

Laser ablation induced agglomeration of Cu nanoparticles in sodium dodecyl sulfate aqueous solution

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Copper (Cu) particles have been fabricated by pulsed excimer laser ablation of a Cu target in a sodium dodecyl sulfate (SDS) aqueous solution. The particles are agglomerated from Cu nanocrystals. Some of the particles are hollow. Comparison to Cu particles produced in water by the same procedure shows that both the SDS and laser-nanocrystal interaction play important roles in the agglomeration process.

(Received June 24, 2009; accepted December 14, 2009)

Keywords: Laser ablation, Agglomeration, Nanoparticles

1. Introduction

Fabrication of metal nanoparticles by laser ablation of solid targets in liquid has attracted much attention during the last decade because of the potential to make small, monodispersed nanoparticles of complex compositions [1-6]. Also, the simple experimental set-up and one-step fabrication process make laser ablation in liquid an alternative to traditional wet-chemical methods, e.g., colloidal methods and hydrothermal methods. The shape and size of the nanoparticles can be modified by varying the laser output wavelength, fluence and/or pulse duration as well as the liquid environment. Generally surfactants added in the liquid in the laser ablation process will reduce the size of nanoparticles [3]. Sodium dodecyl sulfate (SDS) is a widely used anionic surfactant both in wet chemical methods and in laser ablation in liquid experiments [3,7]. The SDS forms micelles when the concentration achieves the so-called critical micelle concentration (about 8.6×10^{-3} M)[8]. This can be used to stabilize the nanoparticles as in the case of gold nanoparticles formed by laser ablation in SDS aqueous solution [3] or of Cu nanoparticles made by chemical reaction in an SDS aqueous solution [7]. In the present work, we found that pulsed excimer laser ablation induced agglomeration of Cu nanoparticles in SDS aqueous solution. Unique microstructures including hollow particles were found in the products.

2. Experimental

A Cu target (Lesker, 2.0" diameter, 99.99%) was immersed in a 0.05 M SDS aqueous solution on the

bottom of a rotating glass holder. The height of liquid was 5 mm. The laser ablation was carried out with a Lumonics KrF excimer laser at 248 nm wavelength and pulse width of 30 ns. The laser operated at 20 Hz and the pulse energy was 70 mJ with 1 mm spot size. Particles were centrifuged and collected after 20 min of ablation time. A comparison sample was made in distilled water (without SDS) by the same procedure.

The morphologies of the products were characterized with a JEOL JSM 6330F field emission scanning electron microscope (FE-SEM) and a Philip CM12 transmission electron microscope (TEM).

3. Results and discussion

Fig. 1(a) shows the SEM images of the Cu particles obtained in SDS aqueous solution. The diameters of the particles were from about 100 nanometers to several micrometers. It can be observed that microparticles generally have different surface morphologies with nanoparticles. Closer examination reveals that the microparticles are agglomerated from many Cu nanocrystals as shown in Fig. 1(b). These nanocrystals are generally polyhedrons; moreover, the nanocrystals combine and pack together to form microparticles. Nanocrystals are seldom seen on the surface of smaller Cu particles. This could result from the laser surface heating and grain growth. Melting point of a particle will decrease with its size, thus smaller Cu particles may be more likely melted by laser heating.

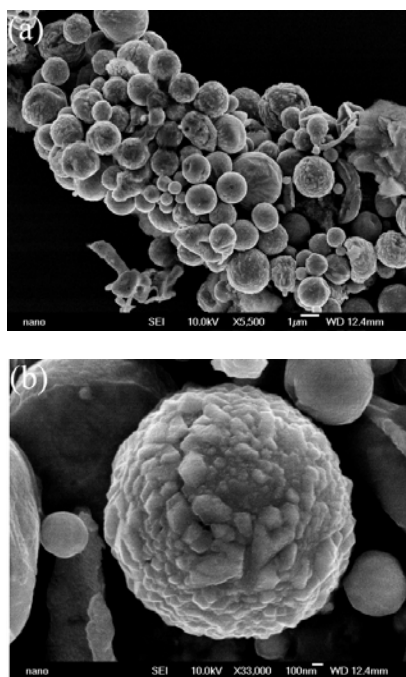


Fig. 1. SEM images of the Cu particles made in SDS aqueous solution. (a) a general view, (b) a typical Cu particle agglomerated from many nanocrystals.

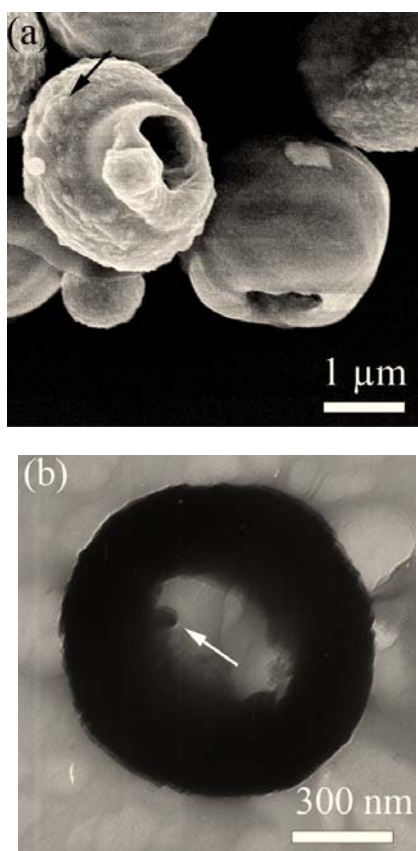


Fig. 2. (a) SEM image of hollow Cu particles, and (b) TEM image of a hollow Cu particle obtained through laser ablation in SDS aqueous solution.

