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FABRICATION OF METAL NANOPARTICLES BY LASER ABLATION

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Abstract

We study producing metal nanoparticles by laser ablation using Nd:YAG laser (Quanta Ray Pro 230-USA) in Q-switch mode. The Ag, Au, Cu nanoparticles were prepared successfully by laser ablation from metal plate in several surfactant solutions. The average size, the size distribution and the plasmon resonance absorption spectrum of the metal nanoparticles were observed in different laser ablation procedures such as different laser intensities and different laser irradiation times. We also studied laser induced particle size control by plasmon resonance. Using the second harmonic wavelength (532nm) of Nd:YAG laser which is near the plasmon resonance absorption of gold nanoparticles (520nm) we can control average size of gold nanoparticles and produce gold nanoparticles with average size from 3 to 7nm. The experimental results are in good agreement with theory and showed advantages of the laser ablation method.

Keywords: laser ablation, plasmon resonance.

I. INTRODUCTION

In recent years, many techniques such as chemical reduction, electrochemical reduction, radiolytic reduction, laser ablation... have developed to prepare nanoparticles.

Among these techniques, laser ablation technique is found to be simple and most versatile for metal and semiconductor nanoparticles. Metal nanoparticles produced by laser ablation aren't contaminated by reductant. In this paper, we report our preparation of metal nanoparticles such as gold, silver and copper by laser ablation in different aqueous solutions. We studied the influence of surfactant concentrations, average laser powers and laser irradiation times on the average size and size distribution of prepared metal nanoparticles. The characterization of metal nanoparticles was observed. Gold nanoparticles were prepared in water and ethanol with different concentrations. Silver nanoparticles were prepared in SCD. Although several metal nanoparticles have been fabricated until now, Cu nanoparticles are difficult to produce since they oxidate or aggregate easily. However, we produced successfully Cu nanoparticles from a metal copper plate in isopropanol both in the presence and absence of PVP Polyvinyl pyrrolidone (C6H9NO)n (PVP, a stabilizer and a surface modification agent) by laser ablation.

II. EXPERIMENTS AND RESULTS

The schema of our laser ablation system is shown in Fig.1

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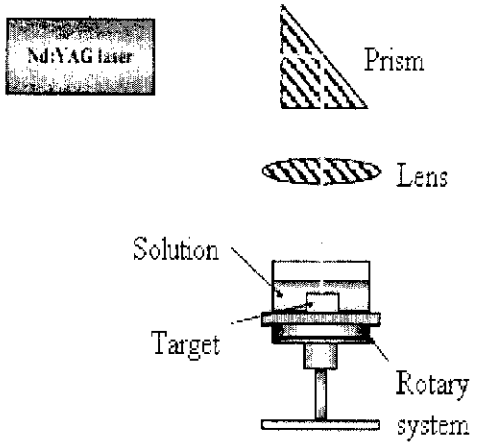


Fig.1: *Experimental arrangement*

A metal plate (99,9% in purity) is placed in a glass cuvette filed with 10ml aqueous solution of surfactant. Laser beam from the Quanta Ray Pro 230 Nd: YAG laser in Q-switch mode was focused on the metal plate by a lens having the focal length of 150mm. The laser was set to give laser pulse with duration of 8 ns and repetition rate of 10Hz. To make the ablation uniform and to avoid the texturing effect, the metal plate is rotated during the laser ablation.

II.1. Preparation of Copper nanoparticles by laser ablation.

Copper nanoparticles were produced by laser ablation of copper plate immersed in isopropanol both in the absence of PVP and in the presence of PVP with different concentrations. The Quanta Ray Pro 230 Nd: YAG laser is set to give fundamental wavelength (1064 nm) and pulse energy of about 80mJ. The solution becomes colored under action of the laser beam.

We first studied to prepare Cu nanoparticles in solution of isopropanol. Copper nanoparticles were prepared by laser ablation with different laser powers. The UV absorption spectra of the colloidal copper in isopropanol were shown in Fig.2.

