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# Facile synthesis of gold nanoribbons by L-cysteine at room temperature

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**Highly crystalline gold nanoribbons have been synthesized via a simple method by L-cysteine reduction of aqueous chloroaurate ions at room temperature, without additional capping agent or surfactant. Based on transmission electron microscopy (TEM) and UV-vis absorption studies for the intermediate products, the formation of gold nanoribbons is regarded as a kind of oriented attachment growth.**

Gold nanoribbon, L-cysteine, oriented attachment

There is an increasing scientific interest in the synthesis of one-dimensional (1D) metal nanostructures, such as nanowires and nanoribbons (or nanobelts), due to their potential applications in nanoelectronics, optoelectronics, magnetics and other fields[1]. Among these 1D nanostructures, highly crystalline nanoribbons have been intensively studied because they may be an ideal system for studying the fundamental electrical and optical transport processes. Although many methods have succeeded in synthesizing oxide and sulfide nanoribbons[2–4], reports on the preparation of metal nanoribbons are very few and it is still a challenge for materials scientists. Xia et al. prepared silver nanobelts by refluxing an aqueous dispersion of silver nanospheres[5]. Sastry et al. described the synthesis of highly oriented gold nanoribbons through the reduction of aqueous chloroaurate ions by 4-hexadecylaniline Langmuir monolayer[6]. Han et al. fabricated gold nanobelts by a sonochemical route in the presence of $\alpha$-D-glucose[7]. Qi et al. synthesized gold nanobelts by the reduction of $HAuCl_4$ with ascorbic acid in aqueous mixed solutions of the cationic surfactant cetyltrimethylammonium bromide and the anionic surfactant sodium dodecylsulfonate[8]. However, the necessity of several organic compounds or the assistance of additional ultrasound, high temperature or Langmuir monolayer may complicate the reaction system. It is therefore desirable to develop more convenient approaches. Recently, Lee et al. extended the previous research about aspartic acid's unique ability to form gold nanoplates[9], and reported a simple aspartic acid synthesis of gold nanoribbons and nanowires in aqueous solutions[10]. Herein, we show that another kind of amino acid, L-cysteine (Cys), also exhibits the novel shape control over the crystal growth: gold nanoribbons can be synthesized through Cys reduction of aqueous chloroaurate ions at room temperature without additional capping agent or surfactant. Based on the TEM and UV-vis absorption studies for the intermediate products, the formation of gold nanoribbons is regarded as a kind of oriented attachment growth.

In a typical synthesis, 100 μL of 1% aqueous solution of hydrogen tetrachloroaurate was mixed with 20 mL of $2\times10^{-5}$ mol/L Cys solution, stirring for 30 min. Then the mixture was allowed to stand at room temperature for more than 48 h without stirring. No additional reducing agent, capping agent or surfactant was needed.

The morphologies of the gold products are characterized by TEM. Figure 1(a) reveals that the gold products

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present ribbon-like shape with the width 20—45 nm. The contrast in the overlap region of the gold nanoribbons clearly indicates the extremely thin thickness of the gold nanostructures (Figure 1(b))[6]. The inset of Figure 1(a) is the electron diffraction pattern from a single gold nanoribbon. The hexagonal symmetry of diffraction spots is a clear indication that the ribbon-like faces are bound mainly by {111} planes. And the presence of the relatively weak 1/3{422} diffraction spots, which should be forbidden for perfect face-centered cubic (fcc) structure, can be attributed to different factors, such as the presence of atomically flat surfaces[11], surface reconstructions, twin planes and stacking faults parallel to the flat facets associated with dynamical effects of electron diffraction[12,13]. The high-resolution TEM (HRTEM) image of a typical nanoribbon is consistent with the result of the electron diffraction, showing a highly crystalline structure with the fringe spacing measured to be 0.24 nm (Figure 1(c)), which agrees with the 3×{422} superlattice spacing of gold crystal[14]. The X-ray diffraction (XRD) pattern for the sample exhibits reflections characteristic of fcc gold (JCPDS No. 04-0784), revealing that the products are composed of gold (Figure 1(d)).

