872 *Chem. Mater.* **2004,** *16,* 872−876

Wet Chemical Synthesis of Silver Nanowire Thin Films at Ambient Temperature

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Received October 27, 2003. Revised Manuscript Received December 12, 2003

Novel silver nanowire thin films, which consist of interwoven bundles of single-crystalline silver nanowires about 30−40 nm in diameter, have been successfully synthesized on glass wall by mild chemical reduction in aqueous solutions of poly(methacrylic acid) at room temperature. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and UV−vis absorption spectroscopy have been used to characterize the obtained silver products. It was found that there existed a competition between precipitation of spherical particles, precipitation of individual nanowires, and formation of silver nanowire films. It was revealed that the negatively charged glass surface provided heterogeneous nucleation sites for the growth of bundles of silver nanowires. Appropriate pH values and polymer concentrations were crucial for the growth of dense silver nanowire films on the glass wall. A polymer-mediated heterogeneous nucleation and growth process has been proposed for the formation of the unique metal nanowire thin films.

Introduction

Recently, many efforts have been devoted to the controlled synthesis and assembly of metal nanowires because of their potential use as interconnects or active components in fabricating nanodevices and their important roles in investigating a variety of physical phenomena.[1] In particular, the preparation of silver nanowires has received much attention because bulk silver exhibits the highest electrical and thermal conductivity among all metals and the performance of silver in many applications could be potentially enhanced by processing silver into one-dimensional (1D) nanostructures.[2] For the 1D growth of silver nanowires by chemical or electrochemical depositions, "hard templates", such as carbon nanotubes,[3] porous polycarbonate[4] and alumina[5] membranes, and mesoporous silica,[6] and "soft templates", such as DNA chains,[7] peptide nanotubes,[8] rod-like micelles,[9] and hexagonal liquid-crystalline phases[10] have been employed. To avoid the step of template removal, several direct solution-phase approaches to silver nanowires by using surface-capping reagents have been explored. For example, silver nanowires have been successfully synthesized by chemical reduction in the presence of gelatin protein[11] and a variety of functional polymers[2,12,13] or with use of citrate as both reductant and capping agent in the absence of a surfactant or polymer.[14] However, these templateless methods were often characterized by relatively low yields or elevated synthesis temperatures. Moreover, silver nanowire arrays or films have not been obtained directly by these solution-phase approaches, although some metal nanowire arrays or films have been produced by electrodeposition against templates.[10,15] Here, we report a novel room-temperature synthesis of silver nanowire thin films on glass wall by chemical reduction in aqueous solutions of poly(methacrylic acid) (PMAA), which is remarkably simple and mild, reminiscent of the classic silver mirror reaction.

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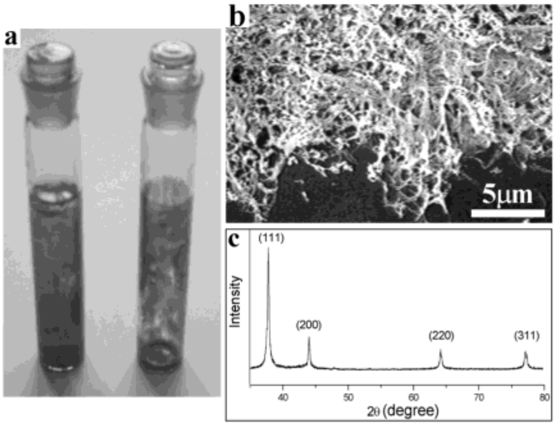

Figure 1. (a) Photo of wet (left) and dry (right) glass tubes with silver nanowire thin films on the glass wall. (b) SEM overview of a free-standing silver nanowire thin film. (c) XRD patterns of Ag nanowire thin films.

Experimental Section

Silver nanowire thin films were readily synthesized by reducing $AgNO_3$ with ascorbic acid in aqueous solutions of PMAA ($M_w = 6500$, sodium salt, Aldrich) at room temperature (ca. 22 °C). In a typical synthesis, 9 mL of solution containing PMAA (30 mg) and ascorbic acid (0.2 mmol) was prepared in a glass tube (~1.2 cm in diameter), which gave a pH value of about 3.6. Then, 1 mL of 0.2 M $AgNO_3$ was added with shaking, which gave a final PMAA concentration of 3 g L^{-1} and final reactant ($AgNO_3$ and ascorbic acid) concentration of 0.02 M. After mixing, the solution was allowed to stand for 24 h, leading to the gradual formation of a translucent gray film on the inner wall of the glass tube. The film product was scratched off the glass wall, washed with water, and characterized. In the experiment, the polymer concentration was varied between 0.3 and 6 g L^{-1} and the pH value of the solution was adjusted between 2.0 and 6.0 with HNO_3 or NaOH before the $AgNO_3$ solution was added.

