One-Step Synthesis of Au Nanoplates with the Assistance of Formaldehyde

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Abstract. In this work, a facile method has been developed to fabricate Au nanoplates in one step through heating formaldehyde and HAuCl₄ aqueous solution. The obtained Au nanoplates are single crystal with an average edge length of approximately 160 nm. And the formation of plate-like Au nanostructures is because of the adsorption of formaldehyde on the surfaces of Au nanostructures, leading to a similar surface energy of {111} and {100} facets.

1. Introduction

In the past decades, gold nanostructures have been widely studied due to their unique size and morphology dependent electronic, chemical, physical, and optical properties [1]. To date, a myriad of gold nanostructures, such as nanoparticles, nanorods, nanorings, nanowires, nanodisks, nanocubes and branched nanocrystals, have been synthesized [2, 3], and they are widely used in the fields of catalysis, biomedicine, biosensing, imaging and photoelectronic devices [4, 5].

Two-dimensional (2D) Au nanoplates have recently attracted much attention among those gold nanostructures, mainly due to a strong plasmon band of these 2D nanostructures in the Near Infrared Ray (NIR) region. Nanoplates with plasmon bands in the NIR region are very sensitive to the changes of small morphology and close environment, providing possible applications in cancer hyperthermia, sensing, imaging, and biological assays [6]. Meanwhile, 2D nanoplates with long edges and sharp vertices present enhanced electric field at the vertices and anisotropic electrical conductivity [7]. Therefore, they are excellent candidates of information storage, photonics and optoelectronics, metal enhanced fluorescence and surface enhanced Raman scattering [8]. Additionally, Au nanoplates are also good substrates for tip-enhanced Raman scattering measurements, because of the atomically flat surfaces of Au nanoplates, easy deposition of analytes on surfaces, and higher enhanced factor between gold surfaces and metal tips. It is also reported that Au nanoplates provides new possibilities for fundamental studies and potential applications in catalyzing, and new nanodevices [9].

Nowadays, a variety of methods have been exploited to get these anisotropic Au nanoplates. The most common method for the formation of Au nanoplates is the seed-mediated approach [10]. In this method, nanoparticles with the diameter of 3-6 nm are prepared firstly, and then they are mixed with a solution of HAuCl₄, reducing agent and surfactant. Another conventional method is the polyl process, in which the Au nanoparticles are generated by heating a mixed solution of HAuCl₄, surfactant and ethylene polyol above 120 °C for several hours. Aldehyde group is formed in this method when the reaction temperature is higher than 100 °C.[11] It is reported that this aldehyde group can be used to reduce AuCl₄⁻ and the intermediate induced by oxidized aldehyde group plays an important role in the formation
of Au nanoplates[12]. However, the above seed-mediated method is complex, in which two separate steps are needed, including formation of Au nanoparticles and growth of Au nanoplates. As for the polyol process, the reaction temperature is high, which is energy-intensive and unsafe.

Here, we developed a simple one-step method to fabricate Au nanoplates with the assistance of formaldehyde. The morphology and crystal structure of obtained Au nanoplates were analyzed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Also, the formation mechanism was discussed.

2. Experimental Section

2.1. Materials and Chemicals
Formaldehyde (36.5-38%) was purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) was purchased from Alfa Aesar. All the chemicals were used without further purification.

2.2. Preparation of Au Nanoplates
The reaction solution was prepared by adding 1 mL formaldehyde and 0.5 mL of 10 mM HAuCl₄·3H₂O into 9 mL deionized water. Then the reaction solution was heated at 40 °C for 5 h. After the heat treatment, the final product was obtained by centrifugation at 6000 rpm for 30 min.

2.3. Characterization
Au nanoplates obtained from previous steps were first ultrasonicated for 3 min as the pre-process for characterization, making sure that the Au nanoplates were well dispersed in solution. The ultrasonic cleaner used in our research was KS-120D. Before the characterization of TEM, 10 μL of the well-dispersed products was dripped on carbon-coated copper grids. Then TEM and High-resolution TEM (HRTEM) images were taken by using a JEOL JEM ARM200F. For the characterization of SEM, a drop of these nanoplates was placed on a 1 x 1 cm² silicon slide. After the samples dried, SEM images were collected by a FEI Nova NanoSEM 450.

3. Results and Discussion

![Figure 1](image1.png)

**Figure 1.** a) The typical TEM image of Au nanoplates. b) TEM and c) SEM images of an individual Au nanoplate.
In this work, Au nanoplates were fabricated in one step with the help of formaldehyde. Fig. 1 shows the morphology of Au nanoplates. As shown in Fig. 1a, the average edge length of Au nanoplates is about 160 nm and the shapes of them include triangle, truncated triangle and hexagon. In Fig. 1b, the TEM image of an individual Au nanoplate exhibits contrast in its surface. This is because of the existence of the internal stress, which is caused by the buckling of the ultrathin nanoplate [13].

Fig. 2a shows the HRTEM image of the Au nanoplate. It demonstrates that the Au nanoplate is single-crystalline. And the fringe spacing is 0.14 nm, which is indexed to \{220\} reflections of face center cubic (fcc) Au [14]. Its corresponding Fourier transform pattern is shown in Fig. 2b. The hexagonal Fourier transform pattern demonstrates that the flat surface of the Au nanoplate is \{11\}\_1\} face, as reported previously [15]. And each nanoplate is bounded by two \{11\}\_1\} planes as the top and bottom faces and a mixture of \{11\}\_1\} and \{10\}_0\} planes as the side faces [15].

**Figure 2.** a) HRTEM image and b) corresponding Fourier transform pattern of the Au nanoplate.

In the formation of Au nanoplates, Au precursors are firstly reduced to Au atoms by formaldehyde. Then Au atoms grow to Au nanostructures with plate-like shape[16]. In the shape control of Au nanostructures, it is reported that the adsorption of an appropriate ligand can control the morphology of nanostructures through interaction between ligands and metal facets[17]. In this research, the surface energy of \{11\}_1\} planes is lower than that of \{10\}_0\} and \{11\}_0\} planes after the adsorption of formaldehyde on surfaces of Au nanoplates. Meanwhile, the surface energy of \{10\}_0\} planes is close to that of \{11\}_1\} planes. Thus, Au atoms grow to Au nanostructures with plate-like shape finally, as reported in previous research[16]. And further study on the formation of Au nanoplates is still in progress.

4. Conclusion
A facile one-step method has been developed to fabricate Au nanoplates through heating formaldehyde and H\text{AuCl}_4\ aqueous solution at 40 °C. The obtained Au nanoplates are single crystal and their average edge length is approximately 160 nm. And the formation of plate-like Au nanostructures is because of the adsorption of formaldehyde on the surfaces of Au nanostructures, leading to a similar surface energy of \{11\}_1\} and \{10\}_0\} planes.

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