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Preparation and characterization of size and morphology controllable silver nanoparticles by citrate and tannic acid combined reduction at a low temperature

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ABSTRACT

In this paper, Ag nanoparticles (NPs) were prepared by using the citrate and tannic acid combined reduction of silver nitrate at 60 °C. Tannic acid is employed as both auxiliary reductant and surface modification agent. The size of Ag NPs can be well under controlled by varying the concentration of tannic acid. The size of Ag NPs decreases from 30 to 10 nm with the decrease of the concentration of tannic acid. The minimum average particle size, 10 nm, could be obtained with the 6 μM of tannic acid under the reaction condition of 60 °C. The products are rod-like, triangle, polygon NPs when the concentration of tannic acid turns to 24 μM. The results show that the obtained Ag NPs at 60 °C are smaller than that of boiling. Moreover, the morphology of the obtained Ag NPs is controllable under the condition of 60 °C. A SERS experiment was conducted for RhB in the presence of Ag NPs prepared at 60 °C, and a clear surface enhanced Raman spectroscopy was recorded.

1. Introduction

Ag NPs can exhibit unique properties as a result of small dimension, high surface area, quantum confinement and other effects [1–3]. In recent years, Ag NPs have been widely applied in the low temperature superconducting material, biological sensors, catalysts material and so on [4–9].

One application of Ag NPs is molecular sensing based on surface enhanced Raman signals. Raman spectroscopy is a nondestructive analytical technique which is based on the effect of inelastic light scattering by molecules. Surface enhanced Raman spectroscopy (SERS) associates with metal surfaces and provides a huge enhancement of Raman intensities with reduced fluorescence backgrounds, making it an ultrasensitive tool of detection. Surface enhanced Raman spectrum, which possesses the surface of the high detection sensitivity, can provide rich interface information, making it become an important tool to study the electrochemical catalysis [10], biomedical monitoring [11], environment inspection [12], and so on.

Accordingly to the applications of Ag NPs, a variety of preparation routes have been reported [13], including chemical reduction [14], microwave dielectric heating reduction [15], ultrasonic irradiation [16], radiolysis [17], electrochemical synthesis [18], and so on. Especially, wet chemical reduction, which has the advantage of easily controllable process, relatively low equipment requirement, short time and high yield, has been widely used in the laboratory and industry [5]. Chemical reduction method generally refers to the process for using reducing agent to reduce silver compounds under the condition of the liquid phase [19,20]. In the past decade, the reports have clearly demonstrated that the electromagnetic, optical and catalytic properties of Ag NPs are strongly influenced by shape, size and size distribution, which are often controlled by the synthetic methods, reducing agents and stabilizers [21,22].

In fact, the synthesis of Ag NPs with different morphologies and sizes using chemical reduction of silver salts has been reported [23,24]. Sodium citrate has been used as the reducing agent in various rapid chemical methods during these studies and most of them usually boil the mixed solution for the synthesis of Ag NPs [25,26]. So, it is very meaningful to synthesize Ag NPs at a low temperature. Z. Yi et al. have already reported the preparation of morphology controllable Ag NPs only using tannic acid and the size of Ag NPs were in the range of 50–500 nm [27]. X. C. Jiang has already used citrate ions as reducing agents and stabilizers, but the ability to stabilize Ag NPs was poor and there were no triangular Ag NPs generated [28].

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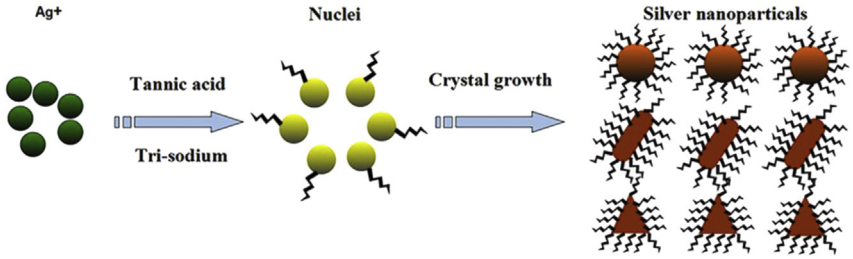

Scheme 1. Proposed preparation process of the Ag NPs.

In this paper, we use tri-sodium citrate as the reductant agent and tannic acid as the auxiliary reductant and stabilizer to prepare Ag NPs with smaller and uniform size at 60 °C, and the morphology of Ag NPs can be easily controlled. To demonstrate the potential use of the Ag NPs prepared by this method, we measured the SERS of Rhodamine B.

