Available online at www.sciencedirect.com

ScienceDirect

Journal of Solid State Chemistry 180 (2007) 2262–2267

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Synthesis and characterization of silver nanowires with zigzag morphology in *N*,*N*-dimethylformamide

Xin He[a], Xiujian Zhao[a,*], Yunxia Chen[a], Jinyang Feng[a], Zhenya Sun[b]

[a]*Key Laboratory of Silicate Materials Science and Engineering, Wuhan University of Technology, Ministry of Education, 122 Luoshi Road, Hongshan District, Wuhan, Hubei 430070, PR China*

[b]*Center for Materials Research and Testing, Wuhan University of Technology, 122 Luoshi Road, Hongshan District, Wuhan, Hubei 430070, PR China*

Received 20 March 2007; received in revised form 25 May 2007; accepted 27 May 2007

Abstract

Zigzag silver nanowires with a uniform diameter of 20 ± 5 nm were prepared by reducing silver nitrate ($AgNO_3$) with *N*,*N*-dimethylformamide (DMF) in the presence of tetrabutyl titanate (TBT) and acetylacetone (AcAc) at 373 K for 18 h. X-ray and selected area electron diffraction (XRD and SAED) patterns reveal that the prepared product is made of pure silver with face centered cubic structure. Transmission electron microscopy (TEM) investigations suggest that the amount of silver nanowires is enhanced with increase in reaction time, and the end-to-end assemblies of silver nanorods are observed during the reaction process. After 18 h reaction, silver nanowires with zigzag morphology are obtained. In this paper, a possible growth process of silver nanowires with this interesting shape is described. Silver nanoparticles with small sizes were obtained by reducing Ag^+ ions with DMF, providing seeds for homogeneous growth of silver nanorods. With the extending reaction time, the synthesized silver nanorods were connected in an end-to-end manner, and the interface between the connections of two nanorods gradually disappeared. The final product shows zigzag morphology with various angles. The angles between two connecting straight parts of zigzag nanowires exhibit an alterable range of 74–151°. These silver nanowires show tremendous potential applications in future nanoscale electronic circuits.

Keywords: Silver nanowires; Zigzag morphology; End-to-end assembly; Solution-phase growth

1. Introduction

Recently, metal and semiconductor nanowires have attracted great attention for their potential applications in the areas of nanofabrication, optoelectronic nanodevices and biological nanosensors [1–5]. Among the various nanostructured materials, silver nanowires or nanorods are the ideal choices, due to their excellent electrical and thermal conductivity and high stability under ambient conditions.

In the last decades, different approaches have been used to synthesize silver nanowires. The template-directed approaches were the most effective and widely used. Macroporous membranes [6], mesoporous materials [7], carbon nanotubes [8], DNA channels [9], organic nanotubes arrays [10] and silica gels [11] have been used as physical templates to guide the growth of nanowires. Though above-mentioned methods can ensure a good control over morphology of final products and allow obtaining metal nanowires with high aspect ratios, the additional removal of these physical templates may complicate the synthetic procedures and limit the scale at which materials can be synthesized. Therefore, solution-phase approaches to prepare one-dimensional metal nanostructures in which mostly the capping reagents or surfactants were applied [12–19] have been developed. The shape of a crystal is determined by the relative specific surface energies associated with the facets of this crystal. To change the free energies of the various crystallographic surfaces and their growth rates, the introduction of

---

*Corresponding authors. Fax: +86 27 87669729.
E-mail addresses: hexin1981@126.com (X. He), zhaoxj@public.wh.hb.cn (X. Zhao).

doi:10.1016/j.jssc.2007.05.023

appropriate capping reagents or surfactants is crucial. Taking into account the above-mentioned elements, the one-dimensional metal nanowires can be obtained by hindering the growth of certain crystallographic planes using appropriate capping reagents or surfactants. Murphy and co-workers prepared silver nanorods and nanowires in the presence of cetyltrimethylammonium bromide (CTAB) [15]. Xia and co-workers have developed a polyol-process to obtain large-scale uniform silver nanowires using polyvinylpyrrolidone (PVP) as structure-directing reagent [16,17]. However, some template-free approaches have also been successfully used to synthesize silver nanowires [20,21]. Since the preparation methods of metal nanowires are largely developed, the coming field of interest is to assemble these nanoscale objects into functional devices. The technological improvements require the nanomaterials to be easily machined in nanofabricating.

