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Facile synthesis of single-crystal silver nanowires through a tannin-reduction process

Xuelin Tian · Juan Li · Shilie Pan

Abstract A facile aqueous-phase approach for the synthesis of silver nanowires is reported, in which tannin ($C_{76}H_{52}O_{46}$) is used as a mild reducing agent for silver nitrate. This synthesis is a root-temperature, seedless process, and does not need any surfactant or capping agent to direct the anisotropic growth of the nanoparticles. The obtained silver nanowires are about 25 nm in diameter and up to 20 μm in length. Unlike the usually reported cases of silver nanowires or nanorods, in which the silver nanocrystals were often generated with a multi-twinned structure, in our experiments the nanowires adopt a single-crystal structure with their growth direction along the [100] axis. Investigations on the influence of different experimental conditions indicate that slow rate of the reduction process is a key factor for inducing the anisotropic growth of the nanowires.

Keywords Silver · Nanowire · Eco-friendly · Tannin · Reduction rate

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Introduction

One-dimensional (1-D) metal nanostructures have attracted intensive attention due to their unique shape-dependent properties and their potential applications in technical areas. They can be used to experimentally investigate the effects of quantum confinement on electronic transport, optical, and other physical properties (Hu et al. 1999; Zhang et al. 2000; Xia et al. 2003; Wiley et al. 2005). They have also been widely exploited to fabricate nanoscale electronic, photonic, sensing, and catalytic devices (Cui et al. 2001; El-Sayed 2001; Tao et al. 2003; Christopher and Linic 2008). Among all metals, silver nanowires are particularly interesting to synthesize and study because bulk silver exhibits the highest electrical and thermal conductivities, and 1-D nanostructures of silver might provide some enhanced properties and applications.

Many chemical methods have been explored to prepare silver nanowires, for example, electrochemical techniques (Zhu et al. 2000; Peppler and Janek 2007), polymer-directed synthesis (Xiong et al. 2003; Shen et al. 2007), template (i.e., mesoporous materials (Huang et al. 2000), alumina membranes (Wang et al. 2008), carbon nanotubes (Govindaraj et al. 2000), porous polycarbonate (Tian et al. 2003), DNA chains (Wei et al. 2005), and peptide nanotubes (Reches and Gazit 2003)) directed synthesis and hydrothermal process (Sun and Li 2005; Wang et al. 2005). A most impressive method is the PVP-assisted polyol process at elevated temperature (Sun et al. 2002a, b; Skrabalak

et al. 2008). The authors synthesized high quality silver nanowires with uniform morphology and pointed out the unambiguous crystal structure: penta-twinned structure bounded by five {100} side surface and 10 (Bardhan et al. 2009) end surfaces, with [110] as the common axial direction of the five subunits as well as the growth direction of the nanowire. Seed-mediated, surfactant-assisted synthesis of silver nanowires or nanorods is another typical method (Jana et al. 2001). Although the authors did not indicate the crystal structure of the nanowires, silver nanorods (Ni et al. 2005) and gold nanorods (Johnson et al. 2002) prepared by similar methods were found to adopt the penta-twinned structure. Many other cases in which uniform and straight silver nanowires could be obtained have also given the penta-twinned crystal structure (Caswell et al. 2003; Yu et al. 2004; Sun and Li 2005; Zhang et al. 2005). Formation of this kind of structure can be understood as follows. In the solution-phase synthesis of silver (or gold etc.) nanostructures, the crystallinity of the embryonic seeds (single-crystal vs. multi-twinned particles) plays a crucial role in determination of the morphology of final products (Wiley et al. 2005). Below a certain size, the multiply twinned decahedron has been demonstrated to be the most thermodynamically stable seed, with its surfaces bound almost entirely by the lower energy {111} facets (Marks 1994; Yacaman et al. 2001). If the chemical potential (i.e., driving force) for crystallization locate at a sufficiently low level, multi-twinned particles (thermodynamically more stable, often being decahedra) would be formed rather than single-crystal seeds (kinetically stable). Then the formed decahedral seeds could uniaxially grow and elongate into 1-D penta-twinned nanocrystals through preferentially deposition of free silver atoms on the twin defect sites, which represent the reactive active regions (Sun et al. 2002a, b; Wiley et al. 2005). As the formation of twinned seeds during nucleation and growth of noble-metal nanocolloids is expected for most reaction conditions (Lofton and Sigmund 2005; Elechiguerra et al. 2006), this decahedron-induced 1-D growth might be a general mechanism in the cases where driving force for crystallization is weak and there is no too strong adsorption action to the original seeds.

