One-step growth method of silver nanowires in aqueous environment

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Abstract
Silver nanowires were successfully prepared by one-step growth method in aqueous environment. The suitable pH value is a key factor for the successful preparation of silver nanowires. The concentration of silver nitrate precursors also affects the yield of silver nanowire. We studied the growth mechanism of silver nanowires in detail. This is a classic Ostwald ripening process. The final silver nanowires are face-centered-cubic (FCC) phase. The morphologic parameters of the silver nanowires were observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Its size is about 7 μm long and about 45 nanometers in diameter. This experiment provides an effective method for the preparation of silver nanowires in aqueous environment. It has important potential applications in biological detection and physical devices.

1. Introduction

Metal nanostructures have attracted much more attention for their unique optical properties [1]. Among them, as an important representative of metal nanomaterials, silver nanostructures have been widely concerned by researchers [2–4]. It has many peculiar properties. There is a lot of research in nanoelectronics [5–10], nanophotonics [11–13], optical imaging [14, 15], nanodevices [16–18], nano-silver paste [19, 20], nanoscale biological applications [21, 22] and so on. The properties of silver nanostructures vary with their morphologies and sizes [23–25]. For example, the zero-dimensional silver nanoparticles (such as cube, polyhedron and spherical nanoparticles) will appear multiple resonance modes with the increase of size [26, 27]. Compared with other metal nanomaterials, the multiple modes of silver nanoparticles are more sensitive to size and easier to control. The silver nanorods have also been investigated for their easily regulated local surface plasmon resonance (LSPR) properties in the ultraviolet region [28–30]. In addition, the one-dimensional silver nanowire structure also has many unique properties. The high electrical and thermal conductivity of bulk silver, for example, offers advantages in nanowires. Wang’s group also successfully prepared the special silver nanorings which can be as good nanoantennas [31, 32].

More and more silver nanostructures with various morphologies have been prepared. The preparation methods of silver nanowires are also varied [33–40]. These preparation methods generally fall into two categories: either template-directed [41–46] or template-free [47, 48]. For example, the Ag nanowires have been prepared by electroplating into an anodic aluminium oxide (AAO) [45, 46]. The method requires controlling the aperture of AAO template to control the size of nanostructures. In general, most of these free-form samples are prepared in the polymer environment, that is, the polyols such as ethylene glycol as the preparation solvent and poly(vinyl pyrrolidone) (PVP) as the modifier to prepare silver nanostructures [49, 50]. Most experiments require high reaction temperature in the organic environment, which should be more than 100 °C [2].
Therefore, it is a developing trend to try to prepare silver nanostructures in aqueous environment with low temperature.

In this paper, we used a small amount of cetyltrimethylammoniumchloride (CTAC) as surface modifier, ascorbic acid as reducing agent, and silver nitrate (AgNO₃) as precursor to prepare silver nanowires in aqueous environment. The growth temperature is 60 °C. We investigated the growth mechanism of silver nanowires by controlling the growth time. And the composition of the initial sample was analyzed by energy-dispersive x-ray spectrum (EDXS). The growth parameters were studied by adjusting the volume of NaOH and AgNO₃ solution. The morphology of the silver nanowires was studied by using the transmission electron microscope (TEM) and scanning electron microscopy (SEM). This is an effective method for the preparation of Ag nanowires in aqueous environment. This is of great help for augmentation of Ag nanostructures for potential biological applications.

2. Experimental section

The synthesis process of Ag nanowires was that mixed 2 ml of water with 0.5 ml of CTAC solution (0.2 M) and stirred at 60 °C. Then we added amount of sodium hydroxide (NaOH) solution (0.1 M) to the mixed solution. And we studied the effect of NaOH on the growth of silver nanowires by changing its volume. After the mixture was well mixed, 1 ml AgNO₃ solution (8 μM) and 1 ml CTAC (60 mM) and ascorbic acid (80 mM) mixture were simultaneously injected drop by drop. The reaction was stirred at 60 °C and stopped after 3 h. The final products were collected by centrifugation (3600 rpm for 6 min). And the precipitate was dispersed in 3 ml of water. The colloidal solution is the Ag nanowires.

