



## Facile synthesis of networked gold nanowires based on the redox characters of aniline

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### ABSTRACT

Metal nanowires are often used in the study of electron transport properties, electronic device technology and many other fields. We have reported a facile while effecting an approach to networked gold nanowires by taking advantage of the redox characters of aniline at different pH values. The effects of different synthetic parameters, such as mole ratio of HAuCl<sub>4</sub> to aniline, pH value, on the shape and size of the final gold products are investigated. Based on the experimental data, a possible growth mechanism is also proposed. This work probably contributes to not only the fundamental research of shape-controlled nanostructures but also new methods of producing nanoscaled metal wires for nanodevice study.

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### 1. Introduction

Metal nanostructures have been quite attractive due to its unique optical [1,2], electronic [3,4], magnetic [5] and other properties. And the physical and chemical properties are highly dependent on the shape of the nanostructures [6,7]. As a result, shape-controlled synthesis of metal nanostructures is becoming one of the hottest fields in the recent years. Metal nanowires are often used in the study of the electron transport properties and electronic device technology [8,9]. Many methods to obtain metal nanowires reported before were based on physical method which is costly and greatly depends on the apparatus [10]. As a contrast, wet chemical method plays an important role in shape-controlled synthesis of nanostructures in virtue of high output, multiplex routes [11–13], less cost, etc. Hence, to develop a facile wet chemical synthesis method of metal nanowires will be of great significance.

Herein, based on the redox characters of aniline at different pH value, we reported a facile while effective method of synthesizing networked gold nanowires by aniline reducing chloroauric acid. This work will contribute to the fundamental research of shape-controlled nanostructures besides developing new methods to produce nanoscaled conducting wires for nanodevice study.

### 2. Materials and methods

Aniline was purchased from Shanghai Lingfeng Chemical Ltd. and was purified by atmospheric vacuum distillation. Chloroauric acid HAuCl<sub>4</sub>·4H<sub>2</sub>O was obtained from Shanghai NO.1 Chemical Factory

and sodium hydroxide was purchased from Shanghai Jiuyi Chemical Ltd. Both of them were used as received. The networked nanowires were synthesized as following. Briefly, the chloroauric acid was dissolved in water at 25 μM with pH adjusted by sodium hydroxide to 7.0, and heated to 80 °C during a course of 30 min. To 100 ml of this solution, 1 ml of 7.5 mM aniline in water was added under vigorous stirring. The solution was stirred at 80 °C for 2 h. Then the resulting suspension was centrifuged several times and the rinsed samples were redispersed in DI water for further characterization.

The resulting gold nanostructures were characterized by TEM (JEM-2000EX, JEOL) operating at 120 kV. HRTEM images and SAED pattern were characterized by JEOL JEM-2010 TEM operating at 200 kV. XRD spectra was recorded by D/Max RA circumgyration X-ray diffraction instrument (Cu target, λ = 1.5405 Å). Ultraviolet-visible-near-IR (UV–vis–NIR) absorption spectra were recorded by a SHIMADZU UV-3150 spectrophotometer.

