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Preparation and Size Characterization of Silver Nanoparticles Produced by Femtosecond Laser Ablation in Water *

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Femtosecond laser ablation of silver plate placed in water is used to produce nanoparticle suspension. The method is easy to operate and the suspension is relatively stable. The optical properties and the size distribution of the suspension are studied with UV–vis absorption spectroscopy and dynamic light scattering, respectively. The shape of the nanoparticles is investigated by an atomic force microscope, which is near spherical. There are two kinds of nanoparticles, small particles with diameter about 35 nm, and large particles with diameter about 120 nm.

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Noble metal nanoparticles have attracted much attention because of their unique size-dependent optical properties, magnetic properties, catalytic properties and etc.[1−3] The size-dependent properties of silver nanoparticles make them suitable for many applications in various areas such as catalytic, optical and antibacterial applications.[4,5] Nanoparticles of different sizes and shapes have been prepared by many kinds of technologies including chemical and physical technologies.[6,7] Compared with the chemical methods, physical methods are contamination-free. Silver nanoparticles are synthesized by using many methods such as chemical, sonochemical, radiolytic reduction.[8−10] Recently, pulsed laser ablation method has been adopted to generate nanoparticles.[11−14] Laser ablation in vacuum or in a background gas has been widely used for fabrication of various nanopowders in gas phase[12] and laser ablation in solution has become a promising method for the preparation of metal and metal alloy nanoparticles, and some network structures.[13,14] In comparison with chemical methods, laser ablation needs to add less surfactant for capping of colloidal particles, so that purer nanoparticles can be achieved. Furthermore, nanoparticles can be produced in many kinds of solutions, which may be used for nanoscale fabrication and the dispersion control of nanoparticles.[15−17] Nanosecond pulsed laser ablation has been widely studied, but there are few reports of femtosecond pulsed laser ablation. In this Letter, we employ a femtosecond laser to generate silver nanoparticles. Our results show that the femtosecond laser ablation can produce silver nanoparticles suspended in water. There are two kinds of silver nanoparticles, small nanoparticles with diameter about 35 nm and large nanoparticles with diameter about 120 nm. The amount of the small particles is much larger than the amount of the large particles.

Silver nanoparticles were prepared by pulsed laser ablation of a silver plate which was 0.5 mm thick with a purity of 99.99%. The plate was mechanical polished, and then it was washed by deionized water several times to remove impurity from the surface. The silver plate was placed on the bottom of a 25 ml beaker filled with 10 ml deionized water. The laser system was a femtosecond pulsed laser which consists of a femtosecond laser seed (Spectra-Physics, MaiTai, 700 mW, 800 nm, about 100 fs, 80 MHz) and a regeneration amplifier (Spectra-Physics, Spitfire). The output laser had a repetition at 1 kHz with pulse width of 120 fs and wavelength of 800 nm. The output power of the femtosecond laser was measured by a laser power meter (Spectra-Physics, 407A). During the procedure of laser ablation, the target was rotated manually to ensure uniform ablation and to avoid texturing effect. The Gaussian laser beam was focused by an optical convex lens whose focal length was 75 mm. The UV-Vis absorption spectra of silver colloid solution were immediately measured by a spectrophotometer (Ocean Optics, HR4000). The size distribution of silver nanoparticles was measured by dynamic light scattering (DLS, Brookhaven, BI-9000AT). The shape of silver nanoparticles was observed by an atomic force microscope (AFM, Digital Instruments, NanoScope

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After several minutes of ablation, the colour of the water turned into yellow. This phenomenon matched the case of the formation of silver nanoparticles by nanosecond laser ablation. Metal nanoparticle colloid shows different colours, for the absorption spectra of metal nanoparticles are size- and shape-dependent due to surface plasmon resonance.[18] The size and shape of nanoparticles can be qualitatively described by the peak position and shape of the absorption spectrum. For example, the peak position of gold nanoparticles absorption curve has a red-shift when the particles are larger. The spherical particles have a single-peak absorption spectrum, while the elliptical or cylindrical particles have a double-peak absorption spectrum. The optical absorption curve of mono-dispersed particles is narrow, while the optical absorption curve of wide size distribution is broad. It is expected that the absorption peak of silver nanoparticles locates around 400 nm.

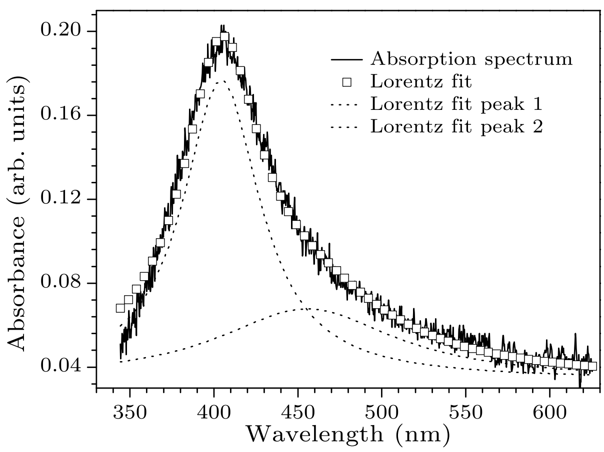

Fig. 1. Absorption spectrum of silver nanoparticles produced by 5min laser ablation (800 nm, 120 fs, 1 kHz, 20 μJ/pulse).

