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Synthesis and layer-by-layer self-assembly of silver nanoparticles capped by mercaptosulfonic acid

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Abstract

Spherical silver nanoparticles capped by mercaptosulfonic acid with a diameter of about 8 nm were prepared by a simple chemical reaction. The resulting silver nanoparticles were characterized by UV–vis spectroscopy (UV–vis) and transmission electron microscopy (TEM). Using layer-by-layer (LBL) self-assembly technique, the multilayer films containing silver nanoparticles and polycation poly(dialyldimethylammonium chloride) (PDDA) were successfully fabricated. The fabrication process was monitored by UV–vis spectra and the morphology of the multilayer films was investigated by atomic force microscopy (AFM). The cyclic voltammogram (CV) measurements further confirmed that the silver nanoparticles had assembled into the multilayer films successfully. Surface-enhanced Raman spectroscopy (SERS) measurements showed that the multilayer films containing silver nanoparticles could serve as SERS-active substrate.

Keywords: Silver nanoparticles; Mercaptosulfonic acid; Layer-by-layer self-assembly; Multilayer films; SERS

1. Introduction

In the last few years, research on metal nanoparticles is developed rapidly due to their size-dependent optical, magnetic, and catalytic properties, which are different from bulk materials [1–5]. Most of studies on metal colloids have focused on silver, gold, and copper colloids. In many aspects, the properties of colloidal silver and gold are quite similar, but silver colloid exhibited superior catalytic activity [6] and improved enhancement factors for SERS [7]. The history of the synthesis of silver colloid dates back to the 19th century [8]. Compared with gold colloid, the silver colloid is more difficult to prepare as monodisperse solutions of a pre-specified size. Up to now, a number of methods have been reported for preparing silver colloid, including chemical reduction [9–12], photochemical means [13], γ irradiation [14], and laser ablation of bulk silver surfaces [15]. Among these methods, chemical reduction is most common, and a variety of reductants have been used, such as citrate, ethylenediaminetetraacetic acid, dye molecules, and $NaBH_4$. Although those methods have proven to be successful, exploring the optimum synthesis methods of the silver colloid is still a challenge.

The LBL self-assembly technique, first introduced by Decher in 1991 [16], provides an elegant way of controlling the composition of the resulting assemblies and the thickness of an individual layer on the nanometer scale. Recently, metal nanoparticles are often used as functional building blocks for the construction of nanostructured LBL films. So we predict that this kind of thin film could represent a great potential for broadening the selectivity of the matrix of SERS experiments.

SERS is an extremely powerful microanalytical technique that is currently receiving a great deal of attention due to its potential application toward a wide range of problems. In particular, it is extensively used in the fields of biomedicine [17], thin-film characterization [18], and trace analysis [19].

In the present work, we describe another simple and convenient method for the synthesis of silver colloid, namely, the silver nanoparticles were prepared with mercaptosulfonic acid as the stabilizer, which made the resulting nanoparticles negatively charged in aqueous solution. In addition, based on electrostatic interactions, the multilayer films containing silver nanoparticles could be fabricated by the LBL self-assembly method. SERS measurement indicates that the thin films

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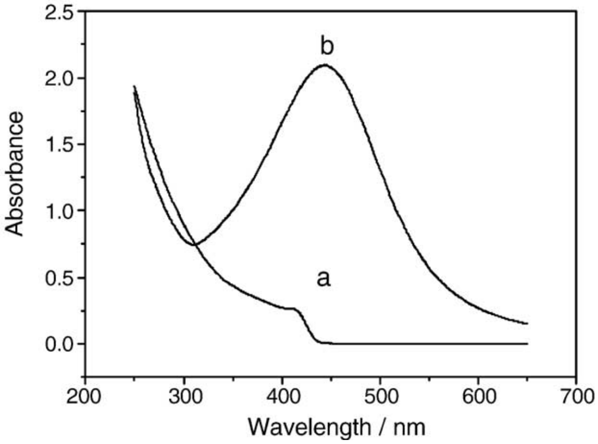

Fig. 1. UV–vis absorption spectra of AgI colloid before adding of $NaBH_4$ (a) and Ag colloid after adding of $NaBH_4$ (b).

prepared by the present method may be a new candidate for SERS substrate.