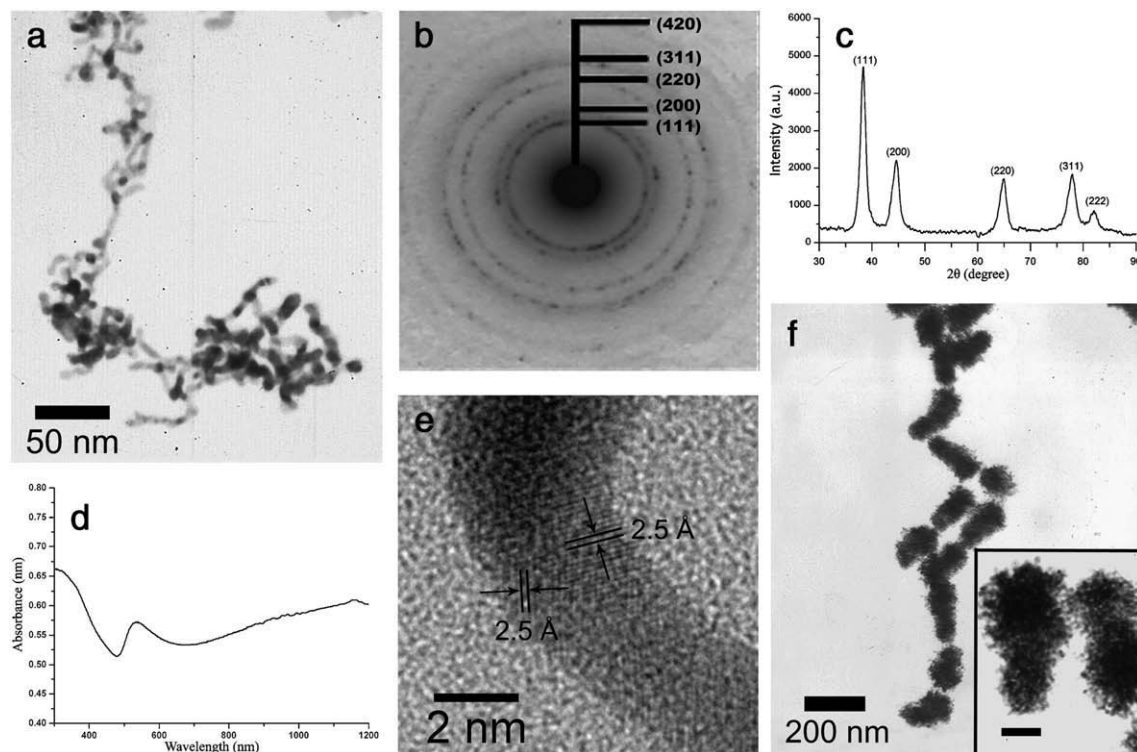
### 3. Results and discussion

During the addition of sodium hydroxide, the chloroauric acid solution faded gradually. After the aniline was added, the reactant turned to salmon pink immediately and then gray blue bit by bit. It is showed distinctly by the TEM micrograph that the nanostructure is crooked nanowires with a 2D networked fabric (Fig. 1a). HRTEM image of part of the nanowire reveals that it comprises caudate gold nanoparticles with crystal facets in different directions, and gold atoms depositing in the clearance of particles to form nanowires (Fig. 1e). Corresponding SAED pattern shows the annular diffraction spots of {111}, {200}, {220}, {311} and {420}, validating the nanowires have a polycrystalline structure (Fig. 1b). Fig. 1c throws out the identical powder XRD pattern of the gold nanostructures. The five Bragg

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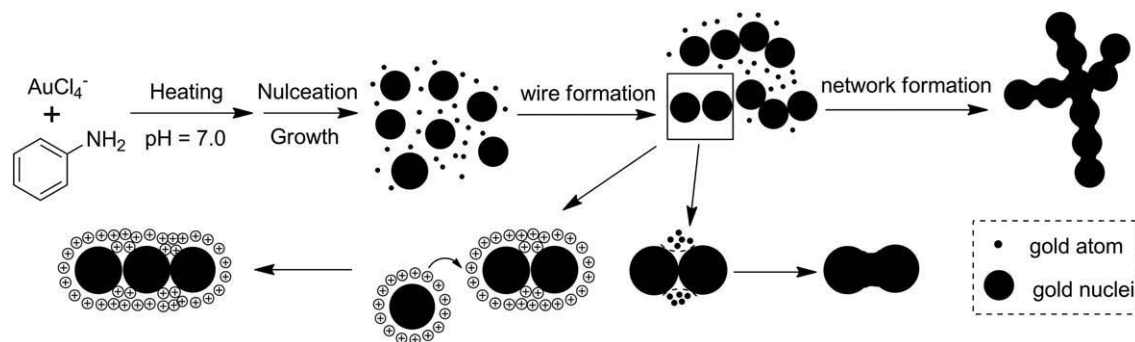
**Fig. 1.** (a) TEM image, (b) the corresponding SAED pattern, (c) XRD pattern, (d) UV-vis-NIR absorption spectra, and (e) HRTEM image of the gold nanowires obtained at 80 °C, pH 7.0. (f) TEM image of the paramecium-like gold nanoaggregates obtained at 80 °C, pH 5.6. The inset of (f) is a magnified image of the paramecium-like gold nanoaggregates, bar 50 nm.