In this synthesis, gold nanoribbons are formed spontaneously and no additional reductant, ultraviolet irradiation, or electrochemical method is required. That is, Cys can not only be used as reducing agent[15], but also show a special shape control over the crystal growth, implying that the biologically related small molecules may have a profound influence on the gold crystal growth[9,10]. To gain insight into the kinetics of formation of the gold nanoribbons in this experiment, nanoparticles at the intermediate stages of the growth process are characterized by TEM and UV-vis spectros- copy. Figure 2 show the TEM images and UV-vis ab- sorption spectra of samples taken from the reaction mixture at different stages. It can be seen that when ag- ing for 2 h, many small nanoparticles with the diameter of ~3 nm are observed to assemble into chain-like struc- tures (Figure 2(a)). With the aging time prolonged to 6 h, ribbon-like shape appears in some regions of the chain-like assembly (Figure 2(b)). This is corresponding to a weak and broad absorption peak at about 550 nm in the UV-vis spectrum (Figure 2(c)). With the reaction proceeding, the intensity of the UV-vis absorption gradually increases. After 48 h, we find that a certain amount of $AuCl_4^-$ still remains in the reaction solution through a colorimetric method using HBr acid (Figure 3)[16]. However, when the initial concentration of Cys in

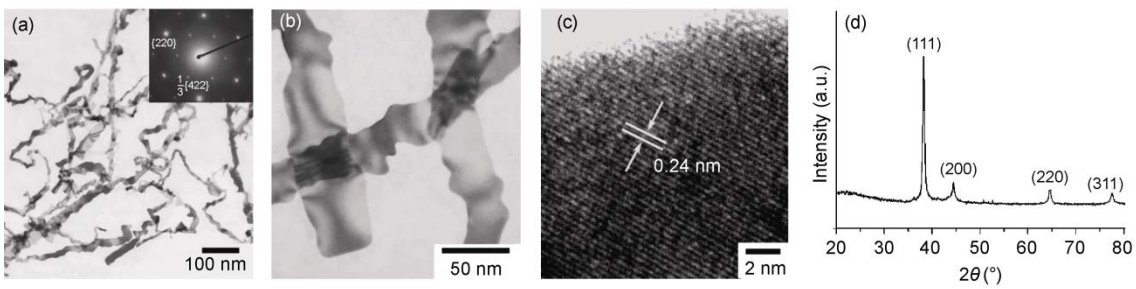


**Figure 1** TEM images of gold nanoribbons with (a) lower and (b) higher magnification, (c) HRTEM image, (d) XRD pattern. The inset of (a) shows the corresponding SAED pattern.

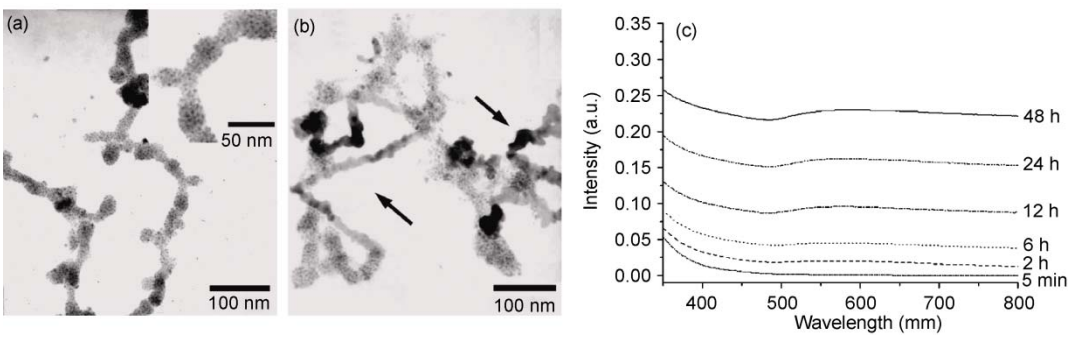


**Figure 2** Typical TEM images of the intermediates after aging for (a) 2 h and (b) 6 h. The inset in (a) is the higher magnification. The arrows in (b) mark the ribbon-like shape in the chain-like assembly. (c) Time evolution of UV-vis spectra indicating the continuous formation of gold nanoribbons.

