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Surface-enhanced Raman scattering of *p*-hydroxybenzoic acid in pure Ag colloids produced by laser ablation

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Abstract

'Chemically pure' Ag colloids were prepared by laser ablation of Ag plate in pure water. The Ag colloids have good stability and the Ag nanoparticles in the colloids have homogeneous size distribution. Compared with the Ag colloids produced by chemical reduction methods, there was no any extraneous component ions in the colloids produced by laser ablation. Synchronously, we obtained much higher quality SERS spectra of PHBA molecules in the Ag colloids produced by laser ablation, the study of the adsorption behavior of *p*-hydroxybenzoic acid (PHBA) in the Ag colloids by surface-enhanced Raman scattering (SERS) indicated that the Ag colloids system was highly efficient substrate for SERS investigation.

Keywords: Laser ablation; Surface-enhanced Raman scattering (SERS); *p*-Hydroxybenzoic acid; Ag nanoparticles; Adsorption

1. Introduction

Surface-enhanced Raman scattering (SERS) is a highly sensitive technique for probing the interfacial phenomena and the behavior of molecules adsorbed on metal nanoparticles surface [1–5], and because the SERS uses photons as probes, which results in high-sensitivity spectra without damage to samples, revealing rich information concerning the interactions between adsorbate and base, it has become an important method of in situ investigation of thin films and interface in many fields [6–8]. Presently, the metal colloids served as SERS-active substrates are often prepared by chemical reduction methods, such as using sodium borohydride or trisodium citrate as reductants to produce Au, Ag colloids [9,10]. These methods are simple and rapid, and the enhancement effects of SERS are very obvious. However, during the process of producing the metal colloids, the presence of residual oxidation products and extraneous ions in the colloids can cause uncontrolled aggregation and diffusive double layer on the metal nanoparticles surface, which will disturb the adsorption behavior between the molecules and the metal surface. All of these will bring out many complex factors for analyzing the physical and chemical mechanism of SERS. So, it is essential to prepare 'chemically pure' mental colloids to avoid interference of extraneous ions in the application of SERS.

In this paper, we ablated Ag plate in redistilled deionized water using Nd:YAG pulse laser and obtained 'chemically pure' Ag colloids. Comparing with the other methods, the preparation of Ag colloids using pulse laser ablation has these advantages. (1) Short cycle of preparation with simple operation. Usually, within 30 min, different nanoscaled Ag particles can be obtained by varying output energy of the pulse laser. (2) Pure products with regular forms. The metal nanoparticles are formed directly with mental atoms and mental clusters without any reductants, so no any extraneous ions would be imported into the metal colloids during the preparing process. Via the TEM image, the distribution of the Ag nanoparticles was observed and measured, and most of the nanoscaled Ag particles have regular forms with globularity, which are suitable for theoretical calculation. Furthermore,

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the pure Ag colloids were used as SERS-active substrate, and high-quality SERS spectra were obtained through PHBA molecules serving as SERS probe. Comparing with the Ag colloids produced by chemical reduction, the studying in our experiment indicated that, without any extraneous in the ablated Ag colloids, the much stronger adsorption effects between the Ag nanoparticles obtained by laser ablation and molecules of PHBA can cause highly efficient SERS signals. Moreover, the further investigation indicates that the adsorption behavior of PHBA molecules absorbed on the Ag nanoparticles surface changed with the concentration of PHBA solution, in this paper, the reasons were also analyzed.

2. Experiment

2.1. Preparation of Ag colloids

2.1.1. Laser ablation method

Prior to ablation, Ag (1 mm thickness, 99.99%, Aldrich) plate was purified by the diluted nitric acid. Then, the plate was rinsed in ultrasonic washer with redistilled deionized water for 10 min. After that, the Ag plate was fixed at the center of a quartz cell filled with 30 ml of redistilled deionized water. The laser beam was adjusted by a 200 mm focusing lens to make the laser facula on the Ag plate to be ∼2 mm (diameter). The irradiation by the laser with 1064-nm line was continued for 20 min with an energy output 300 mJ per pulse. Finally, gray-brown Ag colloids were obtained (**LA *Ag Colloid***).