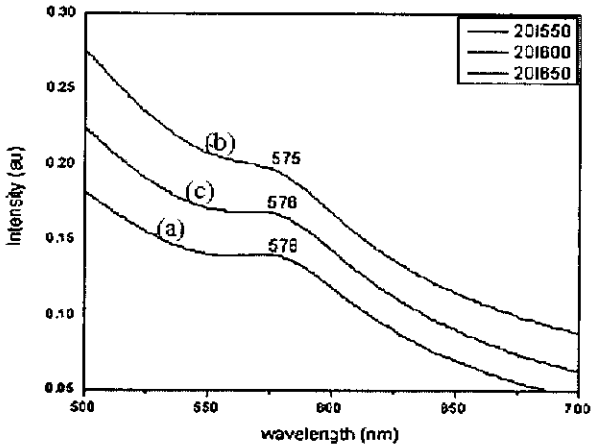
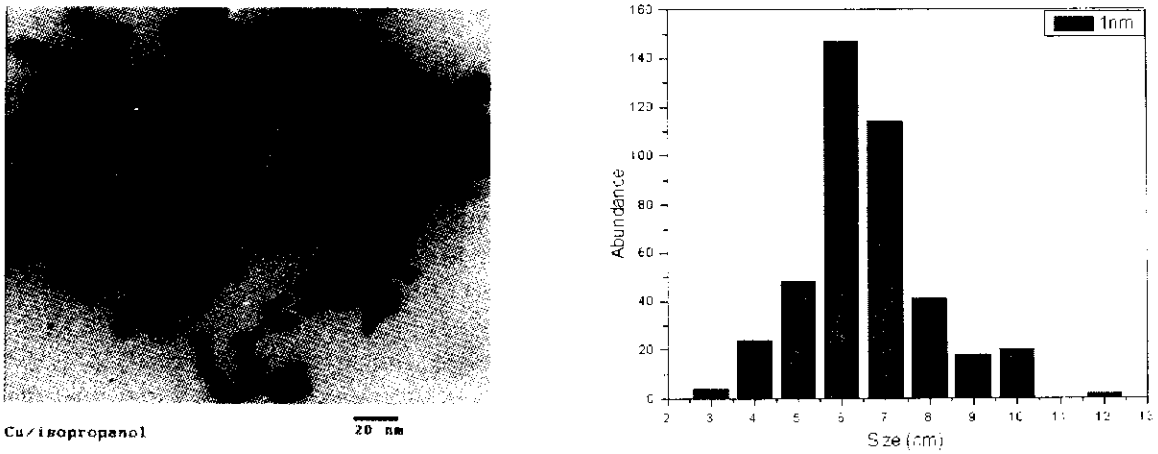


Fig.2. *Absorption spectra of copper nanoparticles in Isopropanol with the different average laser powers 550 mW(a), 600 mW(b) and 650 mW(c).*

The characteristic absorption peak around 576 nm appeared and the resonance peak position changed little with the average laser powers of ablation. According to Mie's theory the resonance peak of nanoparticles is red-shifted when their size increases [4]. The results showed that the laser power density of ablation influences not only the abundance but also the size of nanoparticles. There was no indication of the absorption around 800 nm, which is typical of copper oxide nanoparticles. [5]

The copper nanoparticles produced in isopropanol with the average laser power of 600mW was observed by a transmission electron microscope (JEM 1010-JEOL) (Fig.3).



(a) *(b)*

Fig.3. *The electron micrograph (a) and size distribution (b) of copper nanopracticles produced by laser ablation in isopropanol*

The TEM image and size distribution show that the average particle diameter of copper nanoparticles produced in isopropanol is about 6 nm. The samples prepared in isopropanol without PVP remained stable for more than a week.

In order to prepare protected cooper nanoparticles we used solution of PVP in isopropanol. Copper nanoparticles were prepared by laser ablation of the copper plate in PVP solutions of different concentrations.

