Ultrasound-Assisted Self-Regulation Route to Ag Nanorods

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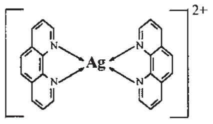
An ultrasound-assisted self-regulation route was reported to prepare silver nanorods. Ag nanorods were obtained from a mixture of $AgNO_3$ and gallic acid, with 1,10-phenanthroline as a type of coordination agent to regulate the products, under the ultrasonic condition.

In the past few years, one-dimensional (1D) nanostructured materials have attracted considerable interest of recent scientific research, due to their unusual properties and potential applications.[1,2]

Many methods have been used to prepare 1D silver nanomaterial, such as nanorods and nanowires. Some scientists synthesized Ag nanowires by electrochemical methods.[3–5] Some templates, such as mesoporous silica and carbon nanotubes, were also used to prepare Ag nanowires.[6–8] Otherwise, 1D silver nanomaterials could be synthesized in emulsion or polymetric systems.[9–12] All these methods needed complicated process, so we tried to use a type of self-regulation method to prepare 1D silver nanomaterials.

It is known that 1,10-phenanthroline can coordinate with Ag^{2+} to form a type of stable complicated Complex **1**, $[Ag(C_{12}H_8N_2)_2]^{2+}$,[13] which is a d^9 complex, taking a approximate square-planar geometry, with steric inhibition on its plane.



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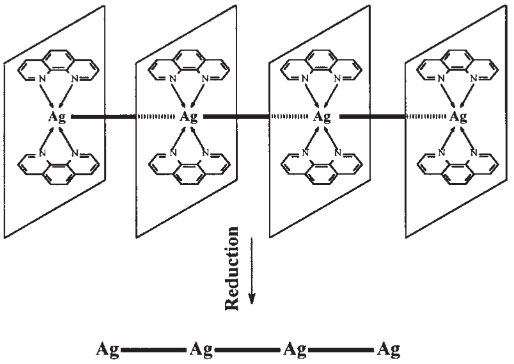
Thus a linear alignment of $[Ag(C_{12}H_8N_2)_2]^{2+}$ is expected. It is thought the Ag^{2+} ions in **1** can be reduced to elemental Ag, which is preferential to grow along the vertical direction to the parallel planes and form nanorods, due to their steric inhibition on the planes. This procedure can be thought as a self-regulation one of the product morphology, as Scheme 1 shows.

However, how can we obtain the Ag^{2+} ions in the reaction system? It was reported that Ag^+ ions could be oxidized to Ag^{2+} ions by oxygen under conditions of ultrasound.[14,15] Moreover, considered about the velocity of reduction, gallic acid was chosen to reduce $[Ag(C_{12}H_8N_2)_2]^{2+}$ to elemental Ag. Based on this strategy, an ultrasound-assisted self-regulation route was reported to prepare Ag nanorods: with H_2O as solvent, 1,10-phenanthroline as coordination agent, $AgNO_3$ and gallic acid as reactants, Ag nanorods were obtained. This process is described as follows.



Scheme 1.

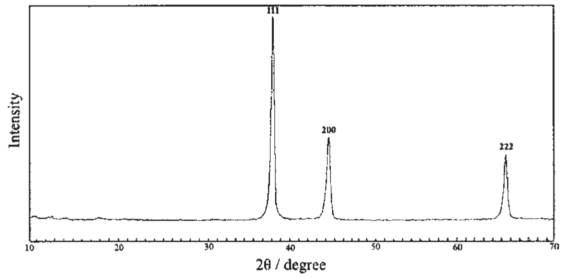


Figure 1. XRD pattern of Ag nanorods.

$$4Ag^+ + O_2 + 4C_7H_6O_5 \xrightarrow{\text{1,10-phenanthroline}} 4Ag + 4C_7H_4O_5 + 2H_2O + 4H^+$$

In a typical procedure, $AgNO_3$ (0.420 g, 2.47 mmol), and 1,10-phenanthroline (0.99 g, 4.99 mmol) were loaded into a 125-mL jar that was then filled with H_2O up to 40% of the total volume. In succession, the jar was placed in a commercial ultrasonic cleaning bath (18 KHz, 250 W) and irradiated. The solution turned bright yellow due to the formation of **1**. Then 2 mL gallic acid solution, in which gallic acid (0.400 g) was dissolved and diluted to 50 ml with H_2O, was added to the jar. The irradiation was maintained for 3 h. The precipitate was filtered and washed several times with diluted HCl ($1\ mol\cdot L^{-1}$), distilled water and absolute ethanol. The product was dried in a vacuum at 60 °C for 2 h.

