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One-step Synthesis of Shape-controllable Gold Nanoparticles and Their Application in Surface-enhanced Raman Scattering

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Gold nanoparticles (NPs) of various shapes were synthesized by a one-step method at ambient temperature in the presence of NaCl. 2-mercaptosuccinic acid (MSA) was used as both reducing agent and stabilizing agent. The shapes of gold NPs were controllable by simply tuning S/Au ratio (S is from MSA molecule, and S/Au ratio is controlled by tuning the volume of added MSA solution), and triangle, polygonal and spherical nanoparticles were obtained. This result suggested a new way to consider the effects of MSA on the growth of nanoparticles, which showed that MSA is a strong capping agent and facilitates more uniform growth of nanoparticles in every dimension. And other important factors on nanoparticles growth including NaCl and temperature were discussed. Furthermore, a typical probe molecule, 4-aminothiophenol (4-ATP) was used to test the surface-enhanced Raman scattering (SERS) activity of these gold NPs and the results indicated good Raman activity on these substrates. And the enhancement factor (EF) at 1078 cm^{-1} (a_1) was estimated to be as large as 6.3×10^4 and 5.5×10^4 for triangular plates and truncated particles, respectively.

KEY WORDS: Nanoparticle; Shape; Controlled synthesis; Surface-enhanced Raman scattering (SERS)

1. Introduction

Shape control of nanoparticles has received much consideration due to the strong relationship between shape and chemical, physical, thermal, optical, electric, magnetic, and catalytic properties of nanoparticles[1−12]. Up to now, a variety of chemical methods have been developed to synthesize various shapes of nanostructures including rods[13−15], wires[16], triangular plates[17,18], belts[19], hollow spheres[20] and cubes[21,22]. In particular, gold nanoparticles have attracted much attention for their numerous applications in the areas of catalysis[23−25], sensors[26−30], and surface-enhanced Raman scattering (SERS)[31,32]. Many methods have been reported to synthesize various shapes of gold nanostructures including electrochemistry[33,34], templating[35,36], photochemistry[14,37], and seeding[13,15] method. However, these methods more or less involve templates, seeds, and complex procedures. A simpler solution-based route processed at room temperature is becoming more and more attractive due to its mildness, simplicity and lack of equipments. The most successfully synthesized shape-controllable nanoparticles are those of silver and have been achieved by typical routes. For example, Im et al.[38] have reported the high yield of silver nanocubes by introducing a small amount of hydrochloric acid to the conventional polyol synthesis; Wiley et al.[39] also have synthesized right bipyramids of silver by adding NaBr to a polyol synthesis. However, the challenge of shape control for gold has been met with only limited success. For example, shape control of gold nanoparticles has been achieved by a heating treatment strategy[40]. As for solution methods, various stabilizers are necessary to prevent the aggregation of nanoparticles, so polymers, ligands, surfactant, *etc*., have been sufficiently studied. 2-mercaptosuccinic acid (MSA) has been one of popular stabilizers in the synthesis of gold nanoparticles[41,42], but in which MSA only acts as a stabilizer. By heating reaction solution at 100 °C, gold nanowires have been obtained, in which MSA acts as both stabilizing agent and reducing agent[43,44]. And Niu et al.[45] have reported the one-step seed-mediated growth of 30−150 nm quasispherical gold nanoparticles with MSA as a new reducing agent. However, up to now, the actual function of MSA in controlling the shape of nanoparticles at room temperature has not been extensively studied. Here we found that MSA can act as both reducing and capping agent even at ambient temperature. Therefore, it is very important to study the fundamentals of MSA in the growing of gold nanoparticles, because the understanding of fundamentals can help us design new materials and better synthesis methods.

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In this paper, we have described a simple solution-phase method to synthesize different shapes of gold nanoparticles at room temperature (RT). MSA acts as both capping and reducing agent. The shapes of gold nanoparticles can be controlled by changing the S/Au ratio (S is from MSA molecule, and S/Au ratio is controlled by tuning the volume of added MSA solution) and adding of NaCl. Through the study of the influence of S/Au ratio on the shapes of nanoparticles, the roles of MSA in the growth of nanoparticles are clearly discussed. It is found that these triangular plates can be used as good SERS-active substrates with 4-aminothiophenol (4-ATP) as a test probe.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$, 99%) and NaCl (A.R.) were obtained from Beijing Chemical Reagent Factory (China). 2-mercaptosuccinic acid (MSA, 97%) was bought from Fluka. 4-aminothiophenol (4-ATP) was obtained from Aldrich. Ultrapure water (≥18.2 MΩ cm) was used throughout the experiments.