2.1.2. Chemical reduction method

In 500 ml of redistilled deionized water, 90 mg of silver nitrate was dissolved and the solution was heated to boiling. The 10 ml of a 1% trisodium citrate aqueous solution was added into the boiling silver nitrate solution dropwise, accompanied by vigorous stirring. The mixed solution was kept boiling for a further 10 min. Finally, green-gray Ag colloids were obtained (**CR *Ag Colloid***).

2.2. Experimental instrumentations

The Ag was ablated by a Quanta Ray Nd:YAG laser with 10 Hz repetition rate and 6–9 ns laser pulse duration. The maximum output energy of the laser is 800 mJ with irradiation of 1064 nm line. The output energy can be varied and measured by the power meter.

The transmission electron micrograph (TEM) images of the Ag colloids were taken with a H-600 TEM made by the HITACHI corporation after placing several drops of the fresh Ag colloid on Ni–Cu grid. The magnification of the TEM is 1×10^3–3×10^5 in this experiment.

All optical absorption plasmon spectra (SPA) of the Ag colloids were measured with a SHIMADZU Model UV-2401PC UV–visible spectrophotometer. During the experiment, the two kinds of Ag colloids were filled in clean quartz cell for measurement. The scanning region is from 200 to 800 nm, and the slit width of scanning is 0.5 nm.

The Raman spectra were obtained by the H13325 Raman spectrophotometer made by the RENISHAW CORPORATION. The Raman spectra of solid PHBA can be measured directly in the sample platform of the Raman spectrometer, and before measuring the SERS of PHBA molecules in Ag colloids, the Ag colloids and the PHBA solution need to be mixed enough with certain proportion in clean sample cell. Then, we used the capillary tube as carrier to take the mixed solution for obtaining the SERS. The operated wavelength is 514.5 nm. The output laser power in this experiment is from 50 to 100 mW.

3. Results and discussion

3.1. The characterization of Ag nanoparticles produced by laser ablation

When the laser ablated the Ag plate in the redistilled deionized water, the solution became yellow-gray gradually. After 5 min, we took a little of the solution for the TEM measurement, and discovered that the Ag colloids had high dispersibility with homogeneous size distributions for the low concentration of the Ag particles in the solution, and the Ag particles were not easy to aggregate together in the solution (Fig. 1(a)). With the prolongation of ablating-time, the concentration of Ag particles became higher and the degree of aggregation in the Ag solution also became more higher. Finally, the solution appeared gray-brown with the increasing concentration of Ag particles in the solution. Fig. 1(b) shows that most of the Ag nanoparticles were globoid and became aggregated after 20 min-ablating the Ag plate. This kind of Ag colloids were stable for a week without any extra stabilizing agents, and there were no visible sediments in the colloids.

Through analyzing the physical processes and mechanism of pulsed laser ablation of Ag plate. We consider that, in the ablating process, with the incidence of the great higher energy laser beam, the surface of the Ag plate absorbed much energy in very short time, and the most of laser energy of light changed into thermal energy [11], the Ag plate surface was melted or gasified instantly because of the laser intensive thermal effect. Simultaneously, the Ag atoms or clusters overcame the binding energy of the Ag surface and escaped from the Ag plate surface and formed into high-temperature and high-pressure Ag liquid or Ag gaseous group in very short time [12]. Meanwhile, the Ag liquid or Ag gaseous groups caused sharp expansion and transient explosion in redistilled deionized water and then they were solidified into globoid solid Ag nanoparticles by the interaction with the water [12], Finally, a large number of Ag nanoparticles were obtained with regular shapes and homogeneous size distribution in the colloids.