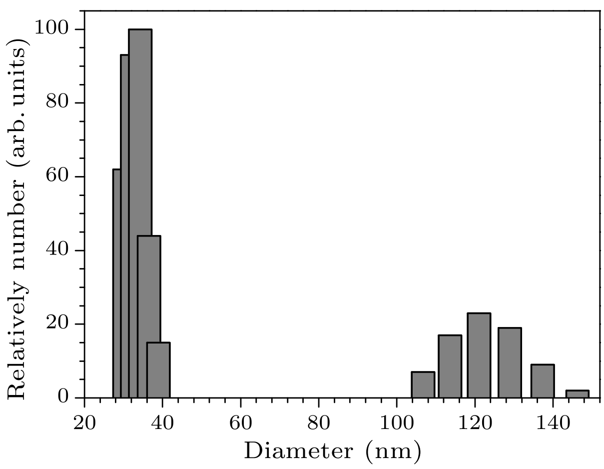

Fig. 2. Size distribution of the silver nanoparticles produced above by DLS.

Figure 1 shows the absorption spectrum of a silver nanoparticles sample that was produced by 5 min laser ablation at 20 μJ/pulse. The solid line is the absorption spectrum of the sample, which has the similar profile with the absorption of silver nanoparticles prepared by colloidal assemblies.[19] The peak position of the spectrum is determined by the diameter of the nanoparticles, and the intensity of the absorption is determined by the amount of the nanoparticles. The absorption at long wavelengths is due to the light scattering of light by big particles. The absorption peak is about 404 nm. The square scatter line is the two-peak Lorentz fit line of the spectrum. The two dotted lines are the two Lorentz fit lines. The two-peak fitted line conforms to the absorption spectrum very well, which implies that there are two kinds of silver nanoparticles in the colloid. The amount of small particles is larger than the amount of big particles.

The size distribution of silver nanoparticles was measured by dynamic light scattering. Figure 2 shows the size distribution of the same sample. This result shows that there are two kinds of particles whose diameters are about 35 nm and 120 nm. As shown in Fig. 2, the amount of small particles is rather larger than the amount of large particles, which is consistent with the result of the absorption spectrum.

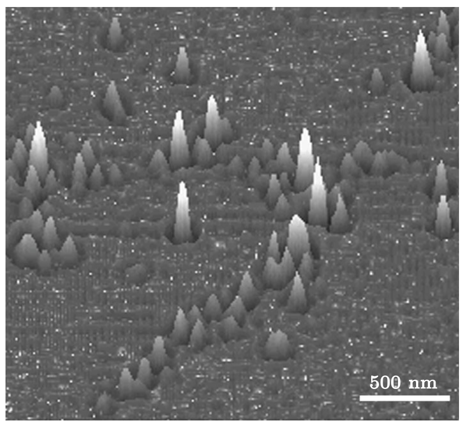

Fig. 3. AFM image of a typical silver nanoparticles sample.

The shape of silver nanoparticles was then characterized by the atomic force microscope (AFM). The specimens for AFM experiments were prepared by depositing a drop of solution containing silver nanoparticles onto mica flakes and letting them dry completely at room temperature. Figure 3 shows a typical AFM image, the particles were near spherical. The diameter of bright particles and dark particles are about 120 nm and 35 nm, respectively.

The aggregation of particles was investigated by absorption spectrum as shown in Fig. 4. The peak of the spectrum has a red-shift implied that the particles are growing larger. The broadening of the spectrum suggests that the distribution of particles becomes wider and wider. The enhancing of the light scattering by particles indicates that more particles aggregate into big particles. The absorption spectrum became stable after ten days.

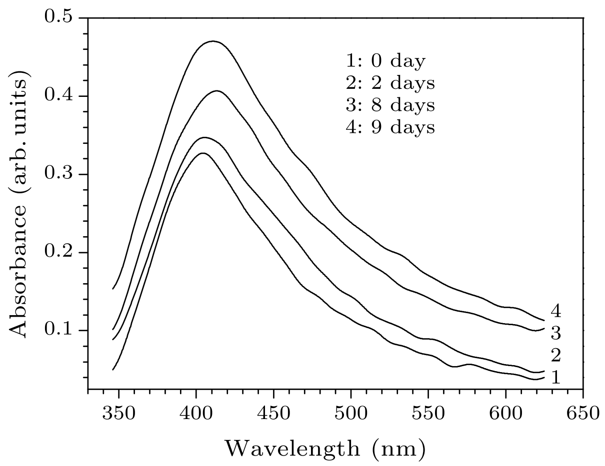

Fig. 4. Time dependence of the absorption spectrum of a typical silver nanoparticle colloid.

In conclusion, silver nanoparticles have been successfully generated by femtosecond pulsed laser in water. The results show that there are two kinds of particles, small particles with diameter about 35 nm, and large particles with diameter about 120 nm, which is different from the case of particles produced by nanosecond laser ablation. The properties of the particles are characterized by AFM, DLS and absorption spectroscopy.

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