Synthesis of Gold Nanoparticle Using Halloysites

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We report that gold nanoparticles were synthesized by reduction of HAuCl₄ using halloysites. The synthesized samples were analyzed by a transmission electron microscope. The results show that the gold nanoparticles have strip-like, subcircle, and irregular shape, which are single crystals or polycrystals. Their shapes and sizes are relate to the different halloysites. Reduction of Au³⁺ may be related to the surface dangling bonds of halloysite nanotubes. Our research results show that a simple, room-temperature, and green synthesis of the nanocomposite of halloysite nanotubes and gold nanoparticles are possible. The nanocomposite may have the advantages of both the nanocomposite of halloysite nanotubes and gold nanoparticles, which may be widely applied to physical, chemical and biological field. [DOI: 10.1380/ejssnt.2009.813]

Keywords: Synthesis; Gold nanoparticle; Reduction; Halloysites

I. INTRODUCTION

Gold nanoparticles have a lot of wonderful physical and chemical properties and have many important applications in physical, chemical and biological field. The synthesis methods of gold nanoparticles included template method, wet chemical synthesis, electrochemical method, scanning probe lithography, photochemical method and sonochemical synthesis. A classical synthesis method is gold nanoparticles prepared by reduction of HAuCl₄. The most common reducing agent is sodium citrate [1–5]. Other reducing agents included sodium borohydride, tannic acid, white phosphorus, and ascorbic acid, etc. [6,7,8,9,10,11]. A new method is that gold nanoparticles prepared by reduction of HAuCl₄ using photosynthetic bacteria or extract of rhodopseudomonas capsulata [12]. However, the synthesis of gold nanoparticles using halloysites has not previously been reported. In this paper we report that gold nanoparticles prepared by reduction of HAuCl₄ using halloysites. Our research results show that the synthesis of the nanocomposite of nanotube halloysite and gold nanoparticles by the method is possible. This will be a simple, room-temperature, and green synthesis method.

II. EXPERIMENTAL

Two samples of halloysites originated from Hunan (sample A) and Jiangsu (sample B) of China respectively. The synthesis method of gold nanoparticles using nanotube halloysites was as follows. The 2.5 ml of 1% aqueous HAuCl₄ solution was added into a 250 ml graduated flask. Purity water was added to the calibration graduation of the flask. HAuCl₄ used in the experiment was analytical reagent grade (AR) that has ideal quality for the experiment. Two 10 g halloysite samples (samples A and B) and 100 ml of purity water were respectively added into two beakers. Then, 1 ml of HAuCl₄ solution was respectively added to the beakers, stirred uniformly. After 1 day, the samples were analyzed by transmission electron microscope (TEM). TEM samples were prepared by dip-coating a solution of the samples on carbon-film Cu grids. TEM analyses were performed on a JEM-2010HR instrument (JEOL LTD, Japan) equipped with an energy dispersive spectrooscope (EDS, Energy TEM 200, OXFORD-INCA).

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FIG. 1: EDS spectrum of the gold nanoparticles.

FIG. 2: TEM image of the gold nanoparticles and the halloysite nanotubes in sample A.
FIG. 3: (a) TEM image of the gold nanoparticles and the halloysites in sample B and (b) enlarged image of black arrow area in (a).

at an accelerating voltage of 200 kV in the Instrument Analysis Center of the Sun Yat-sen University. Pictures were digitized using a CCD camera. Figure 1 shows EDS spectrum of the gold nanoparticles.

III. RESULTS

Figure 2 shows the halloysites and the gold nanoparticles synthesized using the halloysites of sample A. The halloysites are straight or curved tubes with 20-200 nm in length and 2-7 nm in diameter. The length to width ratio is from 10:1 to 30:1. The gold nanoparticles are strip-like and the sizes are 30-100 nm in length and 5-20 nm in diameter. The black arrow in Fig. 2 indicates growing of gold nanoparticles between two halloysites and their shapes and sizes depends on the free space of two halloysites. This is one of its remarkable characteristics on

Fig. 2. It suggests that (1) reduction of Au$^{3+}$ may be related to halloysite nanotubes, and (2) the different shapes and sizes of gold nanoparticles may be prepared by selecting different halloysites.

The halloysites in sample B are straight tubes with 0.35-1.5 µm in length and 0.05-0.25 µm in diameter that are much greater than those in sample A. There are two sizes gold nanoparticles prepared using halloysites of sample B, which were measured to be 4-8 nm and 16-30 nm in diameter respectively and were distributed on the halloysite tubes. Figure 3 shows 4-8 nm gold nanoparticles with subcircle shape. EDS analysis revealed that the
components of the back particles with subcircle shape in Fig. 3(b) are Au. 16-30 nm gold nanoparticles have irregular shape in samples B (Fig. 4). HREM image indicated that 4-8 nm gold nanoparticles are single crystals and 16-30 nm gold nanoparticles are polycrystals (Fig. 5). The d-spacing of the gold nanoparticle corresponding to the (111) plane was measured to be 0.234 nm in Fig. 5(b). Possibly, the 16-30 nm gold nanoparticles formed by the aggregation of 4-8 nm gold nanoparticles. We think that reduction of Au^{3+} may be related to the surface dangling bonds of halloysite nanotubes. The catalysis of surface atoms having higher chemical activity is reason for reduction of Au^{3+}.

Halloysite nanotubes are a kind of naturally deposited aluminosilicate (Al_2Si_2O_5(OH))_4.nH_2O, chemically similar to kaolin, which have a predominantly hollow tubular structure [13, 14]. The chemical properties of the halloysite nanotubes outermost surface are similar to the properties of SiO_2, while the properties of the inner cylinder core could be associated with those of Al_2O_3 [15]. The Halloysite nano-tubes have properties such as adsorbed, catalytic, etc., which are applied to water treatment, modification of polymer materials, catalysis etc. fields. Our research results show that the synthesis of the nanocomposite of halloysite nanotubes and gold nanoparticles is possible. The nano-composite may have the advantages of both the nanocomposite of halloysite nanotubes and gold nanoparticles. It may be widely applied to physical, chemical and biological field.

The halloysites are a cheap natural product. We can obtain a large amounts of halloysites from the natural deposits. This is different from the artificial synthesized products such as carbon nanotubes. This provides condition for its wide application of the composite materials of halloyssite nanotubes and gold nanoparticles. In addition, the research results showed we may choose the halloysites with different sizes from different area to synthesize gold nanoparticles with special shapes and sizes. We may also synthesize 4-8 nm gold nanoparticles by adding agents such as a surfactant to avoid polymerization.

Now, the most materials relate to gold nanoparticles synthesized by two steps. For example, gold nanoparticles and carbon nanotubes were respectively synthesized in the first step. In the second step, gold nanoparticles were attached to the surfaces of carbon nanotubes [16]. In our study, the synthesis and self-assembly are accomplished by one step at room-temperature, using no the reducing agents such as sodium borohydride, tannic acid, white phosphorus, and ascorbic acid, etc. It will be a simple, room-temperature, and green synthesis method of nanocomposites.

IV. SUMMARY

Gold nanoparticles can be synthesized by reduction of HAuCl_4 using halloysites. Reduction of Au^{3+} may be related to the surface dangling bonds of halloysite nanotubes. Our research results show that the synthesis of the nanocomposite of halloysite nanotubes and gold nanoparticles by the simple, room-temperature, and green synthesis method is possible. The nanocomposite may have the advantages of both the nanocomposite of halloysite nanotubes and gold nanoparticles. It may be widely applied to physical, chemical and biological field.

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