The transmission electron microscope (TEM) images were performed with a JEM-2100PLUS transmission electron microscope operated at 200 kV. Energy-dispersive x-ray Spectrum (EDXS) analysis was performed on an EDAX instrument incorporated in the HRTEM. The scanning electron microscope (SEM) images were performed with a Sigma-500VP scanning electron microscopy operated at 2 kV. The absorption spectra were measured using a TU-1810 UV–vis spectrophotometer. The powder x-ray diffraction pattern of the sample was measured using 3KwPANalytical x-ray Diffractometer Model X pert3.

3. Results and discussions

Figure 1(a) shows the schematic illustration of the Ag nanowires in aqueous environment. The orange spheres represent silver ions (Ag⁺). The green spheres with the curve represent the ascorbic acid molecule. Blue spheres with the curve and purple spheres represent chloride ions (Cl⁻) and hydrophobic ions, respectively. We adjust the pH value of the solution to the proper value by using the NaOH solution. In aqueous solution, the CTAC molecular decomposes into hydrophobic ions and chloride ions. Then the AgNO₃ solution is added into the mixed solution and stirring at 60 °C. In the beginning, the Ag⁺ combined with the Cl⁻ to form silver chloride (AgCl) particles. At the same time, a certain amount of surface modifiers will be attached to the surface of the AgCl nanoparticles. With the increase of reaction time, the AgCl nanoparticles break down and began to form small Ag nanorods and nanoparticles. After 3 h, the large Ag nanowires are formed.

Figures 1(b)–(e) shows the TEM images and EDXS data of the samples after 30 min of reaction. As can be seen from the TEM image in figure 1(b), most of the samples are spherical particles with diameters more than 100 nm at 30 min. These large nanoparticles are AgCl. The small bumps on the surface of these particles are pure Ag nanoparticles. This conclusion can be proved by EDXS measurement. The EDXS data of the 30-minute sample are given in figure 1(c). There is a certain amount of chlorine in it through elemental analysis. The Cl⁻ is derived from CTAC surface modifiers. It’s well known that the AgCl is unstable. It can be clearly seen that the AgCl nanoparticle is rapidly decomposed into silver and chlorine gas under the bombardment of electrons with the transmission electron microscope. Figure 1(d) shows the TEM image of the sample after electron bombardment. Compared with figure 1(b), it can be clearly seen that the original large spherical particles are decomposed into irregular small nanoparticles. These particles can be proved to be pure silver by EDXS. Figure 1(e) shows the EDXS data of samples after bombardment and the corresponding ratio of element content. By comparison with figure 1(c), we can see that there is very little chlorine (0.33%) in it, while the content of silver still accounts for a large proportion. Figure 1(f) shows the XRD pattern of the sample with reaction time about 30 min. The XRD results show that the sample is a mixture of AgCl and Ag nanoparticles. This result is consistent with the EDXS result. The crystalline structure of AgCl is cubic phase (see JCPDS file No. 00-001-1013).