The present work reports the procedure which allows preparing silver nanowires with zigzag morphology of various angles by solution-phase method. By reducing $AgNO_3$ in ethylene glycol with the addition of PVP, this interesting morphology of silver nanowires was also reported elsewhere [12,22]. However, considering the formation mechanism, the zigzag morphologies reported in the preview were formed in two different ways: (a) the straight silver nanorods were connected in an end-to-end manner, and with obvious spacing between them [12], (b) the silver nanowires are bent into various angles due to the presence of obstacles and rough Cu substrates [22]. The situation in our experiment is different from both of them. It is regarded that the obtained end-to-end assemblies of silver nanorods could develop into long nanowires showing zigzagging behavior without any spacing between two nanorods. In the paper, a possible formation process of silver nanowires with this interesting morphology is also described.

2. Experimental

2.1. Preparation

All chemicals were of the highest quality commercially available: *N*,*N*-dimethylformamide, silver nitrate, tetrabutyl titanate (TBT) and acetylacetone were purchased from Shanghai Chemicals Co., Ltd., PR China and used without further purification. The synthesis was performed in an autoclave of 200 ml. The 60 ml of *N*,*N*-dimethylformamide (DMF) and 2 ml of 5 mM $AgNO_3$ in DMF solution were added into the container under mild magnetic stirring. Subsequently, a mixture of 5 mL of tetrabutyl titanate (TBT) and 5 mL of acetylacetone (AcAc) were introduced into the autoclave dropwise over a period of 1 min. After mixing all reagents under ambient temperature, the autoclave was then obturated and heated in silicone oil bath at 373 K for different periods of time. The reaction process was maintained under continuous magnetic stirring. The Ag^+ ions were reduced by DMF progressively and it was revealed by the color change of the mixed solution. As the reaction time extended, the mixture gradually turned turbid and a grey–brown suspension was obtained, indicating the appearance of silver nanowires [23]. The as-prepared suspensions were centrifuged at 3000 rpm for 30 min and washed with ethanol to remove the supernatant. The gray–green precipitates were obtained and dried for 24 h in a drying oven at 333 K and characterized by different measurement ways.

2.2. Characterization

To characterize the composition, the microstructure and the purity of the as-synthesized products, X-ray diffraction (XRD) patterns were recorded using a D/max-RB rotating (Rigaku) powder diffractometer equipped with a graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The UV–Vis absorption spectra of the as-prepared precipitates re-dissolved in ethanol were recorded using a Japanese UV–Vis spectrophotometer (Shimadzu), modeled UV-1601. The morphologies of the products were observed by JEM-2010 transmission electron microscopes (TEM) with an accelerating voltage of 200 kV. The selected area electron diffraction (SAED) was also conducted on the microscope of JEM-2010. HRTEM measurements were carried out with JEM-2100F electron microscopes operating at 200 kV with samples deposited on a carbon coated copper grid.

3. Results and discussion

The morphology and dimension of the synthesized product are shown in Fig. 1a. It can be seen that the product treated at 373 K for 18 h is mainly composed of uniform nanowires with diameter of 20 ± 5 nm and lengths up to ~600 nm. A few large particles with irregular shapes are also found in the final product. In addition, an interesting phenomenon that the nanowires exhibit zigzagging behavior is easily observed in the TEM image. A discussion on this observation is reported in the present work. The inset in Fig. 1a is the half SAED pattern of the corresponding nanowires, indicating the crystallographic structure of these nanowires. The calculated spacing distances are 2.345, 2.041, 1.433 and 1.288 Å, which correspond to (111), (200), (220) and (311) plane of metallic silver, respectively. They can be indexed to face centered cubic silver (JCPDS File No. 04-0783 from ASTM).