Here we show a simple aqueous-phase method, in which tannin is used to reduce silver nitrate at room temperature, to prepare uniform silver nanowires without the assistance of any surfactant or capping agent. The nanowires were characterized to be a single-crystal rather than conventional penta-twinned structure, which was presupposed to be for the mild reducing condition and no existence of any capping agent in our reaction system. Our method has the following strong points relative to previous reports: (1) the fabrication procedure is extremely simple and environment-friendly; (2) the products adopt single-crystal structure, which might lead to enhanced properties as well as applications in comparison with multi-twinned silver nanowires. Recent discoveries have proved the crystallinity of the metal nanostructure also significantly affects their physical and chemical properties such as mechanical strength, chemical stability (Lu et al. 2004; Elechiguerra et al. 2005). So this kind of single-crystal nanowires could be potential candidate for technical applications and further property investigations (Mohanty et al. 2007).

Experimental section

At room temperature, 10 mL of 5 mM $AgNO_3$ aqueous solution was mixed with 10 mL 1 mM tannin aqueous solution in a 100-mL conical flask. After mixing, the solution was shaken to be homogeneous and was then allowed to stand for 12 h under ambient conditions. The obtained gray-blue reaction mixture was centrifuged at 4,000 rpm for 30 min. The precipitate was washed with ethanol and deionized (DI) water for several times, and was redispersed in DI water for further characterization. Due to the irregular particles mixed within the products, the exact yield of the silver nanowires is difficult to calculate. According to the obtained solid silver products and the scanning electron microscopy (SEM) characterization, the yield of silver nanowires is estimated to be 5–10%.

X-ray diffraction pattern (XRD) was recorded on a Philips X' Pert Pro Super diffractometer, $\lambda = 0.154$ 1874 nm. SEM was performed on a JEOL JSM-6700F microscope. Transmission electron microscopy (TEM) was conducted on a Hitachi H-800 microscopy. High-resolution transmission electron microscope (HRTEM) was performed on a JEOL 2010 microscope. UV–visible extinction spectra were measured on Shimadzu UV-2401 PC spectrophotometer.
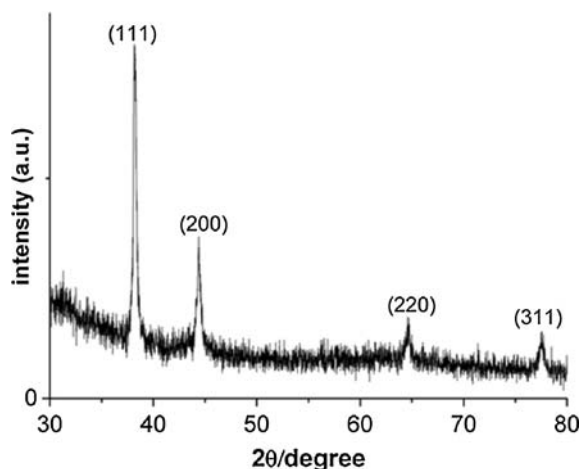
Results and discussion

The XRD pattern of the as-prepared product shown in Fig. 1 exhibits four peaks corresponding to the (111), (200), (220), and (311) diffraction peaks of the face-centered cubic Ag, respectively. No impurity can be detected from this pattern. This indicates that pure crystalline Ag is obtained under the present synthetic conditions.

