the bottom of a glass vessel filled with 40 cc of the liquid. In this study pure acetone and water were used as the liquid environment for laser ablation. The target was kept at 10 mm under the surface of the liquids. To make the ablation uniform and to avoid the texturing effect, the target was rotated during the laser ablation. A pulsed Nd:YAG laser with the fundamental wavelength at 1064 nm, energy of 130 mJ/pulse and pulse length of 10 ns was used for the target ablation. The laser was operated at a repetition rate of 10 Hz and for 5 min. A Gaussian laser beam was focused by a set of optical components and supplied at normal incidence to the surface of the target. After ablation the UV–visible extinction spectra of the colloidal copper solution were immediately measured by a Jasco-530 spectrophotometer. Morphology and size distribution of the particles were characterized by transmission electron microscopy (Philips 200 FEG). Normally, 1000 particles were counted for determination of the size distribution.

3 Results and discussion

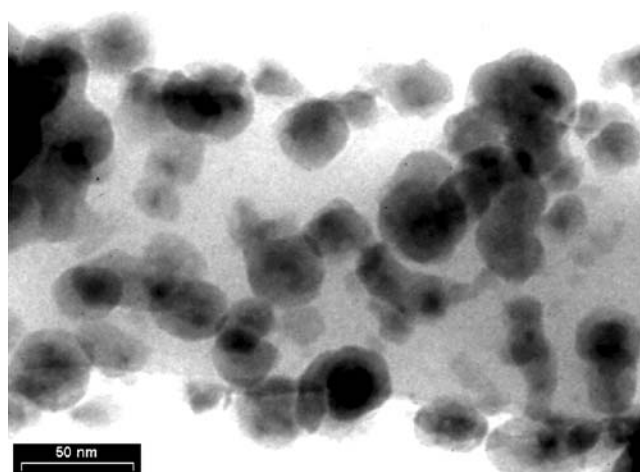
The shape and size distribution of colloidal particles in water and acetone were characterized by transmission electron microscopy (TEM) two weeks after preparation. The specimens for TEM experiments were prepared by depositing a drop of solution containing colloidal copper particles onto

carbon-coated copper grids and letting them dry completely at room temperature. In order to destroy the probable aggregation, prior to the preparation of the specimen, the colloidal solution was shaken ultrasonically for 30 min. It was observed that the particles are nanosized and rather spherical in both media; hence, this means that the aspect ratio is close to 1.

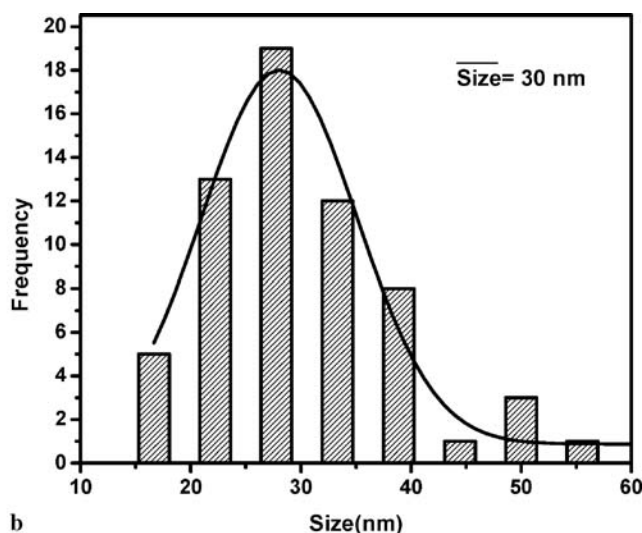
Figure 1a illustrates a typical bright-field TEM image of colloidal copper particles which were synthesized in deionized water. The histogram of the size distribution is shown in Fig. 1b. It imparts that the size of the particles is between 15 and 55 nm. The size distribution is fitted with a Gaussian curve. It was found that the average diameter of a copper nanoparticle is 30 nm with a standard deviation of 14 nm. As is seen from Fig. 1a, the image of some particles can be divided into two areas with different contrast and we believe that it is related to the core shell structure of the particles. This is very similar to the reported image for the Ni/NiO core shell structure [14]. In addition, the thickness of the shell depends on the size of the particle. The core shell structure is due to oxidation of colloidal copper in water and this is confirmed by the selected area electron diffraction pattern and optical absorption measurement that are discussed below.