A single straight nanowire was further characterized by HRTEM, as shown in Fig. 1b, and the magnified image was placed in the top right corner of Fig. 1b. It can be clearly observed that the spacing of the lattice planes is 0.232 nm, which is consistent with the separation of silver (111) planes. It is well known that the theoretically calculated angle value between (111) and (200) planes is 54.4°. In Fig. 1b, the angle between (111) planes and the longitudinal direction of nanowire is measured for 54.1°.

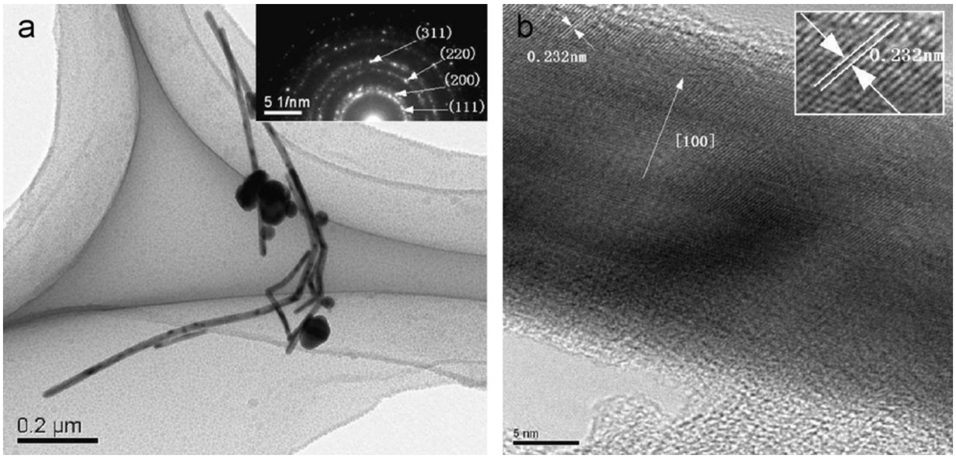

Fig. 1. (a) TEM image of the as-synthesized silver nanowires with a diameter of 20±5 nm. The inset in TEM image is the SAED pattern of the corresponding nanowires, the calculated spacing distances is indexed to face centered cubic silver. (b) HRTEM image of a typical single silver nanowire.

By comparison, it could be supposed that the growth direction of single straight silver nanowire is perpendicular to the (200) planes.

To further confirm the structure of the obtained nanowires, typical XRD patterns of the products treated for 6, 12 and 18 h are shown in Fig. 2. All patterns indicate the presence of four diffraction peaks, which agree well with the (111), (200), (220) and (311) diffractions of face centered cubic silver (JCPDS File No. 04-0783 from ASTM). There are no obvious characteristic peaks of impurities, such as TiO_2 in the prepared products. The result demonstrates that the complex of TBT and AcAc does not hydrolyze in DMF solution. The calculated lattice constants a according to the spacing distance d_g of the $\{111\}$ planes and the equation $1/d_g^2 = (h^2 + k^2 + l^2)/a^2$ [24] are 4.079, 4.083 and 4.081 Å, corresponding to the reaction time of 6, 12 and 18 h, respectively [25]. They are perfectly in agreement with the literature value of 4.086 Å. The result is consistent with the above SAED study, as shown in the inset of Fig. 1a. The final product is all composed of metallic silver, indicating that the high purity of fcc silver could be prepared by this solution-phase method.

In order to investigate the growth process of these silver nanowires, we have carried out the solution-phase reaction at 373 K for different periods of time. Fig. 3a shows the TEM image of the product treated for 6 h. It indicates that the product is mainly composed of particles congregated together with irregular morphology. Fig. 3b exhibits the samples prepared after treating for 12 h. A few nanowires with average diameter of ~20 nm appear, but the agglomerated particles are still present in majority. Comparably, the product treated for 18 h is mainly composed of uniform nanowires, and the amount of agglomeration of large particles with irregular morphology decreases. This is shown in Fig. 1a. It can be concluded that the yield of silver nanowires is enhanced with increase in the reaction time.

