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Synthesis and characterization of L-histidine capped silver nanoparticles

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ABSTRACT

L-histidine capped Ag nanoparticles have been synthesized by a hydrothermal method. Spherical Ag nanoparticles with average diameter ranging from 9 to 21 nm can be obtained by tuning the reaction pH and the reactant ratio. The topography, surface and internal structures of the histidine capped Ag nanoparticles have been characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic light scattering, X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD), Raman spectroscopy and UV–vis absorption spectroscopy. Surface enhanced Raman scattering (SERS) results revealed that the Ag colloid in present study have a structure that the imidazole moiety of histidine is bound on the Ag surface and COO^- group is exposed outward. The as-synthesized Ag colloidal solution was very stable and can be stored at room temperature at least one month. In addition, it was found that the solution color of Ag colloid can change from yellow to reddish-brown by addition of the $NiCl_2$ solution, which may have potential application for Ni^{2+} detection.

1. Introduction

Synthesis of various metal nanomaterials is an active research area in recent years due to their potential applications in catalysis, electronics, photonics, data storage, optoelectronics, biological labeling, imaging, and sensing [1–6]. Among the studied metals, Ag nanomaterials have received considerable attention owing to its high and broad antibacterial activity, superior electro-optical properties [5,7,8]. Furthermore, Ag nanomaterials have been proved to be a good substrate for surface enhanced Raman scattering (SERS) [9–11]. It has been revealed that the physicochemical properties of Ag nanomaterials depend on their size, shape and surface capping agent [12]. Consequently, synthesis of Ag nanomaterials with different size, shape and surface capping agent is an important research area. Recently, some amino acids capped gold [13,14] and Ag nanomaterials [15,16] have been reported. Amino acids are an important class of biological molecules. They are not only the building blocks of protein, but also the important additive in food. Thus, they can be considered as an ideal class of biocompatible ligands for capping of Ag nanomaterials. The capping of amino acid for Ag nanomaterials can render them with good water-dispersible characteristic and biocompatibility, which is essential for their applications in biology and bio-sensing. Histidine, one of the most important amino acids, has been extensively studied due to its biochemical importance, and it is known to be involved in various biological processes including enzyme actions and medical applications [17,18]. There has been increasing interest in estimating the stabilities of various geometric forms of histidine due to its potential importance in various metallic–enzymatic reactions [19].

Synthesis of histidine functionalized gold nanoparticles has been explored recently [14,20,21]. Concerning for Ag, the coordination complex of histidine with silver nitrate has been reported previously,and it exhibited a good antimicrobial activity with low toxicity [22]. However, to our knowledge, histidine capped Ag nanoparticles have not been well addressed. So far numerous methods for synthesis of Ag nanoparticles have been reported, and solution synthetic route has been widely used because of its convenience and quickness. However, sometimes the obtained Ag colloids by solution synthetic route were not very stable, which can influence its final applications. Therefore, development of new strategy for synthesis of Ag nanoparticles with good stability and biocompatibility is still required. Hydrothermal synthetic method is a heat-induced chemical reaction process, which is a facile and energy-efficient route to prepare well-crystallized nanomaterials such as for metal-oxide nanoparticles [23], metal-sulfide nanoparticles [24] and metal/carbon nanocables [25]. In this study, we use hydrothermal method to directly synthesize crystalline silver nanoparticles with histidine capping. It is expected that the present method can be extended for synthesis of some other amino acid capped Ag nanomaterials.

2. Experimental section

2.1. Materials

Ultra pure water was used throughout this study and its resistivity was >18 MΩ cm. The used chemicals included silver nitrate ($AgNO_3$),

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aqueous ammonia (25–28 wt.%) L-histidine($C_6H_9N_3O_2$), sodium hydroxide (NaOH), 4-aminobenzenesulfonic acid ($C_6H_7NO_3S$) and sodium nitrite ($NaNO_2$) are of analytical purity.

2.2. Preparation of Ag nanoparticles

In a typical synthetic experiment, a clear Ag $(NH_3)_2OH$ aqueous solution was obtained by adding 0.17 ml of 2% aqueous ammonia into the 0.50 ml of 0.127 mol/L silver nitrate solution. Then, 30 ml pure water was added into the above prepared Ag $(NH_3)_2OH$ aqueous solution, subsequently, 5 ml of 1% histidine aqueous solution was added. The molar ratio of histidine to Ag is 5:1. The mixed solution was vigorous stirred for 10 minutes, and then an appropriate volume of 2 M NaOH solution was added and the solution pH was adjusted to 11.0. Finally, the solution was transferred into a stainless Teflon-line autoclave of 50 mL, and then it has been sealed and maintained at 130 °C for 5 hours. A yellow solution was obtained, which indicated histidine capped Ag nanoparticles were produced. In this case, not all histidine molecules are reacted and bound on Ag nanoparticles. These unbound histidine molecules can be separated with the Ag colloids by centrifugation to remove Ag nanoparticles. Histidine molecules can react with Pauly reagent in the alkaline condition and produce a substance with orange color, which can be used for measuring their concentration. In present study, the concentration of histidine in the supernatant was determined by this spectrophotometry method as previous reported [26,27].