A typical TEM image of colloidal copper in acetone is shown in Fig. 2a. All particles appear in the same contrast. In comparison with the copper nanoparticles in water (Fig. 1), the diameter of the particles is very small and no aggregation has occurred. The histogram of the size distribution is shown in Fig. 2b. It is observed that the size distribution is narrow with the size ranging from 1 to 7 nm. A Gaussian fitting is applied to the size distribution and the mean size of the particles is 3 nm with a standard deviation of 1.3 nm.

A model that was developed before is used to explain the size reduction mechanisms [12, 20]. At first, a pulsed laser beam ablates the target. Ablated materials expand under liquid environments and disperse many of the produced species. Dispersed materials include nanoparticles, small clusters, free atoms and ions. For the first few pulses liquid phase surrounds the ablated plume and some nanoparticles are formed through fast condensation of molten globules, colli-



a



b

FIGURE 1 (a) Typical TEM image and (b) size distribution of colloidal copper nanoparticles prepared in water

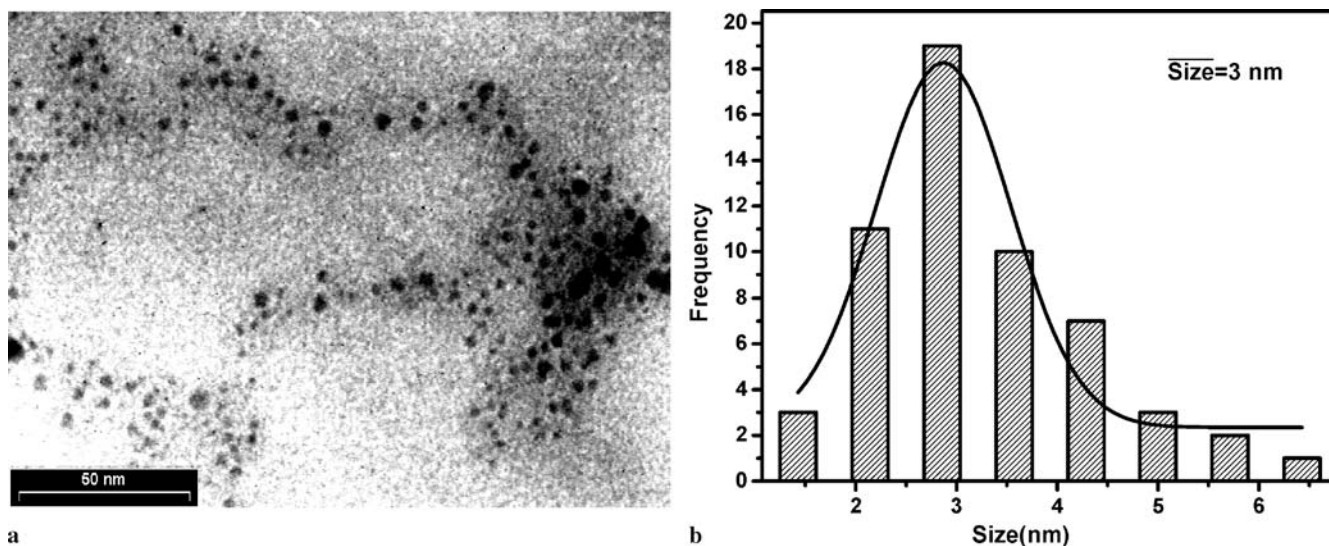


FIGURE 2 (a) Typical TEM image and (b) size distribution of colloidal copper nanoparticles prepared in acetone

sions of plume species with each other or nucleation of small clusters from free atoms [12, 20].