Scanning electron microscopy and TEM characterizations of the centrifuged sample are presented in Fig. 2. As shown in Fig. 2a, the product is the mixture of nanowires and irregular particles. And the nanowires are uniform and straight, with their lengths in the range of 2–20 μm. The TEM images (Fig. 2b, c) show the nanowires are about 25 nm in diameter and exhibit smooth exteriors. Electron diffraction (ED) pattern corresponding to the individual nanowire showed in Fig. 2c is displayed in the inset, which indicates the single-crystal nature of the nanowires with their growth direction along the [100] axis. Further evidence is provided by the HRTEM analyses (Fig. 2d), which unambiguously point out that the nanowires are perfect single-crystal. The regular spacing of the observed lattice plane is 2.0 Å, corresponding to the Ag (200) planes, which is in accordance with the ED result. Additional HRTEM images can also be found (see Supporting Information), and present two sets of lattice fringe with spacing of 2.0 Å that are perpendicular and parallel to the growth direction of the nanowire, respectively. To our knowledge, this is the first report that single-crystal silver nanowires have been found to grow along [100] direction.

Figure 3 shows the UV–visible spectra of the products. The centrifuged sample exhibit two surface plasmon resonance peaks. The shoulder peak at 350 nm is an optical characteristic similar to bulk silver, which has usually been observed for silver nanowires (Wang et al. 2005; Wiley et al. 2005; Shen et al. 2007). The second peak at 390 nm should be the transverse plasmon band of silver nanowires. It is well known that two plasmon modes, transverse and longitudinal modes, are expected for 1-D metallic nanostructures. And for silver nanowires or nanorods with aspect ratio larger than five, the longitudinal plasmon mode would disappear from the visible region (Sun et al. 2002a, b). The transverse mode shows a slight red shift compare to previous results (Sun et al. 2002a, b), which may be due to the affection of the irregular particles in the product and the different solution circumstance.
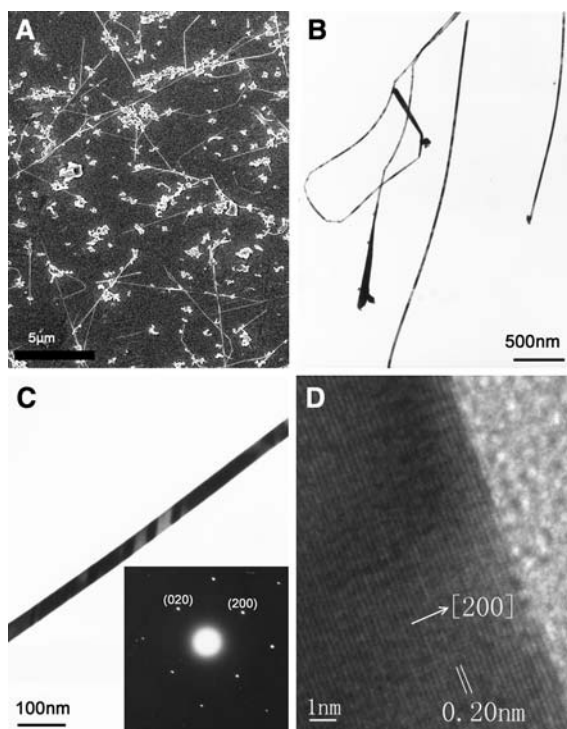
Fig. 2 Electron microscope characterizations of centrifuged sample. **a** SEM image. **b** TEM image. **c** TEM image of an individual nanowire. The inset shows the corresponding ED pattern recorded by focusing the electron beam onto the nanowire. **d** HRTEM image of a nanowire