In the experiments at different pH and reactant ratio, the preparation of Ag $(NH_3)_2OH$ solution and the final hydrothermal reaction process was same as above experiment except that the initial pH condition and the reactant ratio was changed. In one group experiments, the initial pH was fixed at 11.0 and the molar ratios of histidine to Ag at 1.2:1, 2.4:1, 8:1 have been tested. In another group experiments, the initial pH was fixed at 11.8 and the molar ratios of histidine to Ag at 0.3:1, 0.6:1, 1.2:1 and 2.4:1 have been explored. When the synthesis was performed with the molar ratios of histidine to Ag at 0.3:1 and 0.6:1, a lot of black precipitates were produced in the obtained solution. When the synthesis was performed with the molar ratios of histidine to Ag at 1.2:1 and 2.4:1, brownish-red solutions were obtained.

2.3. Characterization

2.3.1. Transmission electron microscopy

The produced Ag nanoparticles were imaged using H-600 transmission electron microscope at 100 kV. The sample for TEM characterization was prepared by placing 5 μl of the as-synthesized Ag colloid solution on a carbon coated copper grid and drying at room temperature.

2.3.2. Atomic force microscopy

30 μl of the histidine-capped silver colloidal solution was dropped on a 0.1% of APTES modified mica surface and washed with pure water three times,then air dried before AFM imaging. All AFM images were obtained in tapping mode under air ambient conditions using a PicoPlus AFM system from Molecular Imaging (MI) Corporation (AZ, USA). NSC35 ultra sharp silicon cantilevers with a nominal spring constant of 4.5 N/m and curvature radius <10 nm from MikroMasch were used, and the cantilever was oscillated at a resonance of 150 kHz. The dimensions of the silver nanoparticles were measured by using the Pico Scan 5.3.3 software.

2.3.3. Dynamic light scattering

The synthesized Ag colloidal solution were determined by ZetaPAL/90plus (Brookhaven Instruments) equipped with a He-Ne laser (632.8 nm, 35 mW).

2.3.4. UV–vis absorption spectroscopy

A shimadzu UV-2550 spectrophotometer was used for the absorption spectrum measurement.

2.3.5. X-ray diffraction

Powder X-ray diffraction patterns were recorded using D/MAX 2200VPC (40 kV/40 mA). The XRD sample was derived from centrifugation of the as-formed silver colloidal solution.

2.3.6. X-ray photoelectron spectroscopy

XPS data was collected by K-Alpha from Thermo scientific. The measured samples were prepared by dropping the concentrated Ag colloidal solution (derived from centrifugation and redispersion of the as-formed silver colloidal solution) on a fresh cleaved HOPG and drying at room temperature.

2.3.7. Raman measurements

Raman measurements were measured with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.). Radiation of 514.5 nm from an air-cooled argon ion laser was used for the SERS excitation.

3. Results and discussion

3.1. Characterization of the synthesized Ag nanoparticles

Fig. 1 shows the representative TEM image of the obtained histidine capped Ag (His-Ag) nanoparticles in the typical experiment. A lot of spherical nanoparticles can be observed. The inset in Fig. 1 shows the size distribution of Ag nanoparticles. The average diameter of Ag nanoparticles is 21 ± 2 nm. The topography of the Ag nanoparticles was further characterized by AFM under air ambient condition. Fig. 2 shows the typical AFM topographic image of the synthesized His-Ag nanoparticles on 3-aminopropyltriethoxy-silane (APTES) modified mica surface. APTES modified mica surface is positive charged [28]

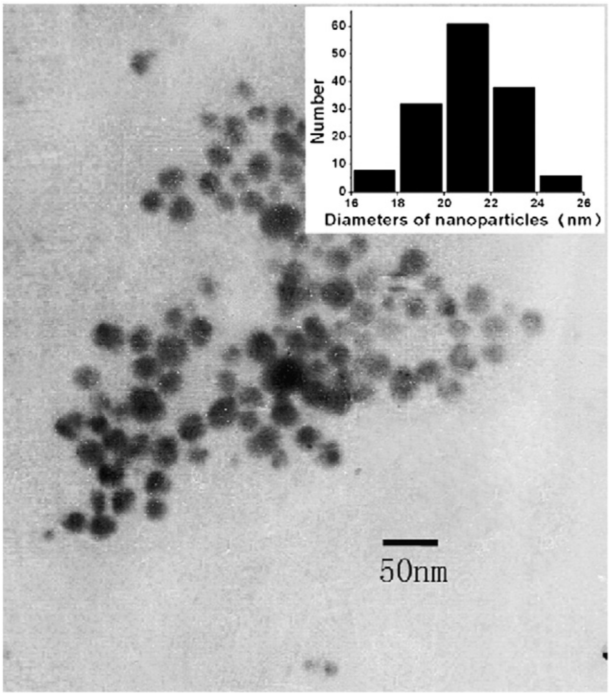

Fig. 1. Shows the representative TEM image of the synthesized His-Ag nanoparticles in the typical experiment. The inset shows the size distribution of Ag nanoparticles (n = 145).