It is known that, in liquids, the nanoparticles are surface charged. Due to interaction of liquid-environment molecules and surface-charged nanoparticles an electrical double layer surrounds the surface of the nanoparticles [12, 20]. After creation and dispersion of nanoparticles, plume–nanoparticle interaction also takes place. This has an important role in the growth mechanism; therefore, in this stage two mechanisms contribute to the nucleation process [12, 20]. The first mechanism is direct nucleation of copper in the condensed plume similar to the first stage. The other mechanism is that the nanoparticles provide growing centers for the next incoming species. Hence, when both mechanisms occur, a broad size distribution is observed. The plume–nanoparticle interaction depends on all attractive and repulsive forces between plume species and nanoparticles such as attractive van der Waals forces that cause growth and/or aggregation and repulsive electrostatic forces due to the overlapping of electrical double layers. The growth rate of the nanoparticles depends on the number of nanoparticles which are formed in the first stage and the molecular dipole mo-

ment of the liquid environment [20]. Molecules with high dipole moment cause more packed and stronger bonds to the surface of the particles; therefore, the electrostatic repulsive force due to overlapping of the electrical double layer of the nuclei and species in the plume prevents further growth [20].

As was clearly seen before, with an increase in the dipole moment of the surrounding molecules the size of the nanoparticles is decreased [12, 20]. Since the molecule of acetone has high dipole moment the growth mechanism through the adding of extra species during ablation showed more effect on the size distribution and restricted the growth mechanisms during ablation. Hence, in acetone, narrow small-size copper nanoparticles were observed.

Figure 3a and b show the selected area electron diffraction patterns of nanoparticles which were prepared in deionized water and acetone, respectively. The pattern of the first consists of four resolved concentric rings. The ring shape of the diffraction pattern exhibits a semicrystal structure. For the case of colloidal copper in deionized water the measured lattice constant agrees with those of CuO(002,11 $\bar{1}$), (200,111), (20 $\bar{2}$) and (020) planes. Figure 3b demonstrates three concen-

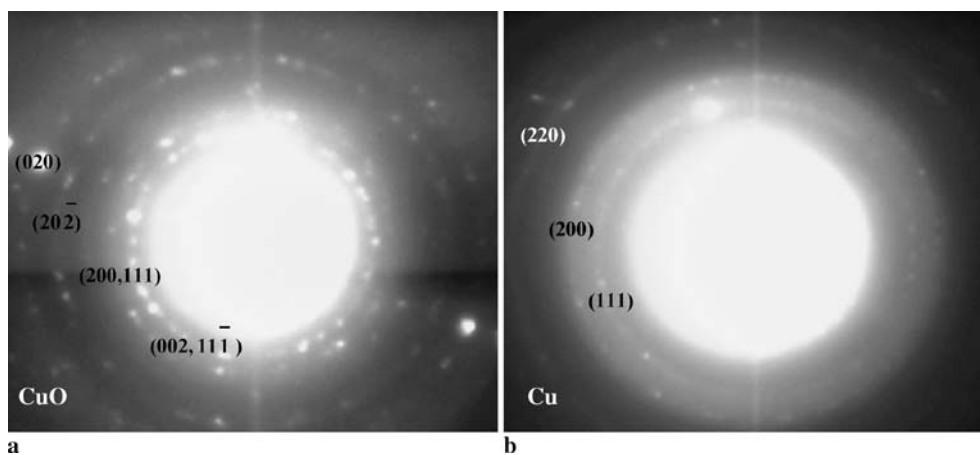


FIGURE 3 Electron diffraction pattern of colloidal nanoparticles synthesized (a) in water and (b) in acetone

tric electron diffraction rings that could be indexed as (111), (200) and (220) planes of copper nanoparticles.

The colloidal nanoparticles in deionized water immediately after preparation had a light green-blue color. After 2 weeks the color of the colloidal particles has been changed to brown-black and complete precipitation had taken place, whereas in acetone the sample was light yellowish and stable even after 10 months. This is another sign for oxidation of Cu in water.

Optical properties of nanoparticles were studied by optical extinction measurements of colloidal copper as a function of time. According to the Mie theory of light absorption and scattering by small particles, a single peak of extinction is expected due to the spherical shape of the particles [21].

