

Facile Synthesis of Gold Nanoplates by Citrate Reduction of AuCl₄⁻ at Room Temperature

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Abstract: Single-crystalline, regular-edged gold nanoplates are synthesized through chemical reduction of AuCl₄⁻ by a suitable amount of citrate at room temperature, without additional capping agents or surfactants. The suitable molar ratio of sodium citrate to HAuCl₄, low reaction temperature and the presence of natural light are critical factors for the formation of the regularly shaped nanoplates.

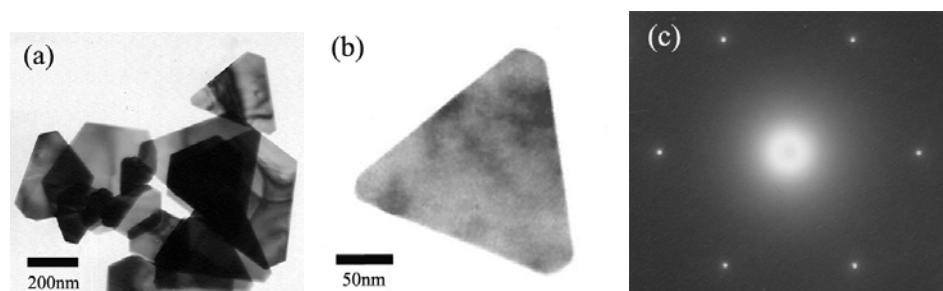
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Metal and semiconductor nanoparticles with nonspherical shapes, such as wires¹, cubes^{2,3} and belts⁴, have been drawing a great interest in scientific community as a result of their physical and chemical properties being distinctly different from conventional spherical particles. Particularly, much effort has been made to synthesize plate-like nanoparticles, which exhibit interesting surface plasmon absorption in the visible-near-infrared (Vis-NIR) region. For the gold nanoplates as concerned, various chemicals such as PEO-PPO-PEO block copolymers⁵, *ortho*-phenylenediamine⁶, dimyristoyl-L- α -phosphatidyl-DL-glycerol⁷ and salicylic acid⁸ have been used as capping agents to control the growing rate of different crystal facets of gold leading to gold nanostructures with plate-like shapes. Recent promising work in this field is the preparation of gold nanoplates by chemical reduction of hydrogen tetrachloroaurate by a reduced amount of sodium citrate in the presence of poly (vinyl pyrrolidone) at a boiling temperature, which kinetically adjusts the reaction pathway to a stepwise self-seeding growth of the nanoplates⁹. In this paper, we describe that with suitable molar ratio of sodium citrate to HAuCl₄, single-crystal, gold nanoplates with regular edges still can be synthesized at room temperature, without additional capping agents or surfactants. The yield of the gold nanoplates is ~60-70%.

In a typical synthesis, 1.3 mL of 1% hydrogen tetrachloroaurate (HAuCl₄·4H₂O) was added to 100 mL of 18 M Ω cm⁻¹ water at room temperature. After 1 min of stirring, 0.4 mL of 38.8 mmol/L sodium citrate was added. The mixture was stirred for an additional 30 min and exposed to the natural light of an ambient laboratory for 16 h. As

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Figure 1 (a) TEM image of the as-prepared gold nanoplates, (b) TEM image of a single truncated triangular nanoplates and the corresponding SAED pattern (c)



a result, we found plenty of particles with brown color suspended in the resulting solution. These particles were collected by centrifugation at 3000 rpm for 20 min and the supernatant were removed. After then, the precipitates were dispersed in deionized water for further measurements.