Figure 2 shows the TEM and SEM images of Ag nanowires at various growth times. As can be seen from in figure 2(a), when the reaction lasted for about 30 min, the large silver chloride nanoparticles were formed, and also a certain number of small Ag nanoparticles were attached to the surface of silver chloride particles. This
result is illustrated in figure 1. Figure 2(b) shows the TEM image of the samples that reacted for about 60 min. The Ag nanowire has been formed at this point in time. However, AgCl particles still existed on the surface of Ag nanowire and in colloidal solution. At the same time, larger and irregularly shaped Ag nanoparticles were formed. When the growth process reached 120 min, there were almost no AgCl particles in the solution, which indicating that all AgCl particles had been decomposed. At the same time, larger Ag nanowires appeared in the solution, as shown in figure 2(c). As the reaction time reached to 180 min, there are Ag nanowires with a
diameter of about 45–50 nm and a length of more than 7 μm. Figures 2(e) and (f) show the SEM images of samples reacting for about 240 min and 400 min. As can be seen from the images, there is no obvious difference in morphology and size between the samples grown at this time and that at 180 min. This indicates that the growth process has been basically completed after 3 h of reaction. The passivation degree of surface modifier CTAC on different crystal surfaces is different, which leads to the growth of anisotropy of nanowires. The growth mechanism of silver nanowires can be explained by Ostwald ripening theory. In the early ripening process, most of the larger silver particles can be guided to grow into uniformly sized nanorods, which then continue to grow into uniform nanowires [35]. Figure 2(g) displays the XRD pattern of the sample. Four FCC peaks at 37.9°, 44.1°, 64.6°, and 77.5° correspond to (111), (200), (220), and (311) planes of silver with face-centered-cubic (FCC) phase (see JCPDS file No. 00-001-1164) [51].

We found that the NaOH was a key factor in the growth process of Ag nanowires. The TEM images were used to explore the experimental results, as shown in figure 3. The volumes of NaOH solution added from figures 3(a) to (d) are (a) 20 μl, (b) 80 μl, (c) 150 μl, and (d) 200 μl, respectively. As seen in figure 3(a), the yield of the Ag nanowire is not high. The Ag nanowires range from 1.5 to 3.5 μm in length and 35 nm in diameter. It contains a large number of Ag nanoparticles, which are regular cubic or tetrahedral structures. The Ag
nanowires shown in figure 3(b) have a high yield with the volume of NaOH solution about 80 μl. The length is about 7 μm and the diameter is about 45 nm. When 150 μl of NaOH solution were added into the reaction solution, the Ag nanowires had a low yield. There just a few short nanowires, and contained a large amounts of irregular nanoparticles. When 200 μl of NaOH solution were added, there was no Ag nanowires formed, only irregular Ag nanoparticles. This may be explained by the fact that in a lower pH value environment, the reaction speed is slow and silver nanoparticles with uniform morphology are more likely to be formed, resulting in a lower nanowire yield. And high pH will make the reaction speed too fast, forming a large number of irregular shape particles. The above experimental results indicate that the pH value is an important parameter for the Ag
nanowires synthesized. High yield silver nanowires can be produced efficiently only with a suitable pH value. The importance of NaOH has been reported in previous studies [48].

In this experimental, we also investigated the effect of the amount of AgNO₃ on the growth of Ag nanowires. The SEM images of Ag nanostructures with different volumes of AgNO₃ solution (0.1 M) are shown in the figure 4. The amount of AgNO₃ added is 10 μl in figure 4(a). As can be seen from the SEM image, only some Ag nanoparticles and a very small amount of Ag nanorods are generated in the results. When the amount of AgNO₃ is gradually increased, the longer nanorods are formed, as shown in figure 4(b). When the amount of AgNO₃ increases to 80 μl, a large number of Ag nanowires are formed, as shown in figure 4(c). This result indicates that high yield Ag nanowires cannot be prepared effectively when the amount of AgNO₃ is small. Figure 4(d) shows the extinction spectra of Ag nanostructures prepared at three different volumes of AgNO₃.

4. Conclusions

The Ag nanowires were prepared effectively at low temperatures. The proper amount of NaOH and opportune amount of silver nitrate are two important experimental parameters. The preparation of silver nanowires was studied by timing sampling. With this method, monodispersed Ag nanowires with the length of more than 7 μm and the diameter of about 45 nm can be prepared. The XRD date indicates that the sample is pure cubic crystal phase. It provides a new and effective method for the preparation of silver nanowires. And the aqueous phase environment makes the sample have better biological application.