Scanning electron microscopy (SEM) was preformed on an AMARY 1910FE microscope operated at 20 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) investigations were conducted on a JEOL JEM-200CX microscope operated at 160 kV and an Hitachi H-9000HAR microscope operated at 300 kV, respectively. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax-2000 diffractometer with Cu Kα radiation. UV−vis absorption spectra were obtained on a Shimadzu UV-250 spectrophotometer.

Results and Discussion

A typical photo of wet and dry glass tubes with silver nanowire films on the glass wall was presented in Figure 1a. It showed that a relatively uniform translucent film was formed on the glass wall in the solution and the film tended to shrink on drying after the solution was evacuated, resulting in a dry film showing irregular holes. A low-magnification SEM image shown in Figure 1b suggested that the film consisted of interwoven fibers. The XRD pattern of the film product (Figure 1c) exhibited sharp peaks corresponding to the (111), (200), (220), and (311) diffraction peaks of the cubic structure of metallic Ag, respectively, indicating that the thin film was composed of pure crystalline silver.

Detailed SEM and TEM characterizations of the obtained silver nanowire thin films were presented in Figure 2. As shown in Figure 2a, the thin film consisted of irregularly stacked bundles of silver nanowires ranging in length from less than 1 μm to larger than 10 μm, most of which seemed to grow from single starting points with a smooth growth front. The high-magnification SEM image shown in Figure 2b suggested that the nanowire bundles consisted of silver nanowires with diameters of about 30−40 nm and showed a certain degree of similarity. Apparently, the bundles of silver nanowires are similar to the bundles of $BaSO_4$[16] and $BaCrO_4$[17] nanofibers grown on glass wall in the presence of polymers; however, no nanowire films have been observed in these barium salts cases. TEM samples were prepared by dispersing a piece of film in water with sonication and dropping the dispersion on copper grids. The TEM image presented in Figure 2c clearly showed the presence of bundles of silver nanowire with lengths up to more than 10 μm. An enlarged TEM image of nearly parallel nanowires was shown in Figure 2d, suggesting that the silver nanowires were ranging in diameter from 30 to 40 nm and exhibited somewhat rough surfaces. Figure 2e showed the TEM image of a single nanowire as well as the related electron diffraction (ED) pattern, which indicated that the nanowire was a single crystal of cubic silver grown along the $[01\bar{1}]$ direction. The HRTEM image shown in Figure 2f exhibited clear lattice fringes with a *d* spacing of about 0.24 nm, which agreed well with the *d*(111) spacing for fcc Ag, confirming that the nanowires were single crystals of cubic silver with $[01\bar{1}]$ as the growth direction.

Figure 3 shows the UV−vis absorption spectrum of the silver nanowires, which was obtained by dispersing the silver nanowire film in water under sonication. The spectrum exhibited a broad plasmon peak centered at ~410 nm as well as a shoulder around 350 nm. It is well-known that two plasmon resonances, the transverse and longitudinal plasmon bands, are expected for anisotropic metallic nanoparticles including silver nanorods.[9] The observed broad peak around 410 nm could be attributed to the transverse plasmon band of the silver nanowires but the expected longitudinal plasmon band did not appear. It is noted that well-resolved longitudinal plasmon band, which is red-shifted with increasing aspect ratio, was observed for uniform silver nanorods with relatively small aspect ratios;[9b] however, the band usually disappeared for silver nanowires with large aspect ratios.[2a,b,14] This result may be rationalized by considering that long silver nanowires usually do not adopt a uniform aspect ratio and they can easily bend or twist in solution, which could significantly decrease the intensity of the longitudinal plasmon band, leading to the disappearance of the band. The shoulder around 350 nm may be attributed to the plasmon resonance of bulk silver,[2a,b] which could result from the interwoven bundles of silver nanowires that were not separated when dispersed in water.

Some insight into the formation mechanism of silver nanowire thin films was obtained by examining the products obtained at earlier stages. After 1 min of mixing, the reaction solution turned dark but no films