Fig. 1 XRD pattern of the as-prepared product
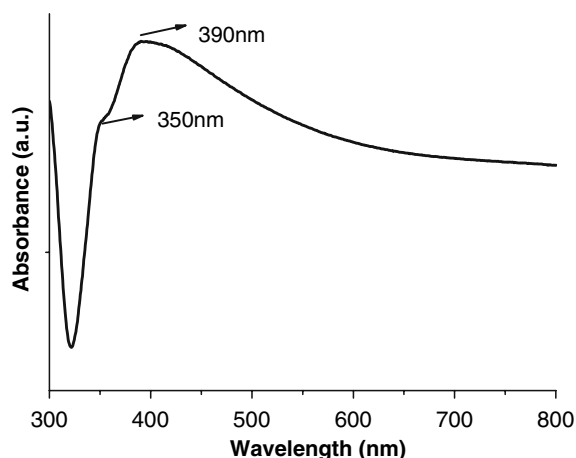
Fig. 3 UV–visible extinction spectra of the products

In our experiments, tannin was used as a weak reducer. It could reduce the Au or Ag salt through the oxidization of its hydroxyl groups (Sun et al. 2004; Tian et al. 2007). As we mentioned above, low driving force for crystallization, i.e., slow reduction rate may favor the formation of twinned silver seeds with decahedron morphologies. Then straight silver nanorods or nanowires might be obtained through the decahedron-induced 1-D growth (Elechiguerra et al. 2006). For getting decahedron seeds, overmuch strong capping agent should be avoided since it could lower the barrier between the single-crystal and the twinned seeds and thus make against the probability of formation of thermodynamic stable twinned decahedra. Based on this consideration, many mild reducing agents could be explored to prepare silver nanowires/nanorods, under the assistance of appropriate or even no capping agent. For example, sodium citrate, glucose, and starch have been successfully used to prepare penta-twinned silver nanowires without introducing any capping agent (Caswell et al. 2003; Yu et al. 2004; Zhang et al. 2005). In our synthesis, we used tannin as a weak reducing agent and did not employ any surfactant or other capping agent; it would be reasonable if the obtained nanowires had adopted the conventional penta-twinned structure. So, the practically obtained single crystal product is a somewhat surprising result. And the decahedron-induced 1-D growth mechanism cannot be applied in our case.

Further experimental investigations indicate that the slow reaction rate is a key factor for the anisotropic growth, since highly anisotropic structures become favorable in a slow reduction process (Mjuulin 1961; Chen et al. 2004). The concentration of tannin was found to exhibit important influence on the morphology of the final products. Figure 4a shows the SEM image of the sample that was synthesized using a procedure similar to the standard synthesis (experimental section), except the concentration of tannin solution increased from 1 to 4 mM. In this case, the reaction rate increased remarkably, and a large number of isotropic nanoparticles were obtained with their size in the range from 20 to 60 nm. No nanowire was found and only a few nanorods mixed within the products. This fact suggested that only sufficiently slow reduction rate could favor the formation of silver nanowires. Other comparative experiments have also approved this suggestion. When a small amount of sodium citrate (1.5 mM on the basis of the total volume of the reaction solution) was introduced to the reaction system at the beginning with other experimental parameters unchanged, the reduction reaction was found to accelerate dramatically, and the products proved to be isotropic particles. Ethanol has been used as the solvent in stead of DI water, which also increased the reaction rate significantly, and the similar products were formed. These facts, which confirmed that sufficiently slow reduction process could favor the formation of highly anisotropic structure, are consistent with a recent report by Xia's group (Chen et al. 2004). Through introducing oxidizing Fe^{3+}/O_2 pair, they slowed the reaction rate of a polyol process to induce the anisotropic growth of single-crystal Pt nanowires. Here, we demonstrate that choosing appropriate solvent and adjusting the concentration of reducer could also efficiently control the reduction rate and facilitate the formation of 1-D nanostructure. And the conception of slow reaction rate induced anisotropic growth should be an important idea for the preparation of 1-D structure for isotropic crystal such as face-centered cubic metal.