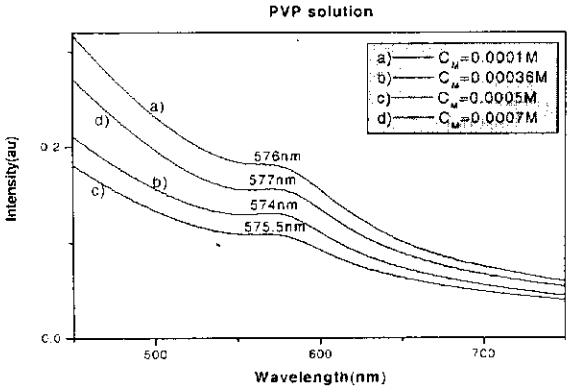
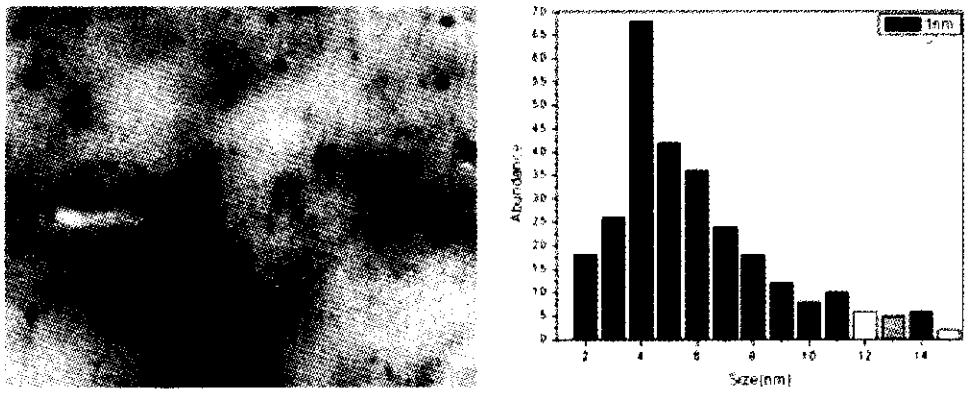


Fig.4. *Absorption spectra of copper nanoparticles in 0.0001M (a), 0.00036M (b), 0.0005M (c) and 0.0007M (d) solution of PVP.*

Figure 4 represents absorption spectra of copper nanoparticles produced in 0.0001M, 0.00036M, 0.0005M and 0.0007M solution of PVP. The intensity peak of absorption band depends on the PVP concentrations. The PVP concentration of 0.00036M gives the resonance peak of absorption band at 574nm (blue-shifted according to Mie's theory) corresponding to the smallest average size of Cu nanoparticles among the above PVP concentrations.

The TEM image of PVP protected copper nanoparticles produced in 0.00036M concentration of PVP is shown in Fig.5a. The data of measured size and size distribution of copper nanoparticles were analyzed and given in Fig.5b.



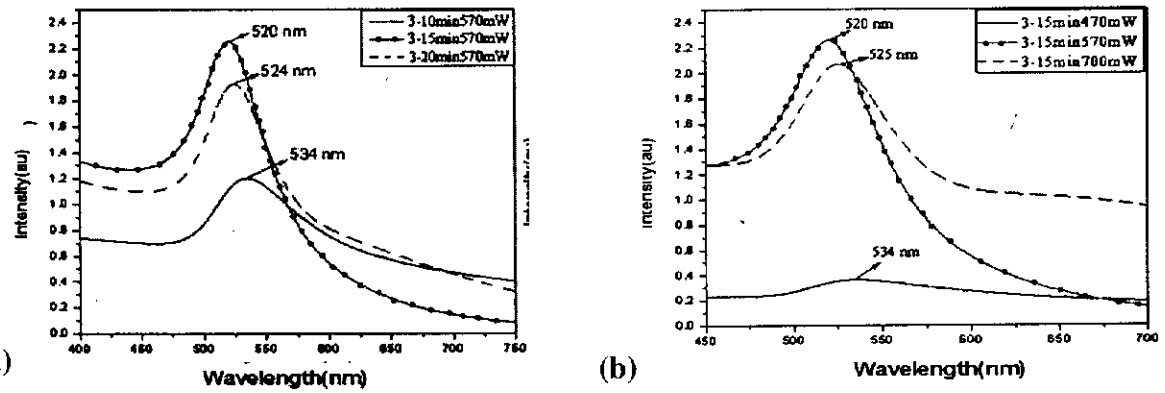
(a) (b)