Hollow particle agglomerates were found in the laser-produced products. Figure 2(a) shows two microparticles with large holes on the surface, the nanocrystals on the surface of the left one can be still identified as pointed by the black arrow, but those on the right have fused together. Figure 2(b) shows the TEM image of a typical hollow particle. The edges of the nanoparticles were identified on the surface, and a nanoparticle is on the inside wall as indicated by the white arrow. The hollow particles are formed due to laser produced bubbles in the liquid, which has been demonstrated in our another paper [9].

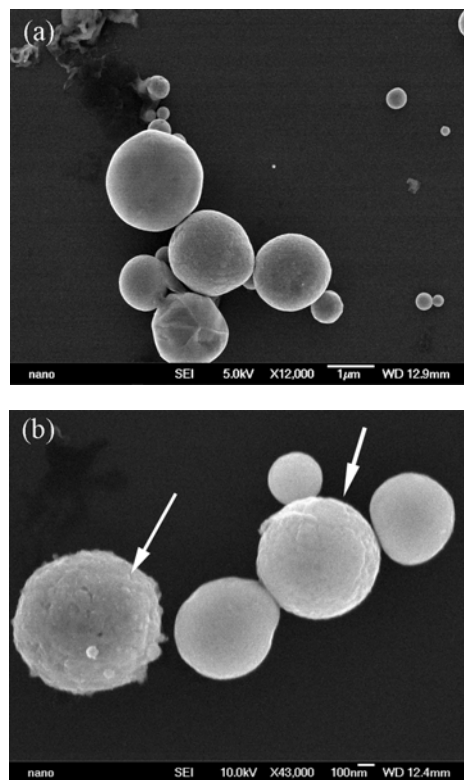


Fig. 3. SEM images of Cu particles obtained through laser ablation in water. (a) most particles have smooth surface, (b) some of the particles are aggregated from very small nanoparticles as indicated by the arrows.

To understand the origin of the agglomeration, Cu nanoparticles were also produced in pure water. As shown in Fig. 3, some of the particles are aggregated by very small nanoparticles as indicated by the arrow, but not as distinct as the agglomeration phenomenon in SDS aqueous solution. Previous reports on laser ablation of Cu in water have shown that dispersed nanoparticles were produced [9,10]. Thus the SDS is critical to the agglomeration. However, SDS was previously shown to promote monodispersion of nanoparticles. Cu nanoparticles produced in SDS aqueous solution by chemical reaction were monodispersed and did not show agglomeration behavior [7]. Therefore, the laser-nanocrystal interaction should play an important subsequent role in the

agglomeration process. The specific factors contributing to the agglomeration mechanism needs further investigation.

4. Conclusions

Cu microparticles aggregated from nanoparticles have been obtained through pulsed laser ablation in an aqueous solution of SDS. Hollow Cu particles were also observed in the products. Electron microscopy analysis shows that both the SDS and laser-nanocrystal interaction play important roles in the agglomeration process. The mechanism of the laser ablation induced agglomeration is under investigation with other materials, laser conditions, and dispersants.

References

- [1] F. Mafune, J. Y. Kohno, Y. Takeda, T. Kondow, H. Sawabe, *J. Phys. Chem. B* **104**, 9111 (2000).
- [2] S. Zhu, Y. F. Lu, M. H. Hong, *Appl. Phys. Lett.* **79**, 1396 (2001).
- [3] F. Mafune, J. Y. Kohno, Y. Takeda, T. Kondow, H. Sawabe, *J. Phys. Chem. B* **105**, 5114 (2001).
- [4] F. Mafune, J. Y. Kohno, Y. Takeda, and T. Kondow, *J. Phys. Chem. B* **107**, 4218 (2003).
- [5] P. Liu, Y. L. Cao, H. Cui, X. Y. Chen, G. W. Yang, *Cryst. Growth Des.* **8**, 559 (2008).
- [6] D. Werner, S. Hashimoto, T. Tomita, S. Matsuo, Y. Makita, *J. Phys. Chem. C* **112**, 1321 (2008).
- [7] X. Zhang, H. Yin, X. Cheng, H. Hu, Qi Yua, A. Wang, *Mater. Res. Bull.* **41**, 2041 (2006).
- [8] D. W. Fuertenau, *J. Colloid Interface Sci.* **256**, 79 (2002).
- [9] Z. J. Yan, R.Q. Bao, Y. Huang, A. N. Caruso, C. Z. Dinu, D. B. Chrisey, *J. Phys. Chem. C* DOI: 10.1021/jp911566a.
- [10] P. V. Kazakevich, V. V. Voronov, A. V. Simakin, G. A. Shafeev, *Quant. Electron.* **34**, 951 (2004).
- [11] P. V. Kazakevich, A.V. Simakin, V. V. Voronov, G. A. Shafeev, *Appl. Surf. Sci.* **252**, 4373 (2006).

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