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Silver nanoparticles prepared by laser ablation and their optical characteristics

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Abstract. Laser-induced thermal explosion of metallic nanoparticles originates from nonlinear optical effect. Nonlinear optical properties of nanoparticle materials depend strongly on their size and shape. Several methods were proposed to produce nanoparticles of a controlled size and well-defined distribution. We studied to prepare silver nanoparticles by laser ablation. The characteristic spectral feature of the silver nanoparticles (peak around 400nm) was found in the absorption spectra measured by a UV-Vis 2450 spectrometer. The size and shape distribution of silver nanoparticles was observed and analyzed by a transmission electron microscope (JEM 1010-JEOL). Two different surfactants were employed namely trisodium citrate dihydrat $C_6H_7Na_3O_7$ and polyvinyl alcohol $(-CH_2-CHOH-)_n$. The size distribution and the UV-Vis absorption spectra of silver nanoparticles depend clearly on the properties and concentration of the surfactant employed. The experimental results were in good agreement with theory and showed advantages of the laser ablation method.

Key words: Surface plasmon resonance, surfactant.

1. Introduction

In recent years, there has been a great interest in the preparation and application of the silver and gold nanoparticles. Under the short laser pulses irradiation in the spectral range of the surface plasmon resonance, metal nanoparticles such as silver or gold nanoparticles are excited to upper electronic states by multiphoton absorption. Through rapid relaxation to their ground state, the absorption photon energy can be conversed into thermal energy. Their temperature rises very quickly to reach thresholds for nonlinear effects such as optical plasma, micro bubble formation, acoustic and shock wave generation and particle fragmentation with fragments of high kinetic energy. The laser-induced explosion of absorbing nanoparticles contributes a potential role for selective damage to cancer cells, bacteria, viruses and DNA...[1] Several methods to prepare metallic nanoparticles suspended in liquid have been developed [2, 3]. The wet preparation methods range from synthesis by chemical reduction in solution, laser irradiation of metallic salt solution to laser ablation of metal plate. The most interest is to produce stable nanoparticles of a controlled size and well-defined distribution. The stability, the size distribution and the abundance of the nanoparticles depend critically on the properties and concentration of the surfactant employed.

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Using a Quanta Ray Pro 230 Nd: YAG laser in Q-switch mode we prepared silver nanoparticles from a metal silver plate in an aqueous solution of surfactant with different concentrations. The average size, the size distribution and the UV-Vis absorption spectra of silver nanoparticles were observed. The optimal concentration of surfactant solutions was determined.

2. Experiments and results

The experimental setup was shown in Fig.1. We placed a silver plate (99,9% in purity) in a glass cuvet filed with 10ml aqueous solution of surfactant. The second harmonic (532nm) of the Quanta Ray Pro 230 Nd: YAG laser in Q-switch mode was focused on the silver plate by a lens having the focal length of 150mm. The laser was set to give the pulse duration of 8 ns, the repetition rate of 10Hz and the pulse energy of 80mJ.

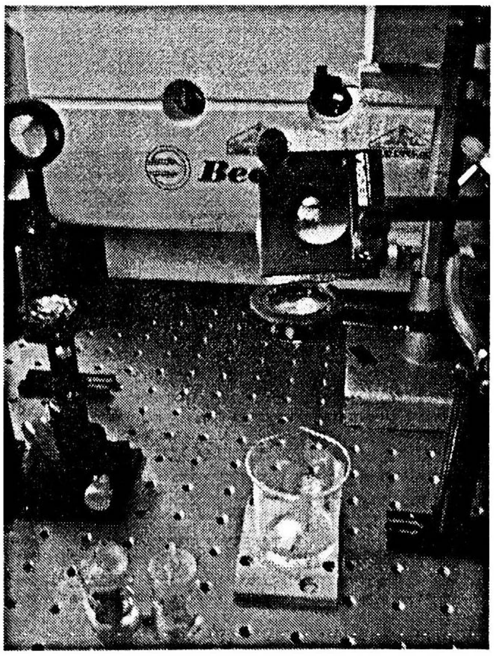


Fig. 1. Experimental setup.