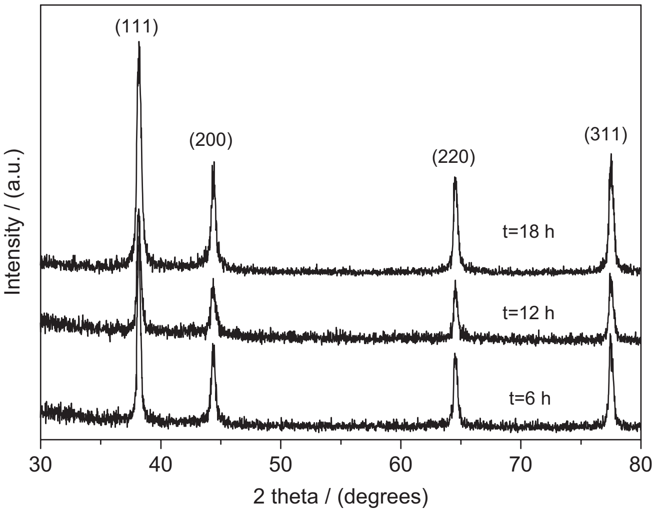

Fig. 2. The typical XRD patterns of the synthesized silver particles treated for 6, 12 and 18 h (all peaks could be indexed to face centered cubic silver).

Fig. 4 shows the UV–Vis absorption spectra taken from the products prepared at 373 K for different reaction time lengths. Mie's theory predicts only a single surface plasmon resonance (SPR) band in the absorption spectrum of metal spherical nanoparticles. Anisotropic metal nanoparticles, on the other hand, could give rise to two or more SPR bands depending on their shape [26]. In our work, a single and asymmetrical absorption band centered at 425 nm is observed for the product treated for 6 h. It suggests that the silver nanoparticles congregated together with broad dimensional distribution are obtained. As the reaction processed, it can be clearly found that the intensity of absorption peak at 350 nm is gradually enhanced. This peak can be attributed to the transverse plasmon response of the long silver nanowires, which is similar to the bulk silver [21,27,28]. While the reaction time is up to 18 h, the presence of broad absorption band centered at 420 nm indicates that the silver nanoparticles also coexist in the final products, and a shoulder in the long wavelength range gradually appear with the increase in reaction time,

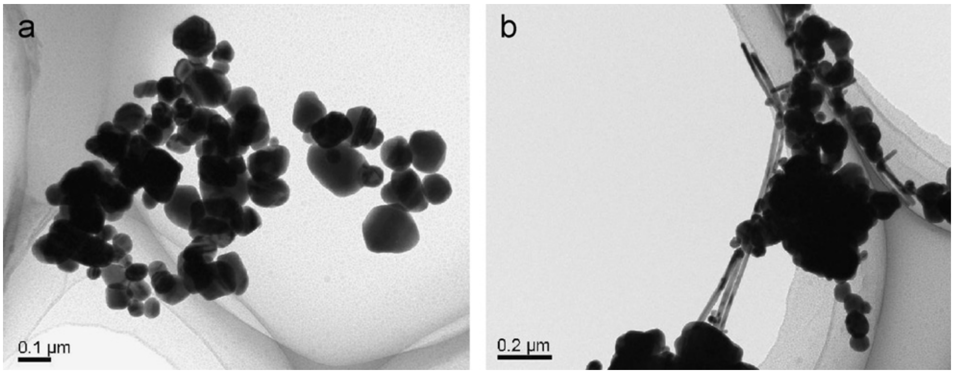

Fig. 3. TEM images of the sample prepared at 373 K for 6 h (a) and 12 h (b).