Fig.5. *TEM image (a) and* size distribution (b) *of PVP protected copper nanoparticles produced in the 0.0036M solution of PVP*

The TEM micrograph and size distribution show that the average particle diameter of copper nanoparticles produced in the 0.00036M solution of PVP is 4 nm with formation rate of 29%. Particle diameter ranges from 2 nm to 15 nm . In the presence of Polyvinyl pyrrolidone (PVP)_(C6H9NO)n on the surface of nanoparticles, the oxygen atoms of C=O group are attached to the Cu atoms on the nanoparticle surface[6]. The PVP protected Cu nanoparticles remained stable more than a month.

The absorption spectra of the unprotected and PVP protected Cu nanoparticles in isopropanol solution exhibit a maximum peak at 578nm and 574nm respectively. This result agrees with the average nanoparticle diameter observed from TEM image, 6nm and 4nm respectively.

II.2. Preparation of gold nanoparticles by laser ablation



(a) (b)

Fig.6. *a) The absorption spectra of gold nanoparticle in water with different times (10 min,15min and 20min); b) The absorption spectra of gold nanoparticle in water with different average laser powers (470 mW, 570mW and 700mW).*

By the same method we successfully prepared gold nanoparticles in water and ethanol solution. The results showed that laser irradiation times of ablation and laser intensity influences clearly the nanopartilces size. Figure 6.a represents absorption spectra of gold nanoparticles produced in water with irradiation times of 10 min, 15 min and 20 min respectively, at the same average laser power of 570mW.

The spectra exhibit the characteristic peak of the surface plasmon band at around 520 nm. This result agrees well with the Mie theory for the surface plasmon peak of Au nanoparticles. When the time of ablation increase from 10 to 15 min, the absorption spectrum peak was blue-shifted (from 534nm to 520nm). According to Mie theory, average size of Au nanoparticles decreases respectively. The TEM image and size distribution show that the average particle diameter of gold nanoparticles produced in water is about 7 nm with average laser power of 570 mW and irradiation times of 15 minutes.

The figure 6.b represents absorption spectra of gold nanoparticles produced in water with average laser power of 470 mW, 570mW and 700 mW respectively, at the same irradiation times of 15 min. When average laser intensity increases from 470mW to 570 mW, absorption peak is blue-shifted from 534nm to 520 nm. However, when laser intensity increases from 570mW to 700mW the absorption peak is red-shifted from 520nm to 525nm. The reason may be the coagulation when the number of Au particles present in water increases with laser intensity.

We continue to produce gold nanoparticles in ethanol solution and investigate affects of ethanol concentration to gold nanoparticles size. When increasing concentrations of ethanol, the absorption peak of the Au nanoparticle sample was red-shifted. This means that the size increases when the concentration of alcohol increases from 0oC. Figure 7 presents the absorption spectrum of gold nanoparticles in ethanol solution with different concentrations at laser intensity of 500 mW and irradiation of 15 minutes.

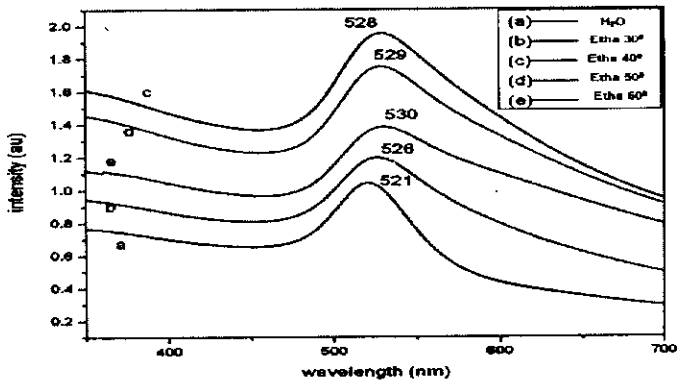


Fig. 7. *The absorption spectra of gold nanoparticles in water and different concentration of ethanol solutions.*

We also studied to use the second harmonic wavelength (532 nm) of laser Nd: YAG which is near the surface plasmon resonance absorption of gold nanoparticles (520 nm) to control the gold nanoparticles size. The results were illustrated in Fig.8.

