



Vapor-phase preparation of gold nanocrystals by chloroauric acid pyrolysis



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ABSTRACT

We report that gold nanocrystals can be prepared from vapor phase using chloroauric acid (HAuCl₄) as the precursor. By tuning the vapor-phase deposition parameters, the size and space distribution of the gold nanocrystals can be well controlled on substrates. Systematic control experiments demonstrate that intermediate AuCl and AuCl₃ products pyrolyzed from HAuCl₄ play an essential role in this vapor-phase deposition process. Compared to conventional wet-chemical synthesis process, vapor-phase process enables direct deposition of gold nanoparticles on solid substrates with better coverage and uniformity, which may find applications in surface-enhanced Raman scattering and plasmon-enhanced photocatalysis.

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1. Introduction

Gold nanostructures have tremendous potential applications due to their unique electronic, optical and catalytic properties [1–6]. Most of their applications are strongly dependent on the size, shape and surface properties of gold nanostructures. Therefore, seeking for controllable methods to prepare gold nanostructures has been an active research area for the past decades. Generally, there are two main well-developed approaches in the preparation of gold nanostructures, *i.e.*, top–down fabrication and bottom-up wet-chemical synthesis. Top–down technique provides freedom of design for planar patterns with high resolution and position accuracy for solid-state-device applications, but it usually involves lithographic process requiring costive vacuum facilities for large-scale fabrication [7,8]. Meanwhile, the fabricated nanostructures are polycrystalline with high surface roughness. Both grain boundaries and surface roughness result in the damping of hot electrons, which may degrade the electronic, optic and catalytic performances of gold nanostructures for applications [1,9,10]. On the contrary, wet-chemical synthesis could provide low-cost and large-scale preparation of monodispersed single-crystalline gold nanostructures with varied morphologies and surface chemistry for solution-based applications, but it requires an additional complicated assembling process for the

specific applications on solid surface. As the nanoparticles tend to aggregate during the drying self-assembly process, it is difficult to obtain highly monodispersed nanoparticles with controlled space distribution on the solid surfaces, which limits the applications of wet-chemical synthesis in solid-state devices. Meanwhile, the surfactants, usually involved in the wet-chemical synthesis process, are difficult to completely remove from the particle surface, which have negative effects on the performance of gold nanoparticles in plasmonic and catalytic applications [11,12]. Therefore, developing alternative methods which have potential to overcome the limits of the existing top-down or wet-chemical techniques for preparing gold nanostructures is still interesting and required.

Vapor-phase synthesis is a versatile, flexible and scalable technique to prepare nanostructures with high crystallinity and clean surface on various substrates [13–16]. Researchers have made many attempts to use vapor-phase method to prepare gold nanostructures. For example, Kim et al. demonstrated the preparation of high-quality single-crystalline gold nanowires via the vapor-transport method using bulk gold pellets as the precursor [16,17]. However, this process requires temperature higher than 1000 °C to vaporize the bulk gold precursor. To lower the synthesis temperature, Igumenov et al. attempted to use metalorganic precursors to prepare gold nanoparticles [18]. In this case, to avoid the deposition of carbon substance, the deposition temperature should be as low as possible and thus it is difficult to obtain gold nanoparticles with high crystallinity.

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In this work, we report a facile vapor-phase deposition process to prepare high-quality gold nanostructures with well-defined shapes using chloroauric acid (HAuCl_4) as the precursor. It has been known that HAuCl_4 is the most widely used reactant in wet-chemical synthesis of gold nanoparticles and can also be *in situ* decomposed into gold via pyrolysis or solution-based aerosol deposition process [19,20]. In our work, we found that HAuCl_4 can be readily decomposed into evaporable products which can further transport to other solid substrates to form gold nanocrystals at relatively low temperature. We demonstrate that the size and space distribution of the gold nanocrystals can be tuned by controlling the deposition parameters in a tube-furnace system. With a systematic study and *in-situ* experiments, a possible mechanism is also proposed to explain this vapor-phase deposition process. With this unique technique, single-crystalline gold nanocrystals without any surface contaminations can be prepared in large scale on solid substrates, which have potential for plasmonic and catalytic applications.