When the concentration of tannin solution decreased from 1 to 0.5 mM (Fig. 4b), silver nanowires could also form by reason of the slow reduction process, but the proportion of them decreased significantly compared to Fig. 2a. This might be due to the lack of sufficient driving force (reducing agent) for the growth of more nanowires. The appropriate concentration of tannin solution has been found to be 1 mM for formation of desired products.
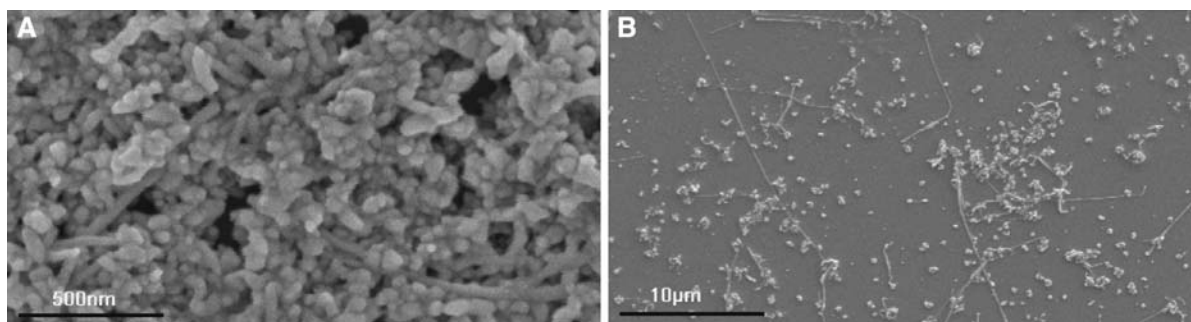
Fig. 4 SEM images of the products in comparative experiments at different concentration of tannin: **a** 4 mM, **b** 0.5 mM

In our synthesis, the silver nanowires grew along the [100] axis and this is reasonable since the (100) facet is not the most chemical stable plane of face-centered cubic structure metal. It has greater surface free energy than (111) facet. So it is easier for the crystallization of the free silver atoms on (100) lattice surface, which could lead to the preferential growth along [100] direction. Although slow reaction rate has been found to be the key factor for the anisotropic growth, precise mechanism is not clear: considering the cubic silver has six equivalent {100} faces, how can the nanocrystals break the symmetry and follow a 1-D growth mode during their growth process? The capping interaction between silver particles and tannin (with its derivatives) is speculated to be another important factor for the anisotropy growth besides the slow reduction rate. Tannin molecules may adsorb on different crystal plane of the silver nanocrystals selectively and thus modify their growth behavior. For example, tannin might act only with the side surfaces of the nanowires effectively and thus induce their 1-D growth. Further experimental investigation is needed to clarify the detailed growth mechanism of the nanowires.

Conclusion

We have demonstrated a surfactant-less, aqueous-phase approach for the growth of silver nanowires at room temperature. Slow rate of reducing reaction is found to be necessary for favoring the anisotropic growth. The obtained nanowires exhibit unique single crystal structures with their growth direction along the [100] axis. This novel structure might means new properties as well as importance in technical applications. Based on the single-crystal nature, the nanowires should have greater chemical stability against atmospheric corrosion, which is meaningful in nanoelectronics (Mohanty et al. 2007). Since many irregular particles mix within the products, improvement of this synthesis procedure has being explored to increase the purity of nanowires. Recently, bio-reduction methods were used to prepare various spherical metal nanoparticles in which tannin, existing in many plants, was employed as the reducing agent (Canizal et al. 2001; Ascencio et al. 2003; Prasad et al. 2007). Our discovery might inspire the further bio-fabrication of 1-D metal nanomaterials in an environment-friendly manner.