Morphologies of the gold products were observed under a JEM-2000EX transmission electron microscopy (TEM) operated at 100 kV. As is shown in **Figure 1a**, the main products were nanoplates. Though the nanoplates randomly overlapped when the sample was dropped on carbon-coated copper grid, the shape of them can be clearly outlined. These nanoplates are 200-500 nm in size along their longest edge, exhibit triangular and truncated triangular shapes with regular edges. The continuous and randomly distributed pairs of bending contours in the flat crystal faces are caused by the warping of the atomic planes with respect to the direction of the incident electron beam¹⁰. **Figure 1b** and **1c** show the higher magnification TEM image of an individual nanoplate and its corresponding selected-area electron diffraction (SAED). In the SAED pattern, hexagonal symmetry of the diffracted spots demonstrates that the Au nanoplate is a single crystal with a preferential growth direction along the Au {111} plane. And the X-ray diffraction (XRD) pattern of the as-prepared gold nanoplates is also displayed in **Figure 2**. An overwhelmingly strong diffraction peak located at 38.4° is ascribed to the {111} facets of face-centered cubic metal gold structures (JCPDS No. 4-0783), while diffraction peaks of other four facets are much weak. It confirms that the nanoplates are mainly dominated by {111} facets, which are preferentially oriented parallel to the supporting surface⁶. Furthermore, **Figure 3** displays a typical UV-Vis spectrum of the gold nanoplates with two surface plasmon resonance (SPR) bands centering at 530 and 940 nm. The presence of the longer wavelength component is a clear indication of anisotropic feature, a result that is consistent with TEM analysis of triangular and truncated triangular nanoplates.

For comparison, when the solution with the molar ratio of sodium citrate to HAuCl₄ changed to 2.5, we can mainly obtain polyhedral nanoparticles coexisting with few nanoplates (**Figure 4**). This suggests that the suitable molar ratio of sodium citrate to HAuCl₄ is a crucial factor in determining the morphology of the final gold nanoparticles.

Figure 2 XRD pattern of the as-prepared gold nanoplates

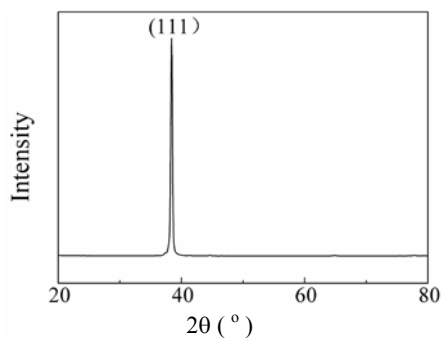


Figure 3 UV-Vis spectrum of the as-prepared gold nanoplates

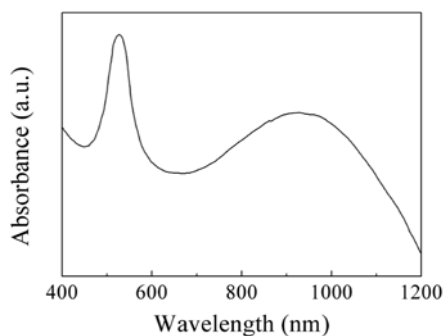
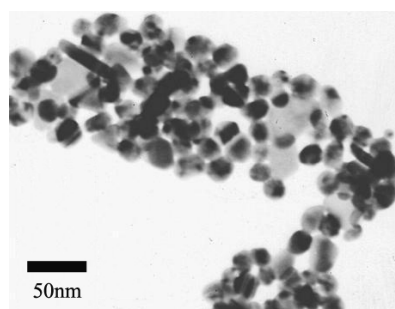


Figure 4 TEM image of gold nanoparticles with the higher molar ratio of sodium citrate to HAuCl_4



The formation mechanism of this synthesis can be assumed as a result of kinetically preferred growth of the superfluous gold ions in the lateral direction of the small gold nuclei⁹. Furthermore, as is known, the temperature has a significant influence on the reduction rate¹¹. At room temperature, the reduction becomes substantially slow and turns into kinetic control, which is suitable for formation of highly anisotropic structures¹¹. So without additional capping agent or surfactant we also can fabricate regular nanoplates.

It is worth mentioning that the presence of natural light is also an important factor

in synthesis of the gold nanoplates. If other conditions were identical, but absence of natural light, the reaction could hardly proceed.

In conclusion, we describe a simple synthesis of single-crystal, regular gold nanoplates with regular edges. This method can be carried out at room temperature and does not need the use of any additional capping agent or surfactant. The suitable molar ratio of sodium citrate to HAuCl_4 , low reaction temperature and the presence of natural light are critical factors for the formation of the regularly shaped nanoplates. Such gold nanoplates may have unique application in gas sensors, the hyperthermia of tumors and other fields.

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