If we assume that only the dipole oscillation contributes to surface plasmon absorption, the extinction coefficient of copper nanoparticles in liquid is given by the following relation [21]:

$$\kappa_{\text{ext}} = \frac{24\pi^2 N a^3}{\lambda} \varepsilon_m^{3/2} \frac{\varepsilon_2(\lambda, a)}{[\varepsilon_1(\lambda, a) + 2\varepsilon_m]^2 + \varepsilon_2(\lambda, a)^2}, \quad (1)$$

where λ is the wavelength of the incident light, N is the number of particles, ε_m is the dielectric function of the medium and $\varepsilon(\lambda, a) = \varepsilon_1(\lambda, a) + i\varepsilon_2(\lambda, a)$ is the complex dielectric function of copper. We suppose that ε_m is frequency independent for liquids. However, the complex dielectric function of copper is a function of the exciting light wavelength. In this case if ε_2 is assumed to be weakly dependent on wavelength then the resonance condition will be satisfied when $\varepsilon_1 = -2\varepsilon_m$. As is seen from the above relation, the position of the extinction maximum is related to several factors, among which the size, dielectric constant of the medium and nature of the dispersed materials are the most important [21]. In addition, the extinction coefficient is also related to the number of particles in the medium. So, variation in the number of particles only affected the extinction intensity whereas change in the size distribution also shifted the peak position.

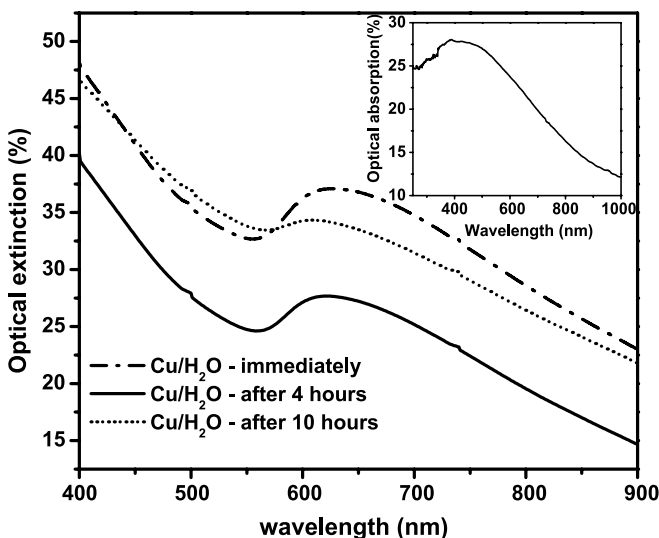


FIGURE 4 Optical extinction spectra of colloidal copper nanoparticles synthesized in water at different times; the *inset* is the optical absorption of the colloidal solution after 2 weeks

Optical extinction spectra of copper nanoparticles in water are shown in Fig. 4. The spectra were measured immediately after ablation, 4 h and 10 h from sample preparation. As is clearly seen, the maximum of the optical extinction appeared at the wavelength around 600 nm, which is related to the surface plasmon resonance of copper nanoparticles in water. During the measurement period a blue shift of the maximum extinction was observed from 626 to 622 nm (after 4 h) and finally to 609 nm. The spectrum after 4 h of preparation, the solid line, shows that the extinction decreases in the entire range of wavelengths, which is assigned to the precipitation of the particles. So, we believe that the small blue shift of the maximum of the optical extinction and the reduction in the intensity are the result of the precipitation of the larger particles. In fact, particle–particle interaction through the Brownian motion causes particles to collide with each other and partial precipitation takes place. After 10 h the optical extinction of the stirred sample shows a slight difference from that measured immediately after preparation. In addition, the optical extinction has a slightly higher intensity at 450 to 570 nm and is less in the remaining range of the spectra compared with the fresh sample. The maximum appeared at 609 nm, which means a reduction in the average of the size distribution and partial oxidation. To explain this observation we should consider two effects. As mentioned before, during ablation and plasma formation many species including electrons, ions, free atoms, small clusters and particles which are called the plume are expanded in the liquid. Very small particles such as atoms and clusters provide nucleation centers and/or impact with the existing particles and result in growth and change in the size distribution. Precipitating of the larger particles may also change the size distribution to a smaller average size. The other effect is the oxidation of colloidal copper due to the reaction with dissolved oxygen in water. The partial oxidation also causes the blue shift because the absorption of the copper oxide increases at the short wavelengths, as clearly seen from the inset of Fig. 4.