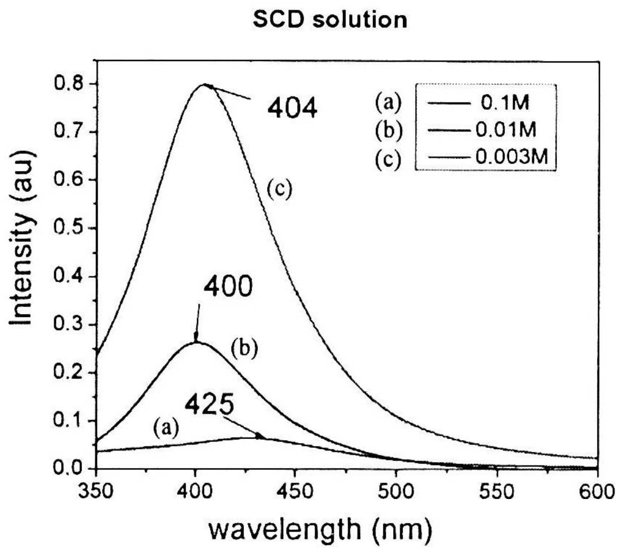


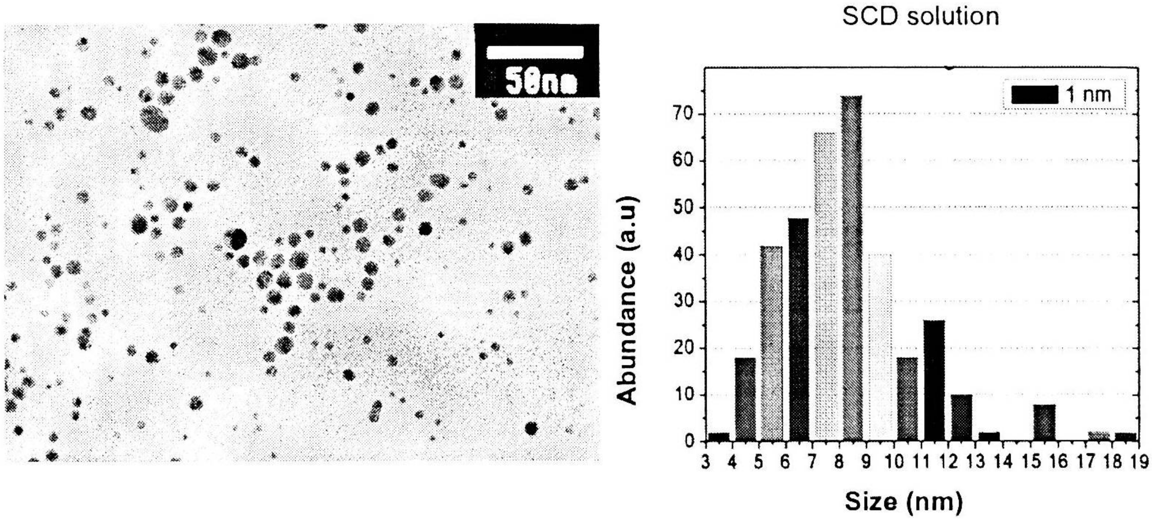
Fig. 2. Absorption spectra of silver nanoparticles in 0.1M (a), 01M(b) and 0.003M (c) solution of SCD.

First, we used trisodium citrate dihydrat $C_6H_7Na_3O_7$ (SCD) as surfactant. Silver nanoparticles were prepared by laser ablation of the silver plate in SCD solutions of different concentrations. Under action of the laser beam on the silver plate the solution of surfactant becomes colored. A small amount of the colored solution was extracted for absorption measurement and TEM observation. The absorption spectrum was measured by a Shimadzu UV-2450 spectrometer. The TEM micrograph was taken by a JEM 1010-JEOL. The size of the nanoparticles was determined by ImagieJ 1.37v software of Wayne Rasband (National institutes of Heath, USA) [4]. The size distribution was obtained by measuring the diameter of more than 500 particles and using Origin 7.5 software.

Figure 2 represents absorption spectra of silver nanoparticles produced in 0.1M, 0.01M and 0.003M solution of SCD. The characteristic absorption peak around 400 nm depends strongly on the SCD concentrations. The optimal SCD concentration is 0.003M.

The electron micrograph of silver nanoparticles obtained by a transmission electron microscope (TEM) was shown in Fig. 3. The spherical shape of the nanoparticles observed by TEM is consistent with the optical absorption peak around 400 nm which originates from surface-plasmon excitation.