The X-ray diffraction (XRD) pattern[16] of Ag nanorods prepared via the ultrasound-assisted self-regulation route is shown in Figure 1. All the peaks can be indexed as cubic Ag. (JCPDS card, NO. 4–783, $a = 4.0862$ Å). No impurities, such as Ag_2O, can be detected.

The morphologies and sizes of as-prepared Ag nanorods were studied by transmission electron microscopy (TEM).[16] Figure 2a and 2b reveal that the products are some nanorods with a diameter of 80 nm. The lengths range from 1250 nm to 2500 nm. The trace of small particles were due to the phenomenon that silver sputtered out immediately when exposed to an electron beam under the transmission electron microscope.[17] A similar phenomenon in a study on gold spheres was reported by Q. Ru.[18]

It is found that the reductant played a crucial role in the formation of Ag nanorods. When NH_2OH was used as reductant,

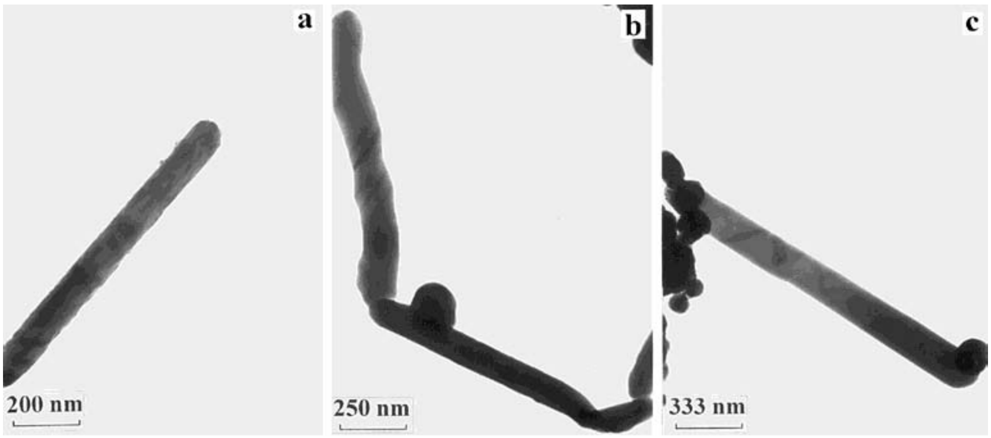


Figure 2. TEM images of (a), (b) Ag nanorods abtained under ultrasonic condition with gallic acid as reductant; (c) Ag nanorods and nanoparticles obtained with NH_2OH as reductant.

the velocity of reduction was too high and the growth of Ag nanorods was not complete. So the product was nanorods and nanoparticles (Figure 2c). The experiment was also carried out in the absence of phenanthroline when other conditions were kept constant, and some silver particles of relative large sizes were obtained. It indicates that phenanthroline is crucial to control the morphology of the product.

In order to investigate the effect of ultrasound on the formation of Ag nanorods, the experiment was carried out with magnetic stirring instead of ultrasound, when other conditions were kept constant. It is found that the products were some nanoparticles, which indicates that ultrasound was necessary to the growth of Ag nanorods. The effect of ultrasound radiation on chemical reactions is due to the very high temperatures and pressures which develop during the sonochemical cavity collapse by a process called acoustic cavitation. There are two regions of sonochemical activity: the inside of the collapsing bubble (I) and the interface between the bubble and the liquid which extends to about 200 nm from the bubble surface (II).[19,20] The Region I had high temperature ($T > 5000\,K$) and high cooling rate ($>10^{10}$ $K{\cdot}S^{-1}$), which was not helpful to the crystallinity of Ag. Moreover, the vapour pressure and the amount of the ionic species were very low inside the bubble, so little product was expected to be obtained inside the bubbles. Therefore, we propose that the formation of Ag occurred at the interface ($T = 1900\,K$) between the bubble and the liquid (Region II), which was helpful to get nanocrystalline products. The crystal growth at the interface was easy to have 1D epitaxy, which was similar to the complex solution-liquid-solid (SLS) proposed for the growth of InP whiskers by T. J. Trentler and W. E. Buhro group.[21,22] Moreover, ultrasound radiation could avoid the aggregation of Ag effectively and promote the oxidation of Ag^+ ions to Ag^{2+} ions.

In conclusion, an ultrasound-assisted self-regulation route prepared silver nanorods. This method can be easily controlled and is expected to be applicable to fabricate other elemental metal or even metal oxides 1D nanomaterials.

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