



Tuning the surface enhanced Raman scattering activity of gold nanocubes by silver coating



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ABSTRACT

Colloidal gold nanocubes coated with a silver nanoshell have been synthesized via the seed mediated growth method. By changing the volume of gold seed and silver nitrate, both the edge length of gold nanocube and the thickness of silver shell could be fine-tuned. The surface-enhanced Raman scattering (SERS) activity of these core-shell structural Au–Ag bimetallic nanocubes has also been investigated by using the rhodamine 6G (R6G) as Raman active probe. It has been found the SERS activity of the silver-coated gold nanocubes greatly depends on their geometry factors. By decreasing the edge length of gold nanocubes or increasing the silver coating thickness, the SERS activity has been greatly enhanced. By comparing with other Raman bands of R6G, the enhancement of the Raman peak corresponding to the C–C–C ring in-plane vibration mode is more sensitive to the geometries of the nanostructure. These improved SERS properties of silver-coated gold nanocubes provide potential application for biologic and chemical sensing based on Raman spectroanalysis.

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1. Introduction

The optical properties of metallic nanoparticles and their application in surface-enhanced Raman scattering (SERS) have been a hot topic in nanoscience and nanotechnology. Because of their unique localized surface plasmon resonance (LSPR) characteristic, the gold and silver nanoparticles have become one of the most active branches in nanotechnology area [1–3]. Gold and silver have wide applications in the field of the biological spectral detection [4,5] with good biocompatibility [6] depending on their unique properties. In addition, the interest of Au and Ag nanoparticle grows rapidly also because of their strong optical absorption, resonance light scattering and local field enhancement in the visible and infrared wavelength regions [7–9]. Therefore, a large number of experiments focus on the investigating of optical characteristic and application of gold and silver nanoparticles.

Raman scattering [10,11], a vibrational spectroscopy technique, has been used to analyze biological organism and human tissue owing to its merit of non-invasion and non-destruction. SERS [12,13] is a surface sensitive phenomenon that results in the enhancement of Raman scattering by molecules adsorbed on rough

metal surface. SERS was first observed by Fleischmann et al. [14] from monolayer pyridine molecules adsorbed on roughened silver electrode surface. SERS is of great importance because of its significant advantage on the studying of biosystem, such as protein [15,16] and nucleic acid [17], and also because of its ability to detect molecule with ultra low concentration, even at the signal-molecule level [18–20]. The mechanism of the SERS could be illustrated by electromagnetic enhancement [21–23] and chemical enhancement [20,24]. The basic principle of the increasing SERS effectiveness lies on the spatially localized regions with strongly enhanced local electromagnetic fields of the metallic nanoscale surface or nanoparticle [25,26]. Thus, many promising nanostructures have been studied for creating hot spots of SERS, such as nanoball [27], nanorods [28], nanostars [29], and other special nanostructures [30]. For example, gold nanocubes, octahedra, and rhombic dodecahedra have been successfully synthesized by Wu et al. [31]. It has been found that these gold nanostructures with non-spherical symmetry are excellent SERS substrates. Especially, the rhombic dodecahedra with a rhombus edge length of 32 nm showed better enhancement of Raman scattering.

With the purpose of combining advantage of the beneficial plasmonic properties of both silver and gold in a single nanoparticle, some Au–Ag bimetallic nanostructure are synthesized [32–37]. By using Au–Ag core-shell nanostructure, SERS has been applied to the sensitive detection of DNA and other biomolecules [38–40]. For example, Au–Ag core-shell nanoparticles are developed to be a

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sensitive biosensor for detecting schistosomiasis japonica by Huang [41]. SERS of Au–Ag core–shell nanoparticles with controlled shell thickness had also been used in the detection of adenosine [39]. It has been found that the strong enhancement and low detection limit could be obtained as the substrate has an Ag shell thickness of 12.4 nm. In recent years, gold and silver nanoparticles with cubic shape have been successfully synthesized [31,42]. In the study of Tsao et al. [42], Au–Ag core–shell nanostructures with cubic, truncated cubic, cuboctahedral, truncated octahedral, and octahedral shape have been synthesized. The size of those Au–Ag core–shell cubes and octahedra could be tuned by increasing the concentrations of reagents. Because of the effect of the gold cores, the major LSPR peak for these nanoparticles are red-shifted compared to Ag particles with similar size. How about the SERS activity of the core–shell structural Au–Ag bimetallic nanocubes? In this paper, we couple the silver and gold as a single core–shell nanostructure. And the SERS activity of the gold nanocubes coated with a silver nanoshell has been studied. It has been found the SERS activity greatly depends on the geometry factors of the silver-coated gold nanocubes. By tuning the edge length of gold nanocube and the silver coating thickness, the SERS activity has been effectively improved.

2. Experimental

2.1. Reagents

The following reagents were used: cetyltrimethylammonium bromide (CTAB) (98%, Sigma–Aldrich), chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) (99.99%, Sinopharm Chemical Reagent Co. Ltd), ascorbic acid (AA) (Tianli Chemical Reagent Co. Ltd), sodium borohydride (Tianjin Kermel Chemical Reagent Co. Ltd), silver nitrate (AgNO_3) (>99.9%, Aldrich), sodium hydroxide (NaOH) (Tianjin Kermel Chemical Reagent Co. Ltd), Milli-Q water (18 M Ω).