We also prepared silver nanoparticles by chemical reduction from an aqueous solution of silver nitrate and trisodium citrate dihydrat $C_6H_7Na_3O_7$ (SCD) which takes the role of both surfactant and reducing agent.



(a) (b)

Fig. 3. The electron micrograph (a) and size distribution (b) of silver nanoparticles produced by laser ablation in 0.003M solution of SCD.

The UV-Vis absorption spectra were presented in Fig.4 for comparison. The absorption spectrum peak of silver particles produced by chemical reduction shifted to 440 nm as compared to 400 nm by laser ablation. The peak width of silver nanoparticles by laser ablation is narrower than that by chemical reduction. This result is in accordance with the measured average size and dispersity. The average size of silver nanoparticles is 8 nm with formation rate of 20% and particle diameter ranges from 4 nm to 12 nm of in case of laser ablation. Meanwhile, the average size is 26 nm with formation rate of 8% and the particle diameter ranges from 5 nm to 45 nm with formation rate changing little in case of chemical reduction .

Trisodium citrate dihydrat $C_6H_7Na_3O_7$ (SCD) is not only a surfactant but also a reducing agent. That may cause unexpectant chemical reactions. Then, we replaced SCD solution by polyvinyl alcohol $(-CH_2\text{-}CHOH\text{-})_n$ solution (PVA) which acts as surfactant only and repeated the experiments. The 532 nm laser beam was focused on a plate of silver in 0.003M, 0.01M and 0.1M PVA solution of 10 mL respectively. As shown in Fig.5, the surfactant PVA concentration which gives the optimal abundance of silver nanoparticles is 0.01M.

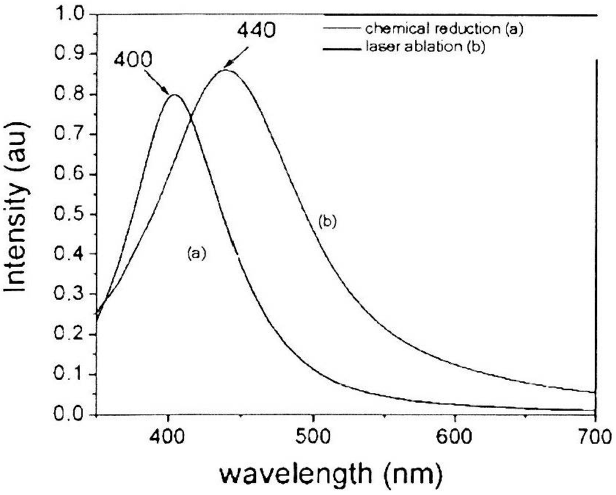


Fig. 4. Comparison of the UV-vis spectra of silver nanoparticles prepared by laser ablation (a) and by chemical reduction (b).

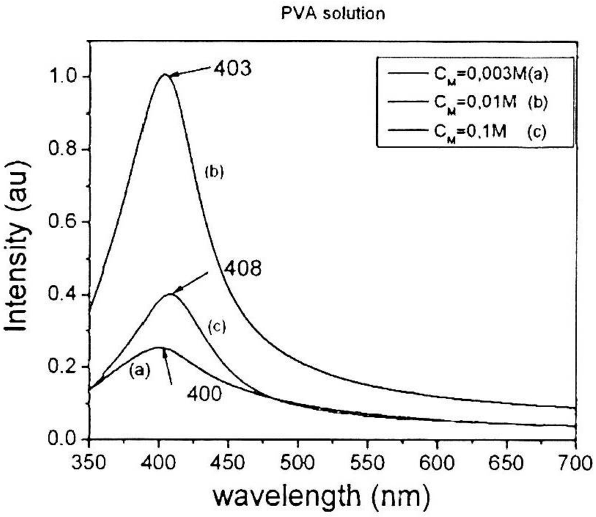


Fig. 5. Absorption spectra of silver nanoparticles produced by laser ablation in a 0.003, 0.01 and 0.1M solution of PVA.

The silver nanoparticles produced in 0.01M concentration of PVA was observed by a transmission electron microscope (JEM 1010-JEOL). The data of measured size and size distribution were analyzed and given in Fig.6. The average size of silver nanoparticles produced in the 0.01M solutions of PVA is 7 nm. The formation rate of silver particles of 6 nm diameter is about 17%. About 67% of silver particles have diameters ranging from 5 to 10 nm.