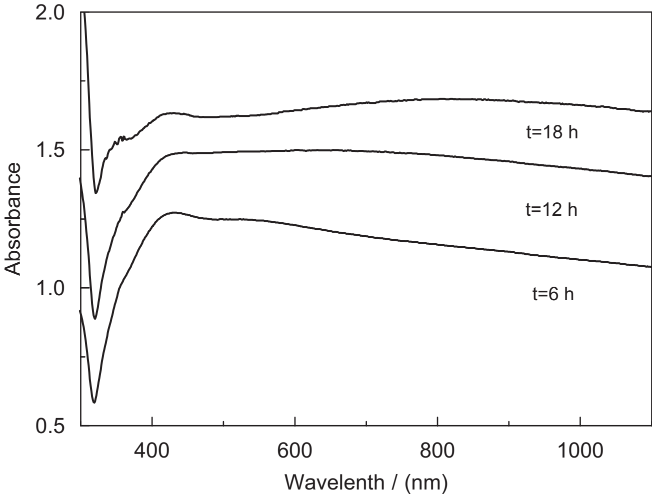

Fig. 4. UV–vis absorption spectra of the samples at different stages of nanowires growth, and three curves correspond to the mixture heated for 6, 12 and 18 h.

implying that the anisotropic silver particles are obtained. The results are in accordance with the above analyses.

Fig. 5a shows the high-magnification TEM image of the product treated for 12 h. It is observed that these silver nanorods with diameter of 20 ± 5 nm are connected in an end-to-end manner, and interface among them is clear. Zhao et al. prepared silver nanowires using a similar approach [21]. They proposed a formation mechanism for silver nanowires and it is that silver nanoparticles spatially direct aggregation along preferred crystallographic axes, once the mixture of TBT and AcAc were introduced into the silver colloids. The as-proposed formation mechanism is just suitable for the growth of the straight silver nanorods in our experiments. However, the formation of silver nanowires with zigzag morphology could not simply be taken to occur because the silver nanoparticles spatially direct aggregation along different preferred crystallographic axes. The reasons for our viewpoints are discussed in the following. The average diameter of the product treated for 6 h is estimated from the X-ray line broadening according to Scherrer's equation $D_{hkl} = k\lambda/\beta \cos\theta$ [29]. The calculated result is 25.49 nm, which is almost equal to the diameter of the product prepared for 12 h (Fig. 5a). This fact suggests that the silver nanorods are very probably formed by assembling silver nanoparticles along preferred direction. However, with the reaction processed, the obvious spacing between two straight parts of silver nanowire gradually disappeared as shown in Fig. 5b. The silver nanowires exhibit zigzagging behavior, and the zigzag nanowire looks like a straight nanowire bent into various angles by certain driving force. A possible path for the formation of these zigzag nanowires is that the zigzag nanowires would probably be obtained simultaneously with the in situ growth of the silver nanowires, like in the growth of the straight nanowires except for orientations. Taking the energy state into consideration, during the growth process of one-dimensional nanoparticles, the straight orientation must be the lowest energy state, which is favorable to the formation of straight silver nanowires, and the zigzag ones are hardly obtained. Therefore, the zigzag nanowires could probably not be shaped in in situ growth process, like in the growth of the straight parts, except for orientations. The theoretical analysis suggests that it is a false hypothesis.

It is very interesting to investigate this fascinating phenomenon in which silver nanowires shaped into diverse angles. The angles between two connecting straight parts of zigzag nanowires vary in the range 74–151°. How to form these silver nanowires with zigzag morphology in the growth process? Based on above considerations, it is supposed that the zigzag nanowires could be probably developed from the end-to-end assemblies. The main supporting evidence is the following. During the formation process of zigzag silver nanowires, the end-to-end assembly of silver nanorods is observed with the product treated for 12 h. But the obvious spacing between straight silver nanorods is absent if the reaction time is extended to 18 h.