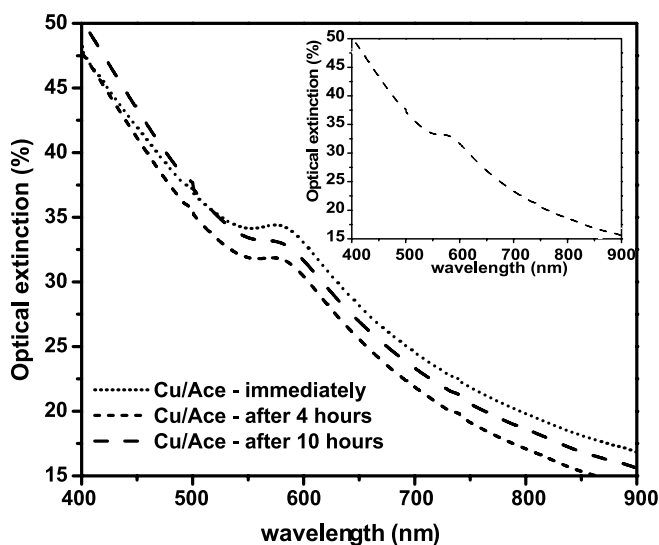


FIGURE 5 Optical extinction spectra of colloidal copper nanoparticles synthesized in acetone at different times; the *inset* is the optical extinction of the colloidal solution after 2 weeks

Figure 5 shows the optical extinction spectra of copper nanoparticles in acetone. For the as-prepared sample in acetone, the maximum of the optical extinction appeared at 575 nm. It also exhibits a blue shift, i.e. at 4 and 10 h after preparation the peak of the optical extinction appeared at 571 and 566 nm, respectively. Since the refractive indices of water and acetone are close to each other and the particles are rather spherical, the optical extinction intensity and the blue shift are affected dominantly by the size distribution.

To study the stability in size and composition, the optical extinction of colloidal copper in water and acetone was measured two weeks after preparation. The optical extinction of copper nanoparticles in acetone as presented in the inset of Fig. 5 shows no change in comparison with that measured after 10 h. This condition was stable even after 10 months. But, optical absorption of copper nanoparticles in water two weeks after preparation showed no surface plasmon resonance peak around 600 nm as is shown in the inset of Fig. 4 due to oxidation to copper oxide (II) nanoparticles. Similar optical absorptions of copper oxide (II) nanoparticles have been reported before [22, 23]. This result is confirmed by the selected area electron diffraction pattern, which is shown in Fig. 3.

In summary, these results demonstrate a method for fabrication of colloidal copper nanoparticles with an average size from 3 to 30 nm. The data show that acetone could be suggested as a good capping agent for copper nanoparticles. It is also helpful to use as the ablation environment for various applications. The pulsed laser ablation of copper in water results in oxidized nanoparticles.

4 Conclusion

In the present work colloidal copper nanoparticles were synthesized successfully by pulsed Nd: YAG laser ablation of copper targets in water and acetone. In addition, stability of the colloidal particles and time evolution of the optical absorption were also investigated. Transmission electron microscopy was employed for characterization of the size and shape of the particles. In both media the particles are rather spherical, and it has been found that the average diameters of the copper nanoparticles are 30 and 3 nm in water and acetone, respectively. Colloidal copper in acetone is generally stable even after 10 months. In water it was precipitated completely after two weeks and colloidal copper changes to oxidized particles. Oxidation of copper takes place due to the

reaction of dissolved oxygen in water with the colloidal particles. Production of the oxide particles was confirmed by selected area electron diffraction and optical absorption spectroscopy. This study also demonstrates a way to control the size and composition of copper nanoparticles by changing the ablation medium.

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