2.2. Fabrication of Au nanocubes and Au–Ag nanocubes

Silver coated gold nanocubes were synthesized by using the method called seed-mediated growth [43,44]. In the first stage, gold seed was produced by mixing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.125 mL, 0.01 M) and CTAB (3.75 mL, 0.1 M) with freshly cold sodium borohydride solution (0.3 mL, 0.01 M). After that, they were putted into water bath with 27 °C lasting 1 h. Then the growth solution was prepared by adding CTAB (1.6 mL, 0.1 M), water (8 mL) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.2 mL, 0.01 M) into ascorbic acid solution (0.95 mL, 0.1 M), which was followed by frequent shake. The last step was adding gold “seed” into the growth solution, and putting the mixture in water bath with 27 °C. This stage lasted for up to nightlong. The colorless solution turned to bright rose. For investigating the relationship between the size of gold nanocubes and SERS effect, we prepared gold nanocubes with different length. In order to obtain the gold nanocubes with different size, gold seed of 20, 30, 40, 60 and 80 μL were respectively added when we prepared the growth solution.

Au–Ag nanocubes were fabricated by using as-prepared Au nanocubes, whose diameter is about 47 nm and the absorption peak is about 540 nm, as the cores. Firstly, in order to remove CTAB on the surface of gold nanocube, 3 mL gold nanocubes were washed twice under the centrifugal condition (7500 rpm, 15 min and 25 °C). Then the washed gold nanocubes were dissolved into CTAB (3 mL, 0.08 M). Next, the vessel was shaken after added AgNO_3 (40 μL of 0.01 M) into it, which was followed by adding ascorbic acid (0.2 mL, 0.1 M) and sodium hydroxide (0.6 mL, 0.01 M) into the solution. Lastly, the reaction solution was put in the water bath with 65 °C lasting 4 h. The bright rose solution turned into orange, then yellow, and then white caused by the thickness increase of the silver shell.

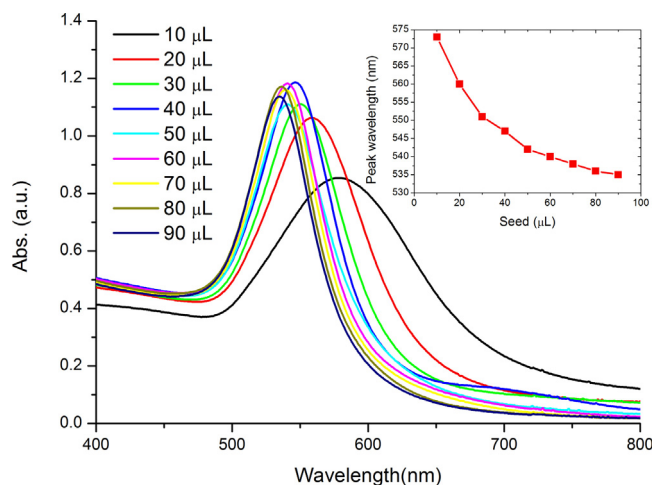


Fig. 1. Absorption spectra of Au nanocubes with different edge lengths. The inset shows the wavelength of the LSPR as a function of the volume of Au seed.

For investigating the SERS effect of Au–Ag core–shell nanoparticles with controllable shell thicknesses, we prepared five samples with different Ag shell by using same size of gold nanocubes. In order to obtain the gold nanocubes with different silver coating thickness, AgNO_3 (0.01 M) with different volume of 20, 60, 100, 200 and 400 μL were added in the solution, respectively.

JEM-200CX transmission electron microscopy (TEM) (JEOL, Japan) and UV-3600 UV–visible spectrophotometer (Shimadzu, Japan) were used to characterize the size, shape, composition and optical properties of Au and Au–Ag nanocubes.

2.3. Raman spectroscopy

One of important applications of nanoparticle is their SERS effect, which could be used in the detection of molecules with low concentration and high sensitivity. In this paper, we use R6G as the probe to study the SERS activity of the Au and Au–Ag nanocubes. Raman spectra were recorded at room temperature by a Raman spectrometer (HORIBA JOBIN YVON, France). The spectra were collected over the range from 400 to 1800 cm^{-1} . A He–Ne visible laser with a wavelength of 633 nm was used as the excitation source. In the measurement, 20 μL of the mixed solution was dropped in a quartz glass substrate at room temperature. We took multiple group measurements at the same location on each sample to ensure the accuracy and stability.

3. Results and discussion

The UV–vis absorption spectra of gold nanocubes with different volume of gold seed are shown in Fig. 1. To avoid oxidation and aggregation of the Au–Ag nanocubes, the samples are reserved in raw-prepared solution or 0.1 M CTAB solution at room temperature. The inserted plot in Fig. 1 shows the wavelength position of the LSPR as a function of the volume of gold seed. In this inset, the volume of gold seed ranges from 10 to 90 μL , which results in the dramatically blue shift of the LSPR peak from 573 to 535 nm. A TEM image of gold nanocubes with an edge length of 63 nm is shown in Fig. 2(a), in which the gold seed is 20 μL and the peak of the absorption spectrum locates at 560 nm. Fig. 2(b) shows a TEM image of gold nanocubes with a edge length of 47 nm, in which the gold seed is 40 μL and the peak locates at 540 nm. These results indicate that the size of gold nanocubes could be tuned by changing the volume of gold seed.

The absorption spectra of gold nanocubes with different silver coating thickness are compared in Fig. 3(a). The as-prepared

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