In order to explain our presumption of zigzagging behavior in detail, another typical two-fold bent nanowire is shown in Fig. 6a. The angle between two straight silver nanorods with a diameter ~25 nm is 116°. Fig. 6b shows the higher magnification of the white rectangle in Fig. 6a. The clearly magnified images of P1, P2, P3 and P4 in

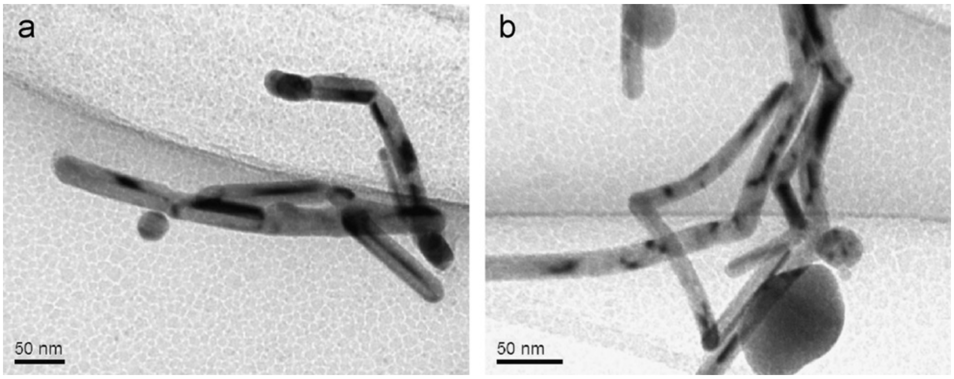

Fig. 5. (a) TEM image of the end-to-end assemblies of silver nanorods with the product treated for 12 h. (b) Higher magnified TEM image of silver nanowires exhibiting zigzagging behavior with the product treated for 18 h.

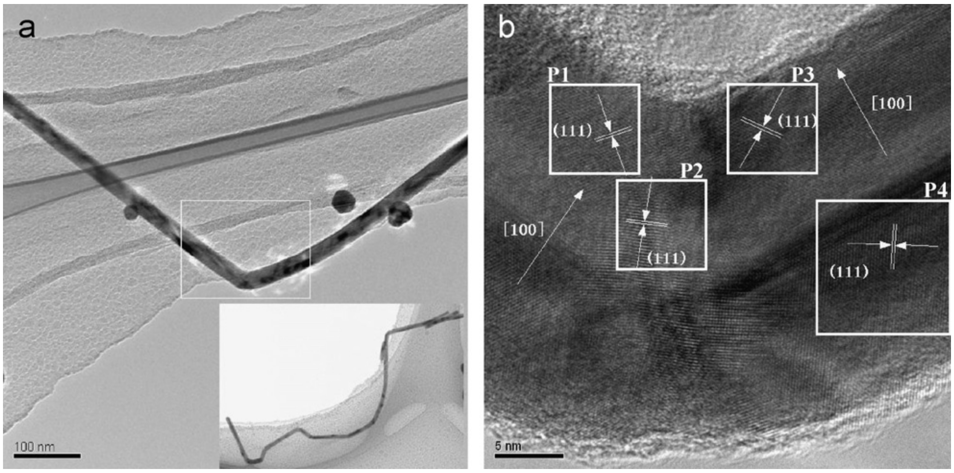

Fig. 6. (a) HRTEM image of a two-fold zigzag silver nanowire. The inset in the image is a multi-fold representation. (b) The white rectangle in image (a) with higher magnification.