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References

[1] Tang Y and Ouyang M 2007 Tailoring properties and functionalities of metal nanoparticles through crystallinity engineering Nat. Mater. 6 754–9
[2] Wiley B, Sun Y and Xia Y 2007 Synthesis of silver nanostructures with controlled shapes and properties Acc. Chem. Res. 40 1067–76
[3] Nagy A and Meszl G 1999 High temperature partial oxidation reactions over silver catalysts Appl. Catal. A 188 337–53
[4] Muench F, Rauber M, Siegmann C, Lauterbach S, Kunz U, Kleebe H J and Ensinger W 2011 Ligand–optimized electroless synthesis of silver nanotubes and their activity in the reduction of 4-nitrophenol Nanotechnology 22 415602
[5] Yan J, Zou G, Wu A, Ren J, Yan J, Hu A and Zhou Y 2012 Pressureless bonding process using Ag nanoparticle paste for flexible electronics packaging Scr. Mater. 66 582–5
[6] Lee T Hand Dickson R M 2003 Discrete two-terminal single nanocluster quantum optoelectronic logic operations at room temperature P. Natl. Acad. Sci. USA 100 3043–6
[7] Nge T T, Nogi M and Suganuma K 2013 Electrical functionality of inkjet-printed silver nanoparticle conductive tracks on nanostructured paper compared with those on plastic substrates J. Mater. Chem. C 1 5235–43
[8] Han M C, He H W, Zhang B, Wang X X, Zhang J, You M H, Yan S Y and Long Y Z 2017 Fabrication of Ag nanowire/polymer composite nanocables via direct electrospinning Mater. Res. Express 4 075043
[9] Yan X Z, Li X, Zhou L, Chu X F, Yang F, Chi Y D and Yang X T 2019 Electrically sintered silver nanowire networks for use as transparent electrodes and heaters Mater. Res. Express 6 116316
[10] Tao Y and Pan D 2019 One-step and low-temperature deposited Ag nanowires/TiOₓ hybrid transparent conductive thin film and its application in antistatic coating Mater. Res. Express 6 076430
[11] Park J, Hwang I C, Kim G G and Park J U 2019 Flexible electronics based on one-dimensional and two-dimensional hybrid nanomaterials InfoMat. 2 53–56
[12] Park S E, Kim S, Lee D Y, Kim E and Hwang J 2013 Fabrication of silver nanowire transparent electrodes using electrohydrodynamic spray deposition for flexible organic solar cells J. Mater. Chem. A 1 14286–93
[13] Mashentseva A, Boroglev D, Zdorovets M and Russakova A 2014 Synthesis, structure, and catalytic activity of a Au/poly(ethylene terephthalate) composites Acta Phys. Pol. A 125 1263–6
[14] Fang N, Lee H, Sun C and Zhang X 2005 Sub-diffraction-limited optical imaging with a silver superlens Science 308 534–7
[15] Lee K and El-Sayed M A 2006 Gold and silver nanoparticles in sensing and imaging: sensitivity of plasmon response to size, shape, and metal composition J. Phys. Chem. B 110 19220–5
Wang Z, Liu J, Chen X, Wan J and Qian Y 2005 A simple hydrothermal route to large
nanowires prepared by modified AAO template method Mater. Lett. 61 900–3
Wang Z, Liu J, Chen X, Wan J and Qian Y 2005 A simple hydrothermal route to large–scale synthesis of uniform silver nanowires
Chem.–Eur. J. 11 160–3
Caswell K K, Bender C M and Murphy C J 2003 Seedless, surfactantless wet chemical synthesis of silver nanowires Nano Lett. 3 667–9
Zhu J, Kan C X, Wan J G, Han M and Wang G H 2011 High-yield synthesis of uniform Ag nanowires with high aspect ratios by introducing the long-chain PVP in an improved polyol process J. Nanomater. 2011 98254
Gao Y et al 2005 Growth mechanism of silver nanowires synthesized by polyvinylpyrrolidone–assisted polyol reduction J. Phys. D: Appl. Phys. 38 1061–7
Liu T, Li D, Yang D and Jiang M 2011 Fabrication of flower-like silver structures through anisotropic growth Langmuir 27 6211–7