reflections clearly correspond to the face-centered cubic structure of metallic gold (JPCDS file, card No. 04-0784). This has already been confirmed by the SAED pattern for the sample as shown in Fig. 1b. The broad X-ray reflection peaks testify the wires were consisted of small gold particles [14]. The mean diameter of the nanoparticles is calculated to be about 6 nm from the line width of the {111} plane diffraction according to Scherrer equation [15].

When sodium hydroxide was added,  $[\text{AuCl}_4]^-$  reacted with  $\text{OH}^-$  to  $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$  [16] and the color of the solution changed as a result. We have studied the resultant nanoparticles when pH of the reaction system was 5.6 and 9.0 for contrast. When the pH was 5.6, the reaction speed increased obviously. As a result, amounts of gold crystal nuclei were produced in a short time and aggregated quickly. In this condition, paramecium-like nanoaggregates were produced (Fig. 1f). But when pH was 9.0, no reaction was observed. We conclude that the reduction potential of  $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$  is much lower than  $[\text{AuCl}_4]^-$ .

In our synthesis system, aniline serves as reducing agent as well as stabilizer which supplies positive surface charge of gold nanostructures [17]. According to the observation of Gospodinova Terlemezyan, aniline is

able to be oxidized to N-phenyl-1, 4-benzquinonediimine ( $\text{C}_6\text{H}_5-\text{N}=\text{C}_6\text{H}_4\text{NH}$ , PBQ) in the whole pH range, but only when  $\text{pH} < 2$ , PBQ could continue being oxidized to polyaniline [18,19]. As reported before [20], in situ produced polyaniline is able to effectively adsorb on the {111} facets and prevents growth on these facets through its multiplex nitrogenous groups, while PBQ does not have these properties. Based on the characters of aniline and the results of the experiment above, we deem that the nanowires formed follow this principle, as shown in Fig. 2. Firstly, PBQ created by oxidation of aniline will not continue polymerizing with aniline to form polyaniline because the pH of the system is 7, which is much higher than 2. Thus, no polymer preferentially adsorbs any existent facets and the resultant nanoparticles run to spheroids, which is stable in thermodynamics. In this pH, there are little  $[\text{AuCl}_4]^-$  and lots of  $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$  in the solution, and  $[\text{AuCl}_4]^-$  is constantly reduced to gold crystal nuclei. At the same time, aniline is oxidized to PBQ and releasing  $\text{H}^+$ , which sets  $[\text{AuCl}_4]^-$  free from  $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$ . Then,  $[\text{AuCl}_4]^-$  goes on being reduced to gold atoms. However, it needs a long time for the pH of the solution to decrease in less than 2 despite of the releasing of  $\text{H}^+$ . Thus, the main components of the solution are PBQ and remanent aniline,