References

Ascencio JA, Mejia Y, Liu HB, Angeles C, Canizal G (2003) Bioreduction synthesis of Eu-Au nanoparticles. Langmuir 19:5882–5886

Bardhan R, Neumann O, Mirin N, Wang H, Halas NJ (2009) Au nanorice assemble electrolytically into mesostars. Acs Nano 3:266–272

Canizal G, Ascencio JA, Gardea-Torresday J, Yacaman MJ (2001) Multiple twinned gold nanorods grown by bio-reduction techniques. J Nanopart Res 3:475–481

Caswell KK, Bender CM, Murphy CJ (2003) Seedless, surfactantless wet chemical synthesis of silver nanowires. Nano Lett 3:667–669

Chen J, Herricks T, Geissler M, Xia Y (2004) Single-crystal nanowires of platinum can be synthesized by controlling the reaction rate of a polyol process. J Am Chem Soc 126:10854–10855

Christopher P, Linic S (2008) Engineering selectivity in heterogeneous catalysis: Ag nanowires as selective ethylene epoxidation catalysts. J Am Chem Soc 130:11264–11265

Cui Y, Wei QQ, Park HK, Lieber CM (2001) Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species. Science 293:1289–1292

Elechiguerra JL, Larios-Lopez L, Liu C, Garcia-Gutierrez D, Camacho-Bragado A, Yacaman MJ (2005) Corrosion at the nanoscale: the case of silver nanowires and nanoparticles. Chem Mater 17:6042–6052

Elechiguerra JL, Reyes-Gasga J, Yacaman MJ (2006) The role of twinning in shape evolution of anisotropic noble metal nanostructures. J Mater Chem 16:3906–3919

El-Sayed MA (2001) Some interesting properties of metals confined in time and nanometer space of different shapes. Acc Chem Res 34:257–264

Govindaraj A, Satishkumar BC, Nath M, Rao CNR (2000) Metal nanowires and intercalated metal layers in single-walled carbon nanotube bundles. Chem Mater 12:202–205

Hu JT, Odom TW, Lieber CM (1999) Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes. Acc Chem Res 32:435–445

Huang MH, Choudrey A, Yang PD (2000) Ag nanowire formation within mesoporous silica. Chem Commun: 1063–1064

Jana NR, Gearheart L, Murphy CJ (2001) Wet chemical synthesis of silver nanorods and nanowires of controllable aspect ratio. Chem Commun: 617–618

Johnson CJ, Dujardin E, Davis SA, Murphy CJ, Mann S (2002) Growth and form of gold nanorods prepared by seed-mediated, surfactant-directed synthesis. J Mater Chem 12:1765–1770

Lofton C, Sigmund W (2005) Mechanisms controlling crystal habits of gold and silver colloids. Adv Funct Mater 15:1197–1208

Lu L, Shen Y, Chen X, Qian L, Lu K (2004) Ultrahigh strength and high electrical conductivity in copper. Science 304:422–426

Marks LD (1994) Experimental studies of small-particle structures. Rep Prog Phys 57:603–649

Mjuulin JW (1961) Crystallization. Butterworth, London

Mohanty P, Yoon I, Kang T, Seo K, Varadwaj KSK, Choi W, Park QH, Ahn JP, Suh YD, Ihee H, Kim B (2007) Simple vapor-phase synthesis of single-crystalline ag nanowires and single-nanowire surface-enhanced raman scattering. J Am Chem Soc 129:9576–9577

Ni C, Hassan PA, Kaler EW (2005) Structural characteristics and growth of pentagonal silver nanorods prepared by a surfactant method. Langmuir 21:3334–3337

Peppler K, Janek J (2007) Template assisted solid state electrochemical growth of silver micro- and nanowires. Electrochim Acta 53:319–323

Prasad K, Jha AK, Kulkarni AR (2007) *Lactobacillus* assisted synthesis of titanium nanoparticles. Nanosc Res Lett 2:248–250

Reches M, Gazit E (2003) Casting metal nanowires within discrete self-assembled peptide nanotubes. Science 300: 625–627

Shen Q, Sun J, Wei H, Zhou Y, Su Y, Wang D (2007) Fabrication of silver nanorods controlled by a segmented copolymer. J Phys Chem C 111:13673–13678