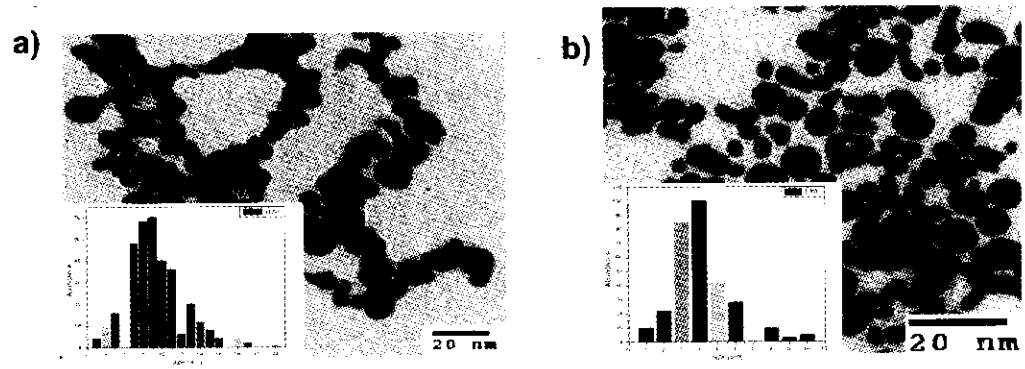


Fig.8. *The electron micrograph and size distribution of gold nanoparticle produced by laser ablation before(a) and after(b) illuminated 532nm wavelength in 60 ^{0} ethanol*

The average sizes of the nanoparticles obtained before the 532-nm laser irradiation is 9.0 nm (Fig 8.a). After the 532 - nm laser irradiation the average size of nanoparticles is 3.5 nm. Under irradiation of a 532-nm laser, gold nanoparticles with any diameters are fragmented into smaller nanoparticles and more dispersed in solution.

II.3. Preparation of silver nanoparticles by laser ablation

Silver nanoparticles were prepared by laser ablation of the silver plate in Trisodium citrate dihydrat C 6H7Na3O7 (SCD) solutions of different concentrations.

The absorption spectra of silver nanoparticles in 0.003M solution of SCD is shown in Fig.9.

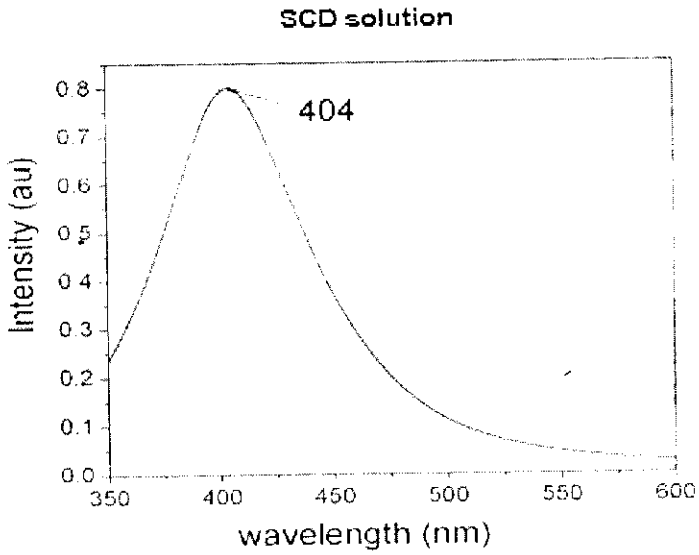


Fig.9. *Absorption spectrum of silver nanoparticles in solution of SCD*

The resonance peak of absorption band around 400 nm characterized for silver noparticles was observed . The TEM micrograph and size distribution of silver nanoparticles prepared by laser ablation in 0.003M concentration of SCD are shown in fig 10. TEM image shows that the average diameter of silver nanoparticle is 7-9nm.