2. Experimental section

2.1. Materials

$AgNO_3$ (99.5%), KI (99%) and $NaBH_4$ (98%) were obtained from Beijing Chemical Co. 3-Mercapto-1-propanesulfonic acid, sodium salt, and poly(dialyldimethylammonium chloride) (PDDA, aqueous solution with a molecular weight of 400,000–500,000) were purchased from Aldrich.

2.2. Instruments

UV–vis spectra were recorded on a GBC Cintra 10_e UV–visible Spectrometer. TEM photographs were measured with a Hitachi 8100 instrument at 200 kV. AFM images were taken with a multimode Nanoscope IIIA (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers. The electrochemical experiments were carried out with a CHI 660A electrochemical workstation (CH Instruments, USA) with a conventional three-electrode cell. The modified glassy carbon electrode was used as the working electrode. The Pt wire and the Ag/AgCl electrode (saturated KCl) were used as the counter-electrode and the reference electrode, respectively. SERS was obtained using a Renishaw 1000 model confocal microscope Raman spectrometer with a charge-coupled device detector and a holographic notch filter. The SERS excitation was provided by the 514.5-nm line of a Coherent Radiation Innova Ar^+ laser. Data acquisition was the result of three 30-s accumulations for R6G.

2.3. Silver colloid preparation

The synthesis process of silver colloid is very simple and can be separated into two parts. First is the preparation of AgI colloid. Second is the reduction of AgI colloid. The detailed synthesis route is described as follows. All glassware used in the procedures were cleaned in a bath of freshly prepared HNO_3–HCl (1:3) and rinsed thoroughly in triply distilled water prior to use. To 50 ml of triply distilled water, 2.5 ml of 0.01 M $AgNO_3$ solution and 5.0 ml of 0.01 M 3-mercapto-1-propanesulfonic acid, sodium salt solution were added with stirring. After 10 min of mixing, 2.5 ml of 0.01 M KI solution was slowly dripped into the above solution with vigorous stirring. After 20 min of further reaction, a light yellow-green AgI colloid was formed. Then, a total of 20 mg $NaBH_4$ was added into the AgI colloid solution, and the reaction mixture was continuously stirred for another 20 min. Finally, the silver colloid was obtained. After adding of $NaBH_4$, the color of the colloidal solution turned heavy rapidly, and the ultima silver colloid is orange.

3. Results and discussion

3.1. Silver colloid formation

The formation process of mercaptosulfonic acid-capped silver nanoparticles was traced by the UV–vis spectra, as shown in Fig. 1. Fig. 1a is the typical absorption of AgI nanoparticles. After the addition of $NaBH_4$, a remarkable absorption band at about 442 nm appeared immediately. When the reaction continued, the peak height increased obviously. After reaction for 20 min, the peak height is nearly unchanged. Fig. 1b is the ultima spectrum of the silver colloid.

Fig. 2 shows the TEM micrograph of the silver colloid. The average diameter of the silver nanoparticles is about 8 nm.

To monitor the stability of the final prepared silver colloid, we measured the absorption spectra of the colloid on different days (not shown here). There was no obvious change in the shape, position, and symmetry of the absorption peak during the initial 15 days, except for the decrease of the absorbance. After the 15th day, the fwhm of the spectrum started to become wider than before, and the peak maximum showed a slight red shift, implying the onset of nanoparticle aggregation. These results demonstrate that the silver nanoparticles colloidal solution can remain stable for about 2 weeks.

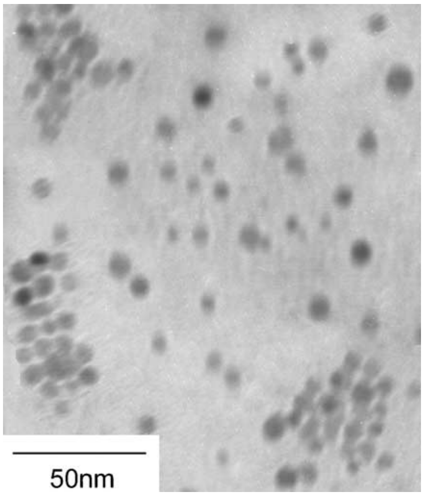

Fig. 2. TEM micrograph of the silver colloid.