Meanwhile, silver nanoparticles produced in the solutions of SCD have diameters ranging from 4 to 12 nm with quite different formation rates and 20% of silver particles have diameter of 9 nm. Comparing the obtained UV-Vis absorption spectra (see Fig.7) we found that the peak width (full width at the haft maximum- FWHM) of silver nanoparticles produced in the solutions of SCD was narrower than the one of silver nanoparticles produced in the solutions of PVA.

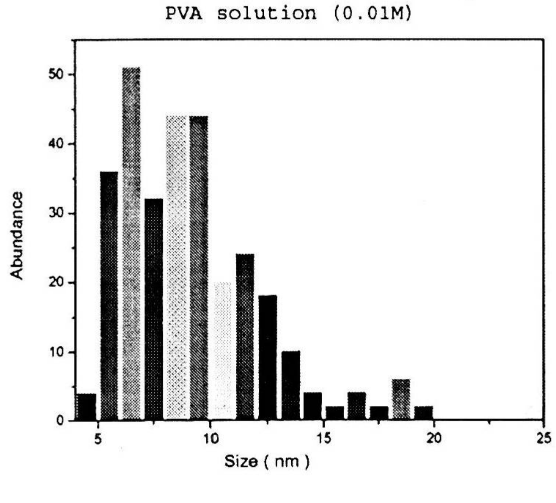


Fig. 6. The electron micrograph and size distribution of silver nanoparticles produced by laser ablation in 0.01M solution of PVA.

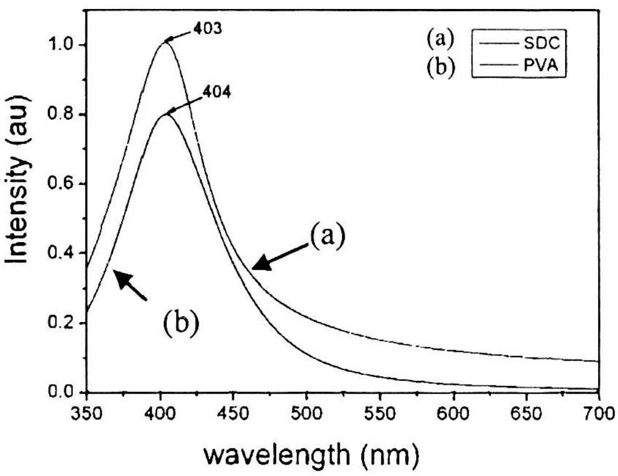


Fig. 7. Comparison of the UV-Vis absorption spectra of silver nanoparticles produced by laser ablation in a 0.003M solution of SCD (a) and in a 0.01M solution of PVA (b).

This result agrees well with the Mie theory for the surface plasmon peak of nanoparticles in UV-Vis absorption spectra. According to the Mie theory, silver nanoparticles of diameters ranging from 1 to 10 nm have the plasmon peak width increasing linearly with the reciprocal of the particle diameter [2,5]. The surface plasmon peak of a lager nanoparticle is more narrowed (intrinsic size effect) [6]. However, when the particle diameter increases further (> 20 nm) the peak width increases with the particle diameter (extrinsic size effect). The absorption spectra of silver particles which have the average diameter of 26 nm produced by chemical reduction were in accordance with the extrinsic size effect

3. Conclusion

We have prepared successfully silver nanoparticles by laser ablation of silver plate in solutions of trisodium citrate dihydrat $C_6H_7Na_3O_7$ (SCD) and polyvinyl alcohol (-CH_2-CHOH-)$_n$ (PVA) respectively. Our results shows that the optimal concentration of surfactant is 0.003M for SCD and 0.01M for PVA. The average size and size distribution of silver nanoparticles were measured. The average size of silver nanoparticles is 7 nm in the 0.01M solutions of PVA and 9 nm in the 0.003M solutions of SCD. In comparison to the results obtained by chemical reduction using silver nitrate and trisodium citrate dihydrat $C_6H_7Na_3O_7$ (SCD), the silver nanoparticles average size produced by laser ablation is smaller. The experimental results were in good agreement with Mie theory.

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