2. Experimental section

2.1. Vapor-phase deposition process

To quantify the amount of gold element in the experiment each time, one gram $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (purity > 99.999%, Sinopharm Chemical Reagent Co., Ltd) was dissolved in 40 ml ethanol absolute, and gold element concentration was ~ 74 mM. For each deposition, 80 μl chloroauric acid solution was loaded into quartz boat. Ethanol solution was feasible to evaporate as vapor phase under the condition of low pressure and mild heating before the decomposition of chloroauric acid. Note that HAuCl_4 solution enables accurate loading of the HAuCl_4 source, which is essential to the vapor-phase deposition process. The tube-furnace system was purchased from Hefei Kejing Corp. HAuCl_4 source together with SiO_2 (300 nm thickness on Si) substrates were put into 60-mm-diameter quartz tube equipped with a rotary pump and carrying gas (N_2). HAuCl_4 precursor was loaded in the upstream and the substrates were put in the downstream. The control of in-tube work pressure was realized by the dynamic equilibrium between injecting N_2 and pump rate. Heating procedure is programmed by micro-computer integrated in the furnace system. For example, the tube furnace was first heated from room temperature to a certain high temperature (e.g. 600 °C) with a constant heating rate (e.g. 40 °C/min), then kept at the high temperature for a certain time, and finally cooled down to room temperature naturally by turning off the heating units.

2.2. Characterization

2.2.1. SEM and HRTEM

The morphology of gold nanoparticles was characterized using Scanning Electron Microscopy (Hitachi S-4800 & FEI NanoLab Helios 600i) with 10 kV accelerating voltage and work distance of 8 mm. The as-prepared gold nanoparticles were on SiO_2 substrates. To prepare TEM sample, we scratched the gold nanoparticles off the substrates to ethanol solution using the edge of a fresh silicon wafer. With ultrasonic bathing, we made the gold nanoparticles dispersed and then dripped the solution onto a copper TEM grid coated with an ultrathin carbon film (~ 10 nm). The high resolution TEM metrology was done by a FEI Titan G2 machine with an accelerating voltage of 300 kV.

2.2.2. EDS and XPS

A HORIBA energy dispersive X-ray spectroscopy attached to HITACHI scanning electron microscopy operated at 20 kV was characterized to target sample. X-ray photoelectron spectroscopy

(Thermo Scientific, ESCALAB-250Xi) was used to study the chemical valence of the materials. Specimens were analyzed in high vacuum environment (10^{-7} mbar, 25 °C) utilizing Al K α at 20 kV with a power of 200 W.

2.2.3. In-situ TEM

The sample for *in-situ* TEM experiment was prepared with HAuCl_4 source temperature at 500 °C but TEM grid was put at room temperature in 9 Torr pressure. *In-situ* TEM experiment was carried out using a JEOL JSM-2010F Transmission Electron Microscope (200 kV accelerating voltage) which is integrated with a digital heating system.

2.2.4. The sample preparation procedures for Raman measurements

We compared the Raman scattering signals between a 50 nm thick gold film and the sample prepared by our vapor-phase deposition method. We immersed two samples into 10^{-5} M Rhodamine-6G (R6G) aqueous solution for 12 h, then rinsed two substrates with ethanol completely and spontaneously dried them at room temperature. The rinsing process ensured the formation of only a monolayer of R6G over the surface of Au.

2.2.5. Raman scattering measurements

Raman scattering spectra of two selected samples were measured on a HORIBA JOBIN YVON HR800 UV Raman Spectroscopy imaging system. The excitation source was 532 nm. Raman signals were collected using a 50x objective (numerical aperture, N.A. = 0.5) under laser power intensity of 0.5 mW and with integration time of 60 s.

2.2.6. Dark-field imaging and scattering measurements

Dark Field imaging and the scattering spectroscopy of single gold nanocrystal were measured on a WITec Confocal Raman Imaging Microscope System alpha 300R. A halogen lamp (15V, 3150 K) with 100 W power intensity was used as white light source and illuminated to the sample via an dark-field objective lens (N.A. = 0.75, 100 \times). All of the samples were measured with the integration time of 20 s. The calculation of dark-field scattering spectrum was referred to the formula as follow:

$$I_{\text{scat}}(\lambda) = \frac{I_{\text{particle}} - I_{\text{sub}}}{I_{\text{halogen}} - I_{\text{dark}}}$$

where $I_{\text{scat}}(\lambda)$ presents the real scattering spectra of single nanoparticle; the spectrum of I_{particle} , I_{sub} , was separately collected from then original particle and surrounding substrate. I_{halogen} , I_{dark} is the spectrum of halogen light source and background count of measurement system, respectively.

3. Results and discussion

3.1. Preparation and morphology characterizations

Fig. 1a shows the schematic of the experimental setup for the vapor-phase deposition process. Fig. 1b shows a scanning electron microscopy (SEM) image of the resultant monodispersed gold nanocrystals with well-defined shapes on a SiO_2 (300 nm thick on Si substrate) surface. We observed that most of the obtained nanocrystals are octahedral, as shown by the enlarged SEM images in Fig. 1b. The trend to form octahedra is because the gold nanoparticles tend to expose their {111} crystal facets due to the energy minimization during the growth process [21]. To further investigate the morphologic uniformity of the synthesized gold nanocrystals, we studied their plasmon resonance properties using single-particle dark-field scattering measurements [22,23]. Fig. 1c shows the corresponding dark-field optical micrograph of the nanocrystals.

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