Skrabalak SE, Wiley BJ, Kim M, Formo EV, Xia Y (2008) On the polyol synthesis of silver nanostructures: glycolaldehyde as a reducing agent. Nano Lett 8:2077–2081

Sun XM, Li YD (2005) Cylindrical silver nanowires: preparation, structure, and optical properties. Adv Mater 17:2626–2630

Sun Y, Gates B, Mayers B, Xia Y (2002a) Crystalline silver nanowires by soft solution processing. Nano Lett 2: 165–168

Sun Y, Yin Y, Mayers BT, Herricks T, Xia Y (2002b) Uniform silver nanowires synthesis by reducing agno3 with ethylene glycol in the presence of seeds and poly(vinyl pyrrolidone). Chem Mater 14:4736–4745

Sun L, Zhang ZJ, Dang HX (2004) Synthesis and characterization of oil soluble ag nanoparticles. Chin J Chem Phys 17:618–622

Tao A, Kim F, Hess C, Goldberger J, He RR, Sun YG, Xia YN, Yang PD (2003) Langmuir-blodgett silver nanowire monolayers for molecular sensing using surface-enhanced Raman spectroscopy. Nano Lett 3:1229–1233

Tian M, Wang J, Kurtz J, Mallouk TE, Chan MHW (2003) Electrochemical growth of single-crystal metal nanowires via a two-dimensional nucleation and growth mechanism. Nano Lett 3:919–923

Tian XL, Wang WH, Cao GY (2007) A facile aqueous-phase route for the synthesis of silver nanoplates. Mater Lett 61:130–133

Wang Z, Liu J, Chen X, Wan J, Qian Y (2005) A simple hydrothermal route to large-scale synthesis of uniform silver nanowires. Chem Eur J 11:160–163

Wang B, Fei GT, Zhou Y, Wu B, Zhu X, Zhang L (2008) Controlled growth and phase transition of silver nanowires with dense lengthwise twins and stacking faults. Cryst Growth Des 8:3073–3076

Wei G, Zhou H, Liu Z, Song Y, Wang L, Sun L, Li Z (2005) One-step synthesis of silver nanoparticles, nanorods, and nanowires on the surface of DNA network. J Phys Chem B 109:8738–8743

Wiley B, Sun YG, Mayers B, Xia YN (2005) Shape-controlled synthesis of metal nanostructures: the case of silver. Chem Eur J 11:454–463

Xia YN, Yang PD, Sun YG, Wu YY, Mayers B, Gates B, Yin YD, Kim F, Yan YQ (2003) One-dimensional nanostructures: synthesis, characterization, and applications. Adv Mater 15:353–389

Xiong Y, Xie Y, Wu C, Yang J, Li Z, Xu F (2003) Formation of silver nanowires through a sandwiched reduction process. Adv Mater 15:405–408

Yacaman MJ, Ascencio JA, Liu HB, Gardea-Torresdey J (2001) Structure shape and stability of nanometric sized particles. J Vac Sci Technol 19:1091–1103

Yu SH, Cui XJ, Li LL, Li K, Yu B, Antonietti M, Cölfen H (2004) From starch to metal/carbon hybrid nanostructures: hydrothermal metal-catalyzed carbonization. Adv Mater 16:1636–1640

Zhang ZB, Sun XZ, Dresselhaus MS, Ying JY, Heremans J (2000) Electronic transport properties of single-crystal bismuth nanowire arrays. Phys Rev B 61:4850–4861

Zhang SH, Jiang ZY, Xie ZX, Xu X, Huang RB, Zheng LS (2005) Growth of silver nanowires from solutions: a cyclic penta-twinned-crystal growth mechanism. J Phys Chem B 109:9416–9421

Zhu JJ, Liu SW, Palchik O, Koltypin Y, Gedanken A (2000) Shape-controlled synthesis of silver nanoparticles by pulse sonoelectrochemical methods. Langmuir 16:6396–6399