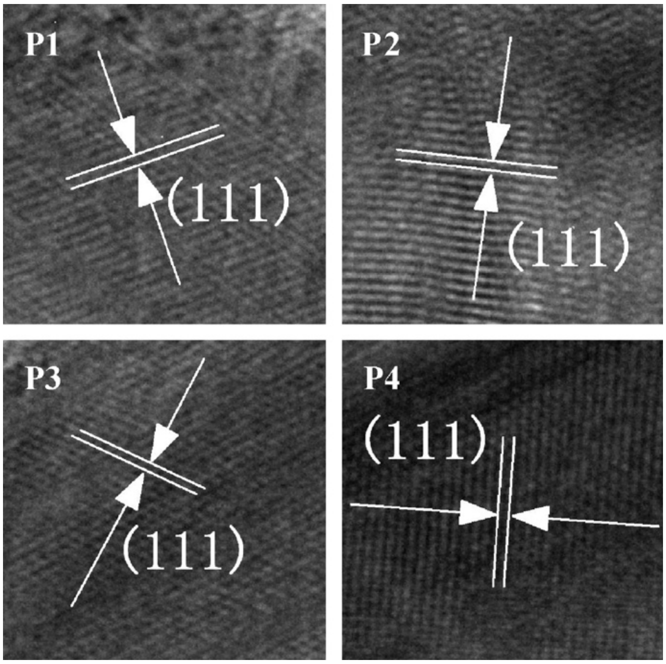

Fig. 7. Much magnified images of P1, P2, P3 and P4 in Fig. 6b.

Fig. 6b are displayed in Fig. 7. The spacing distances of two straight parts of zigzag silver nanowire are all 0.233 nm, corresponding to (111) planes of metallic silver. The angle between (111) planes of the straight part and the longitudinal direction is measured as 54.7°. It is calculated that the angle between (111) planes and the longitudinal direction (54.7°) is almost equal to the one between (111) planes and (200) planes (54.4°). It shows the same situation with the single straight silver nanowire. Therefore, we can conclude that the orientation of two straight parts of zigzag silver nanowire is in accordance with the single straight nanowire, shown in Fig. 1b. In a word, the growth direction of a single straight nanowire and two straight parts of the zigzag nanowire are all perpendicular to (200) planes with the same orientation. Taking the bent part of zigzag nanowire into consideration, the spacing distance of the bent part is also 0.232 nm, corresponding to the (111) planes. It is clearly shown that some line defects of the bent part are easily observed, which are probably developed from the grain boundary between the end-to-end assemblies. The chemical reactivity of the end plane is greater than that of the side plane, leading to different growth rates for different directions. Therefore, small silver nanoparticles tend to be attracted in the end of the silver nanorods to guide the formation of silver nanowires. The end planes of these silver nanorods obtained via spatial aggregation along preferred direction occupy the higher surface free energy than the side one. If the end planes of two nanorods simultaneously attract the same silver nanoparticle, the two-fold end-to-end assembly is obtained, and the different angles between nanorods materialize due to the random direction of each nanorod. If the reaction time is prolonged, the spacing would be filled with the reduced silver atoms. Finally, a zigzag morphology silver nanowire with different angles is formed.

Taking the above facts into account, an integrated possible formation process of zigzag silver nanowires is proposed here. Ag^+ ions firstly are reduced by DMF to form small silver nanoparticles. This organic solvent is a powerful reducing agent against Ag^+ ions. Since the mixture of TBT and AcAc is introduced into the silver colloids, the silver nanoparticles are gradually assembled together to form nanorods along preferred crystallographic axes through arrayed aggregation. However, some silver nanoparticles aggregated together and with irregular morphologies coexist with the nanorods. These as-grown silver nanorods could be connected in the end-to-end manner and separated by the obvious coherent interface among them. With the reaction continually processed, the spacing of the end-to-end assembly between two silver nanorods would be filled with silver atoms, and the silver nanowires exhibiting zigzagging behavior are finally observed. The inset of Fig. 6a shows a multi-fold zigzag representation. The long nanowire shaped into various angles demonstrates that we can provide a promising candidate for fabricating nanoelectronic devices in the future.

4. Conclusions

Silver nanowires with a uniform diameter of 20 ± 5 nm were synthesized by reducing $AgNO_3$ with DMF by introducing the TBT and AcAc. The end-to-end assemblies of silver nanorods were formed during the reaction process, and the obvious spacing between two straight silver nanorods would gradually disappear and probably be filled with silver atoms. As a result, the silver nanowires with zigzag morphology are formed with the product treated for 18 h. The angles between two connecting straight parts of zigzag nanowires can be varied in the range of 74–151°. In the present work, the zigzag silver nanowires could be prepared by a facial chemical solution-phase method, indicating preferential potential for applications in fabricating future nanoelectronic devices.

