Preparation and Characterization of a large-scale gold nanofilm

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Abstract. Large-scale nanofilms were of great interest in the field of nanophotonics, mainly due to their unique optical properties. Two dimensional (2D) large-scale gold nanofilm was fabricated by an interface self-assembly method based on sodium citrate-capped gold nanoparticles (AuNPs). AuNPs was firstly characterized by UV-vis spectra and transmission electron microscopy methods. The prepared large-scale gold nanofilm was characterized by scanning electron microscopy technology. We expected this method and the prepared nanofilm would apply in biosensors and functionalized optical devices.

1. Introduction

Two dimensional (2D) large-scale nanofilm has aroused attention extensively in the field of material science, analytical chemistry, biomedicine and environmental protection in recent years. Many research efforts have been devoted to prepare large-scale 2D nanofilm, including Langmuir–Blodgett compression and transfer methods, soft template and hard template methods, spin-coating method, self-assembly method, and so on [1]. Among them, the bottom-up” self-assembly approaches allow one to controllably fabricate large-area gold nanofilm in a rapid and cost-effective manner, thus attracting considerable scientific interest in recent years [2]. For example, Zhang et al fabricated a macroscopic 2D plasmonic gold superlattices by a process of assembly of high-index faceted gold nanocrystal building blocks (NBBs) at the air–liquid interface. The self-assembled superlattices structure were characterized by Vis-NIR optical and measurements and morphology analyses [3]. Yang et al reported a self-assembly method to prepare Au NPs into monolayers and deposit those monolayers onto arbitrary solid substrates. The SERS enhancement performance and the application of the gold nanostructure were studied in detail [2, 4, 5]. A gold nanofilm prepared by simple vortex mixing of gold colloids and n-hexane was employed to determine trace ciprofloxacin in fish meat [6]. Based on porous silicon (PSi) as template, an Au nanofilm-coated PSi was investigated and established, the authors proved that the composite nanofilm was an excellent SERS substrate [7]. Additionally, it was reported that the shape of the nanoparticles in the assembled nanofilm structure was quite important. Polygon nanoparticles was not the ideal particles for self-assembly [8]. These studies showed that 2D large-scale nanofilms usually have distinct physical and chemical characters that are quite different from those of either single nanoparticles or their bulk material. These features guarantee that Au nanofilm can be developed for use in optoelectronic devices, biochemical sensors, environment air monitors, gene diagnosis and so on. In this context, we preliminarily prepared and
characterized a large-scale gold nanofilm, and expected the as-prepared gold nanofilm to apply in nanophotonics, biomedicine, chemistry and material science.

2. Materials and Methods

2.1. Material
Chloroauric acid (HAuCl$_4$), sodium citrate dihydrate (trisodium citrate or Na$_3$Cit, 99%) were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd. (China). All chemicals were of analytical grade and used without any further purification. Ultrapure water (Resistivity > 18.25 MΩ•cm) was used for all solution preparation and throughout the experiments.

2.2. Instrumentation
A Shimadzu UV-2600 was used to characterize ultraviolet–visible (UV-vis) spectra of gold colloid. All spectra of the colloidal solutions were measured in the range from 300 to 900 nm at a resolution of 0.5 nm. Transmission electron microscopy (TEM) images were measured with a JEOL JEM-2100 electron microscope at an accelerated voltage of 200 kV. The scanning electron microscopy (SEM) images were recorded using a FEI Quanta 250 FEG field-emission scanning electron microscope at high vacuum conditions with a voltage of 30 kV.

2.3. Synthesis of gold nanoparticles
The colloidal gold nanoparticles (AuNPs) were prepared by reducing chloroauric acid with sodium citrate. Typically, 500 μL of 1% HAuCl$_4$ aqueous solution was added into a 50 mL of round-bottomed flask and heated to boiling (about 93 °C). Then, 290 μL of 1% Na$_3$Cit aqueous solution was quickly added. The reaction was performed about 30 min and naturally cooled to room temperature. The as-prepared AuNPs were employed to characterize and prepare the large-scale gold nanofilm.

2.4. Cleaning of glass slide and preparation of gold nanofilms
The cleaning progress of glass slide was reference to previous report [9]. The washed glass slides were dried by nitrogen and for gold nanofilms deposition. The interfacial self-assembly of AuNPs was performed using a previously reported method with a slight modification [10]. The colloidal gold nanoparticles solution was dropwise added to the methylbenzene and ethanol mixture solution (1:1, v:v). Waiting ten minutes, the washed glass slides were employed to raise the large-scale gold nanofilm. Finally, the deposited and transferred large-scale gold nanofilms were dried at room temperature.

3. Discussion
The ultraviolet-visible spectra in Fig. 1A showed that, the maximum ultraviolet–visible absorption wavelength of Au NPs was at 558 nm, and the spectral full width at half maxium (FWHM) was 98 nm. According to the calculated absorption spectrum, this is attributed to nanosized metallic gold particles [11]. Further characterization is obtained by TEM. The corresponding transmission electron microscopy and histogram (Fig. 1B and 1C) showed formation of spherical particles with an average diameter equal to 35 nm and a polydispersity of 28%. In generally, surface modification would be beneficial to prepare nanofilms. However, in order to prove the method can also prepare gold nanofilm at the liquid-liquid interface. We employed this gold colloid without further surface modification.
Fig. 1 Optical characterization and morphology of AuNPs. A) UV-vis spectra. B) TEM image. C) TEM image. Scale bar: 200 nm.

Previous literature has reported that a crack-free, well-ordered and large-area gold nanoparticle films have enormous application potentiality in the field of electronic, photonic, and sensing applications [12]. Fig.2 showed the digital photograph of the prepared large-scale gold nanofilm before and after deposited on glass slides. The large-scale gold nanofilm showed no observable cracks and impurities. These primary results showed that this method can prepare large-area gold nanofilms.

Fig. 2 Optical image of the AuNPs nanofilm before A) and after B) deposited on glass slides.

In order to recognize the microstructure of the nanofilm, a SEM image was exhibited in Fig.3. The surface morphology of gold nanofilm showed that gold nanoparticles have a certain scale of aggregation. However, the whole glass slide was covered with AuNPs. The distance between two particles was only tens of nanometers. The major factors affecting the ordering of the large-area gold nanofilm mostly come from the monodispersity of AuNPs, the rate of the adding and the deposition and transfer process. From these results, it is concluded that the microscopic large-area gold nanofilm could be easily fabricated, but the very tiny scale of ordering need to improved.

Fig. 3 SEM images of large-area gold nanofilms deposited on glass slides substrates. Scale bar: 5 μm
4. Conclusions
In this work, we have synthesized citrate-capped AuNPs and fabricated a large-area gold nanofilm by
directly adding the nanoparticles into methylbenzene and ethanol mixture solution. The structure and
morphology of the large-area gold nanofilm were carried out by optical and SEM images analysis.

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