2. Experimental methods

2.1. Materials

Tannic acid was purchased from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin China). Silver nitrate standard solution (analytical reagent) was purchased from Aoran fine chemical Institute (Tianjin China). Absolute ethanol, KCl, and tri-sodium citrate (analytical reagent) were purchased from Fuchen Chemical Reagent Factory (Tianjin China). Rhodamin B was purchased from Tianli Chemical Reagent Co., Ltd. (Tianjin China). Deionized water was used as solvent for preparing the stock solutions of all reagents. All glass vessels were thoroughly cleaned prior to use with freshly prepared aquaregia and rinsed with deionized water.

2.2. Preparation of Ag NPs

For the preparation of silver nanoparticles, $AgNO_3$ solution and tri-sodium citrate were used, respectively, as a metal salt precursor and a reductant agent. Tannic acid solution was employed as the auxiliary reductant and stabilizer, and the concentration of Tannic acid solution was 6.0 μM, 8 μM and 24 μM, respectively. The preparation route is similar to the reference of [29]. A typical reaction is as follows: 20 ml of 6.8 mM aqueous solution of tri-sodium citrate was mixed with tannic acid, and then heated to 60 °C. The above mixture was added to 80 ml of 0.74 mM $AgNO_3$ solution preheated to 60 °C with vigorous stirring. The mixture was kept at 60 °C for 30 min and boiled for 15 min respectively, cooled down to room temperature and then stored in a dark bottle. The transparent colorless $AgNO_3$ solution mixture was converted to the characteristic pale yellow color after the addition of a required mixture solution containing tri-sodium citrate and tannic acid. The appearance of color was indicated the formation of silver nanoparticles [30].

2.3. Characterization

UV–vis absorption spectroscopy of silver nanoparticles was measured on a UV-2102PC spectrophotometer, and the samples were diluted before being measured. TEM and selected area electron diffraction (SAED) were operated on a High-Resolution Transmission Electron Microscope (JEM-3010, Japan) at an accelerating voltage of 300 kV. The TEM samples were prepared by slowly evaporating a drop of the nano-particle solutions on a copper grid covered by a carbon-supported film at room temperature. Dynamic Light Scattering (DLS) analysis was performed in a Malvern Zetasizer Nano ZS.

Sample preparation for SERS measurements of RhB: RhB was dissolved in ethanol and then diluted in double distilled water to 10^{-9} M. 100 μl this solution were mixed with 900 μl of the Ag colloid and 25 μl of 0.01 M KCl. The mixture was stored at 4 °C for 3 h, and then adsorbed for 20 min on a glass substrate. SERS spectra were acquired using a confocal Raman microscope LabRam HR800 (Horiba Jobin Yvon, Germany) equipped with a HeNe laser line (633 nm). The spectra in the relevant range from 400 to 2000 cm^{-1} were recorded using a 10 s integration time.

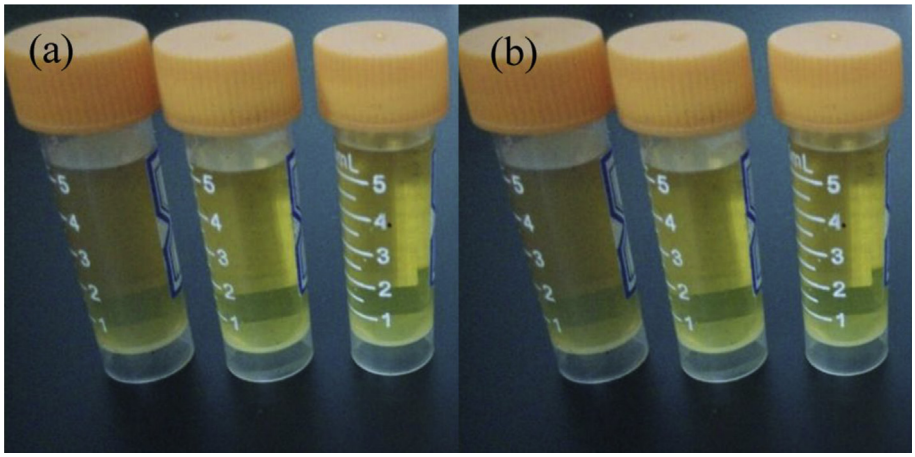

Fig. 1. Silver colloid obtained under the condition of 60 °C (a) and 6 months later (b).