**Fig. 2.** Schematic of the possible formation process of the networked gold nanowires.

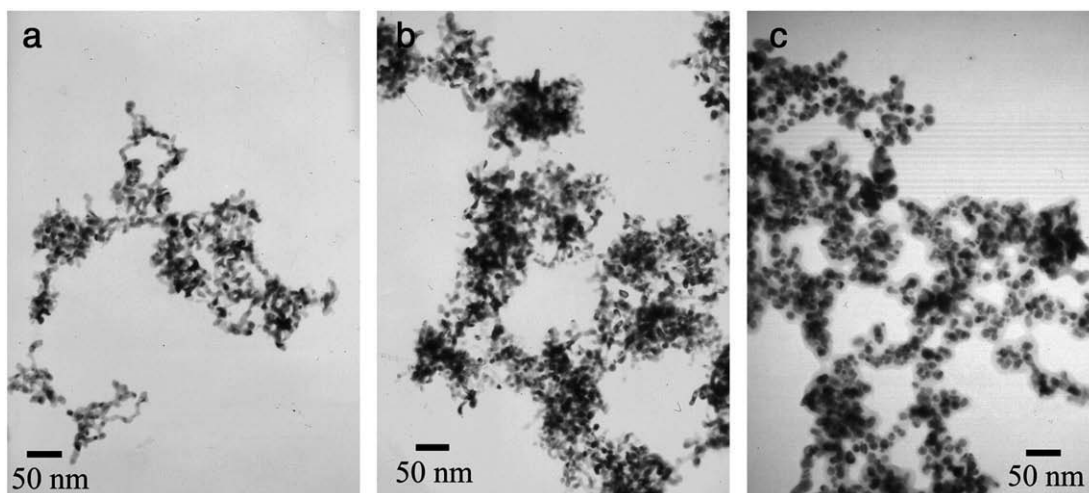


Fig. 3. TEM images of gold products obtained at pH 7.0 with molar ratio (aniline to gold) of (a) 6:1, (b) 1.5:1 and (c) 0.5:1, respectively.

whose adsorption ability is much lower than polyaniline. The gold nanoparticles are unstable due to small size and weak stabilizing ability of PBQ and aniline, and these unstable particles aggregate to linear assembly on account of brownian motion and van der waals attractive force. The linear assembly process is also described in Fig. 2. Firstly, the dimmers of gold nanoparticles are formed, which induce the asymmetric distribution of the surface charges on the nanoparticles. That is, the surface charge density at the joint of a dimer is much higher than that of the other parts of a dimer. Thus, a third particle tends to attack to the head or end face but not side face. This process continues and results in the formation of linear assemblies of gold nanoparticles. At the same time, the concaves between neighbor particles are filled with later-born gold atoms. Afterward, particles in lines form wires [21,22], and at last, nanowires with a 2D networked fabric are produced.

To further substantiate the condition of producing gold nanowires in this system, we studied the resultant nanostructures when changing the quantum of aniline in the original system. We doubled and halved the quantum of aniline while other reactants that remain unchanged, and found that the products were still networked nanowires (Fig. 3a and b). We conclude that it is because aniline is superfluous in the original system and the number of gold crystal nuclei engendered by aniline reducing  $[\text{AuCl}_4]^-$  does not increase or decrease evidently in the two cases. But when changed the proportion of aniline to gold to as little as 0.5:1, many spherical nanoparticles with diameters 10 nm~30 nm were produced (Fig. 3c). It is because the decrease of aniline leads to the decrease of the number of gold crystal nuclei produced, and the relatively ample gold atom supply makes the resultant nanoparticles thermodynamically stabilized large spheres. As a result, linear assembly of gold nanoparticles was not formed.

#### 4. Conclusions

In summary, we have designed a facile one-step method to prepare networked gold nanowires by aniline reducing chloroauric acid in the present of sodium hydroxide. In this method, most  $[\text{AuCl}_4]^-$  is protected by becoming  $[\text{Au}(\text{OH})_n\text{Cl}_{4-n}]^-$  with  $\text{OH}^-$ , and the left  $[\text{AuCl}_4]^-$  is reduced to appropriate amount of gold crystal nuclei at the beginning of

the reaction. Then, the gold crystal nuclei assemble to lines and the slowly later-born gold atoms filled in the concaves between neighbor nuclei. Finally, networked gold nanowires are obtained. In this synthesis system, the reaction properties of aniline are used effectively. This work provides a convenient approach to synthesize networked gold nanowires, and probably contributes to the study of electron transport and electronic devices. Moreover, the work is an example of designed nanoscaled synthesis strategy and may arouse other inspirations in this and other fields.

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