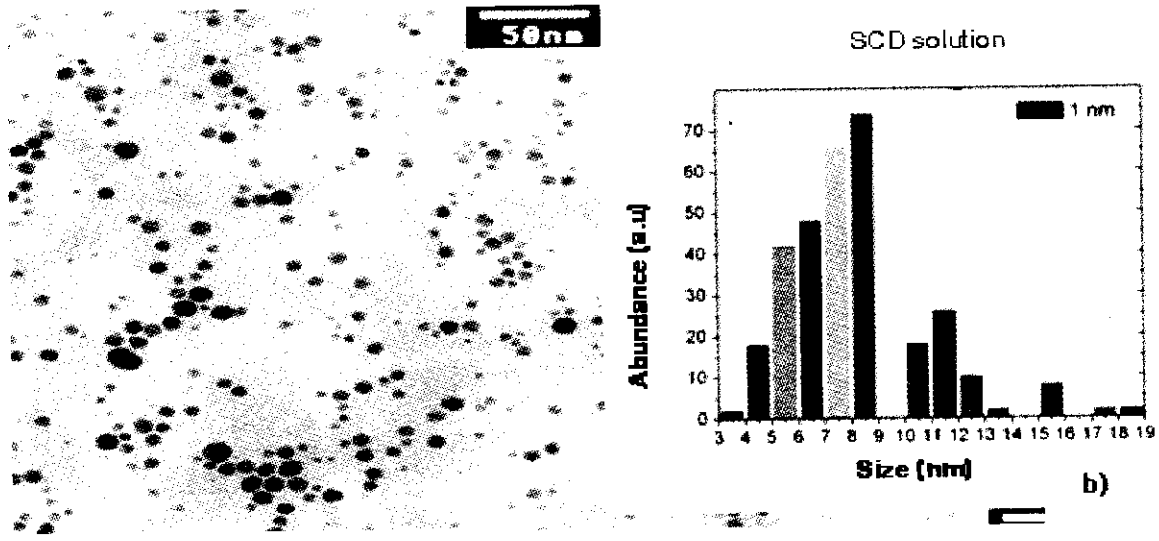


Fig.10. *TEM image (a) and size distribution (b) of silver nanopracticles produced by laser ablation in 0.003M solution of SCD*

III. CONCLUSION

Using the Quanta Ray Pro 230 Nd: YAG laser, we prepared successfully metal nanoparticles such as gold, silver and copper particles. Metal nanoparticles were prepared in different solutions with different concentrations, average laser powers and laser irradiation times to determine suitable metal nanoparticles preparation process. Laser ablation in combination with the laser-induced size control provides a versatile full physical preparation method of size-selected gold nanoparticles without contamination by a reducing agent, which is inevitably used in conventional wet-chemical techniques.

IV. ACKNOWLEDGMENT

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REFERENCES

[1] P.N. Prasad, D.J. Williams, *Introduction to Nonlinear Optical Effects in Moolecules and Polymers*, Wiley, New York, 1991.

[2] H.S Nalwa(Ed). Hanbook of Advanced Electronic and Photonic Materials and Devices, Vol .9, Academic Press, New York, 2001.

[3] R.M.Tilaki, Applied Physics A 88,415-419 (2007)

[4] M.Saito, K.Yasukawa, T Umeda, Y.Aoi Optical Materials 30 (2008) 1202-1204

[5] E.K Athanassiou, RN Grass and U J Stark, Nanotechnology 17 (2006) 1668-1673

[6] Daniel L. Feldheim, Colby A. Foss, Jr, ***Metal Nanoparticles***, The United States of America, 2002.

[7] Lisiecki, F. Billoudet, M.P. Pileni, J. Phys. Chem. 100 (1996) 4160.

[8] Manabendra Chandra, Puspendu K. Das, Chemical Physics Letters 422(2006) 262-266

[9] S. Franzen, Jacob C. W. Folmer, Wilhelm R. Glomm, and Ryan O'Neal, Journal of Physical Chemistry, A, 106, (28), 6533-6540, 2002.