Acknowledgment

This work was supported by the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 705036).

References

[1] Y. Wu, P. Yang, J. Am. Chem. Soc. 123 (2001) 3165.
[2] M. El-sayed, Acc. Chem. Res. 34 (2001) 257.
[3] S. Chung, J. Yu, J. Heath, Appl. Phys. Lett. 76 (2000) 2068.
[4] S. Sun, C. Murray, D. Weller, L. Folks, A. Moser, Science 287 (2000) 1989.
[5] J. Storhoff, R. Elghanian, R. Mucic, C. Mirkin, R. Letsinger, J. Am. Chem. Soc. 120 (1998) 1959.
[6] J. Mbindyo, T. Mallouk, J. Mattzela, I. Kratochvilova, B. Razavi, T. Jackson, T. Mayer, J. Am. Chem. Soc. 124 (2002) 4020.
[7] G. Sauer, G. Brehm, S. Schneider, J. Appl. Phys. 91 (2002) 3243.
[8] Y. Zhang, H. Dai, Appl. Phys. Lett. 77 (2000) 3015.
[9] G. Wei, H. Zhou, Z. Liu, Y. Song, L. Wang, L. Sun, Z. Li, J. Phys. Chem. B 109 (2005) 8738.
[10] B. Hong, S. Bae, C. Lee, S. Jeong, K. Kim, Science 294 (2001) 348.
[11] S. Bhattacharyya, S.K. Saha, D. Chakravoyty, Appl. Phys. Lett. 77 (2000) 3770.
[12] D. Chen, L. Gao, J. Crystal Growth 264 (2004) 216.
[13] B.D. Busbee, S.O. Obare, C.J. Murphy, Adv. Mater. 15 (2003) 414.
[14] J. Gao, C.M. Bender, C.J. Murphy, Langmuir 19 (2003) 9065.
[15] N.R. Jana, L. Gearheart, C.J. Murphy, Chem. Commun. (2001) 617.
[16] Y. Sun, Y. Xia, Adv. Mater. 14 (2002) 833.
[17] Y. Sun, B. Mayers, T. Herricks, Y. Xia, Nano Lett. 3 (2003) 955.
[18] Y. Sun, B. Gates, B. Mayers, Y. Xia, Nano Lett. 2 (2002) 165.
[19] S. Zhang, Z. Jiang, Z. Xie, X. Xu, R. Huang, L. Zhang, J. Phys. Chem. B 109 (2005) 9416.
[20] C. Li, X. Yang, B. Yang, Y. Yan, Y. Qian, Mater. Lett. 59 (2005) 1409.
[21] Q. Zhao, J. Qiu, C. Zhao, L. Hou, C. Zhu, Chem. Lett. 34 (2005) 30.
[22] P. Jiang, S. Li, S. Xie, Y. Gao, L. Song, Chem. Eur. J. 10 (2004) 4817.
[23] Y. Gao, P. Jiang, D. Liu, H. Yuan, X. Yan, Z. Zhou, J. Wang, L. Song, L. Liu, W. Zhou, G. Wang, S. Xie, Chem. Phys. Lett. 380 (2003) 146.
[24] M. Maillard, S. Giorgio, M.P. Pileni, Adv. Mater. 14 (2002) 1084.
[25] X. He, Y. Chen, X. Zhao, X. Zhou, J. Univ. Sci. Technol. B 28 (Suppl. 1) (2006) 205.
[26] B. Russell, J. Mantovani, V. Anderson, R. Warmack, T.L. Ferrell, Phys. Rev. B 35 (1987) 2151.
[27] Z. Wang, X. Chen, J. Liu, M. Zhang, Y. Qian, Chem. Lett. 33 (2004) 1160.
[28] Y. Sun, B. Mayers, Y. Xia, Nano Lett. 3 (2003) 667.
[29] H. Cheng, J. Ma, Z. Zhao, L. Qi, Chem. Mater. 7 (1995) 663.