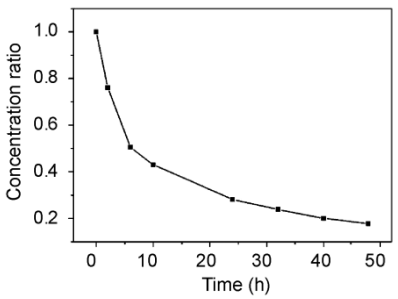


**Figure 3** Time-resolved concentrations of $AuBr_4^-$ in the reaction solution for gold nanoribbons.

the reaction system is increased to $1\times10^{-4}$ mol/L, gold ions are completely consumed after 48 h and only spherical particles are obtained (Figure 4), implying that the relatively excessive chloroaurate has a strong influence on the shape of the product[10,16].

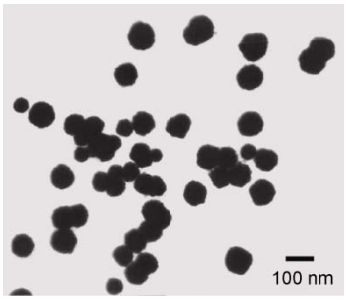


**Figure 4** TEM image of gold nanoparticles synthesized when the initial concentration of Cys is $1\times10^{-4}$ mol/L.

These observations reveal the following two important clues to the formation mechanism of the gold nanoribbons: (1) The nanoribbons grow from chain-like aggregates, which may be caused by three main factors: the weak reducing ability of Cys, the mild reaction condition, and the low molar concentration ratio of Cys to gold ions. The former two factors result in a slow reduction dominated by kinetic control, which is usually responsible for the formation of highly anisotropic structures[17]. As far as the third factor is concerned, the low stability of the nanoparticles due to the insufficient capping of Cys in such a system may also promote the linear aggregation[10,16,18]. (2) The small nanoparticles of the aggregates could rotate to share the same crystallographic orientation with adjacent surfaces, fuse and further crystallize to result in the highly crystalline structures. This phenomenon is named as oriented attachment mechanism, a kind of aggregation-based mechanism, put forward by Banfiled[19] and widely proposed in other reports[18,20–22]. The oriented attachment and growth usually lead to formation of planar defects, including twin planes and other interfaces.

Thus, we can reasonably hypothesize that the formation processes of these gold nanoribbons as follows: First, gold ions are reduced to metallic gold by Cys and form gold nuclei. The nuclei grow into nanoparticles by gathering reduced metallic gold surrounding the nuclei. Due to the insufficient weak reducing agent and the gentle reaction condition, the unstable nanoparticles aggregate linearly. Through oriented attachment, the aggregates gradually fused into highly crystalline nanoribbons. Furthermore, there is something important to be pointed out that though the method employed here is similar to the previous study with amino acids[9,10], the resultant morphology of gold products is much different. The main factor for this difference may be the initial concentrations of tetrachloroaurate, the distinct molar concentration ratio of amino acid to gold ions, and the different reaction kinetics of amino acids with different molecular structures (for example, Cys may have stronger reduction ability through the thiol group than the aspartic acid).

In conclusion, a novel amino acid-based one-step synthesis of gold nanoribbons has been described. The method is simple, conditional gentle and does not need the use of any additional capping agent or surfactant. Moreover, it overcomes the sophistication and high cost of other routes for 1D metal nanostructures fabrication which need organic solvent and the assistance of additional electric field, ultrasound or high temperature, opening up new possibilities for the shape control of other metal nanomaterials. It also provides further insight into understanding the contribution of amino acid residues in biomacromolecules or organisms to the biosyntheses of nanomaterials and the natural process of biomineralization.

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