2.2. Methods

In a typical synthesis, 10 mL of 0.25 mmol/L $HAuCl_4$ aqueous solution was mixed with 0.1 mL of 1 mmol/L NaCl aqueous solution as precursor solution. Seven such precursor solutions were mixed with 0.1, 0.3, 0.5, 0.7, 1.0, 2.0 and 3.0 mL MSA aqueous solution (1 mmol/L), respectively. The S/Au ratio is calculated as 0.04, 0.12, 0.2, 0.28, 0.4, 0.8 and 1.2, respectively. The seven nearly colorless solutions were stayed for 12 h at room temperature. In control experiments, no NaCl was added and the other conditions were the same. The final concentration of NaCl is 7×10^{-3} mmol/L.

2.3. Measurements

All samples for morphology and structure analysis were examined as prepared. SEM images were taken by field emission scanning electron microscopy (FESEM) operated at accelerating voltage of 10−20 kV. UV−vis absorption spectra were taken at room temperature on a Cary 500 scan spectrophotometer. SERS spectra were measured with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, UK). The microscope attachment was based on a Leica DMLM system, and a 50× objective was used to focus the laser beam onto a spot with approximately 1 μm in diameter. Radiation of 514.5 nm from an air-cooled argon ion laser was used for the SERS excitation. All of the spectra reported were the results of a single 20 s accumulation.

3. Results and Discussion

3.1. Role of S/Au ratio in the growth of nanoparticles

3.1.1. UV−vis spectra with different S/Au ratios. It is well-known that metal colloids display the absorption in UV−vis region, which was caused by the excitation of plasmon resonance or interband transition. Therefore, UV−vis absorption spectra can be used to characterize metal colloids. Fig. 1(a) shows the UV−vis absorption spectrum of gold nanoparticles (NPs) that were produced after the reduction process with S/Au ratio of 0.12. The color of the solution changed slowly to blue. After staying for 12 h a weak absorption band appears at around 558 nm, which corresponds to the known surface plasmon absorption band of gold NPs. There is also an obvious absorption at 295 nm, which suggests that a lot of $HAuCl_4$ remains in the products when the S/Au ratio is 0.12. Fig. 1(b)−(d) shows the UV−vis absorption spectra with different S/Au ratios from 0.28 to 0.8. The colors of the solution at these S/Au ratios changed quickly to red, red-mauve and mauve, respectively. The UV−vis absorption spectra show the longitudinal plasmon band red-shift and its intensity increases with increasing S/Au ratio from 0.28 to 0.8. In addition, the UV−vis absorption peak at about 295 nm weakens and finally disappears as a result of the consumption of the residual $HAuCl_4$ as the S/Au ratio increases. It is reasonable that the optical properties of metal NPs are dependent on particle size, shape and environment. Therefore, it is believed that the size and shape of the morphology of gold NPs can be controlled by tuning the ratio of S/Au.

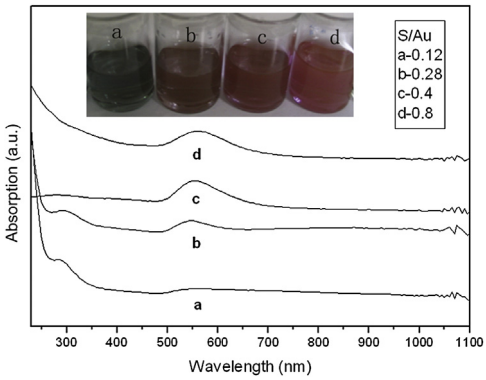

Fig. 1 UV−vis spectra of nanoparticles prepared with different S/Au ratios of 0.12 (a), 0.28 (b), 0.4 (c) and 0.8 (d) in the presence of NaCl, inset is the photographs of the corresponding samples with different colors.

3.1.2. Morphology of gold NPs with different S/Au ratios. Gold NPs have been synthesized by chemical reduction method in the presence of NaCl at room temperature. MSA acted as both capping and reduction agent. Fig. 2 shows a sequence of SEM images with S/Au ratio of 0.12, 0.28, 0.4, and 0.8, respectively. It indicates that the irregular triangle-like NPs have been synthesized at the S/Au ratio of 0.12 (Fig. 2(a)). This phenomenon implies that stabilizer molecules (MSA) are not enough to cover the surface of gold NPs, which results in the formation of irregular NPs. When the S/Au ratio is 0.28, it shows that the dominant products of the reaction are a mixture of triangular plates with the lateral size of 200−300 nm on average and nanospheres, as shown in Fig. 2(b). Under this condition, more gold atoms are reduced by MSA, and the capping agent is also increased although it is still not enough to completely cover the surface of gold NPs. Hence the products of the reaction include not only nanospheres but also uniform triangle particles. When the S/Au ratio is 0.4, the primary products are polygonal NPs with average size of about 65 nm, in which the side edge of the particles is truncated and apt to growth into spherical NPs (Fig. 2(c)). When the S/Au ratio is increased to 0.8, the large spherical gold particles are found as shown in Fig. 2(d). The