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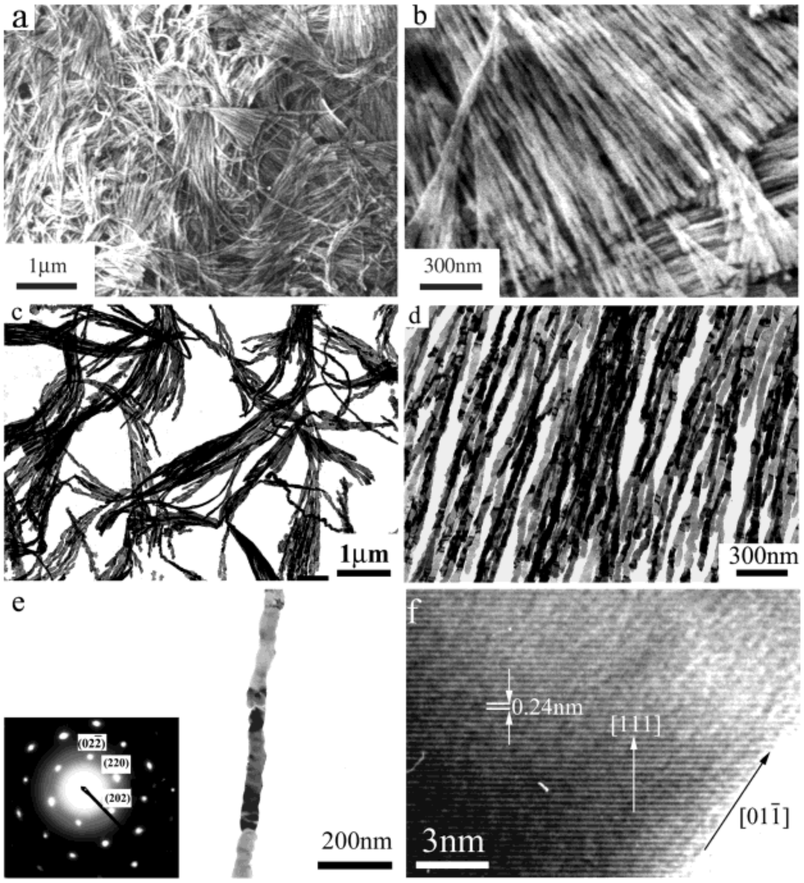

Figure 2. SEM (a,b), TEM (c−e), and HRTEM (f) images of Ag nanowires constituting thin films. Inset of (e) shows the related electron diffraction pattern.

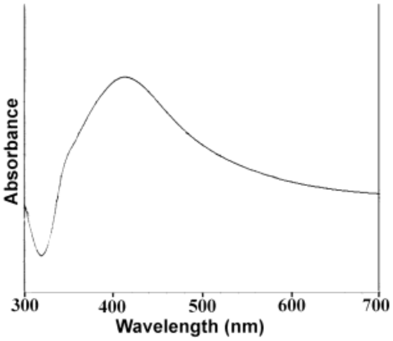

Figure 3. UV−vis absorption spectrum of silver nanowires constituting thin films.

were observed on the glass wall; a TEM sample was prepared by directly placing a drop of the solution on a copper grid. As shown in Figure 4a, the product exhibited a large amount of small nanoparticles about several nanometers with high contrast, which were revealed to be nanocrystals of cubic silver according to the related ED pattern. It was also observed that these silver nanoparticles were surrounded by netlike matter with low contrast, which could correspond to primary silver clusters or aggregates formed upon complexation of the polymer PMAA with unreduced silver ions. It was observed that, with increasing aging time, the solution became more and more clear and a gray thin film formed gradually on the glass wall simultaneously. After 1 h of aging, the solution turned almost clear and a piece of film was scratched off the wall and used for the SEM observation. As shown in Figure 4b, loosely stacked silver nanowire bundles, which showed single starting points and a smooth growth front, were produced. When the aging time was increased to 24 h, relatively dense and complete nanowire films were

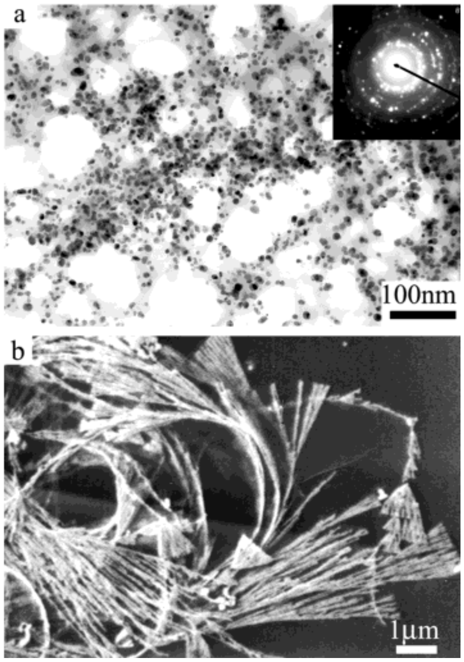

Figure 4. TEM (a) and SEM (b) images of silver products obtained at earlier stages of the formation of Ag nanowire thin films. Aging time: (a) 1 min; (b) 1 h. Inset of (a) shows the related electron diffraction pattern.

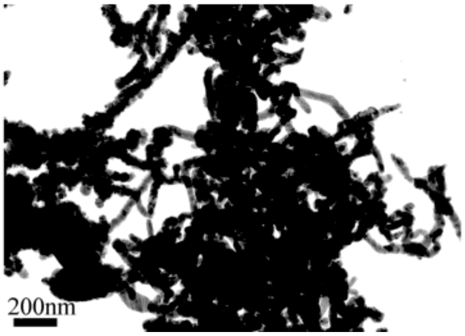

Figure 5. TEM image of silver product obtained in glass tubes under the stirring condition.

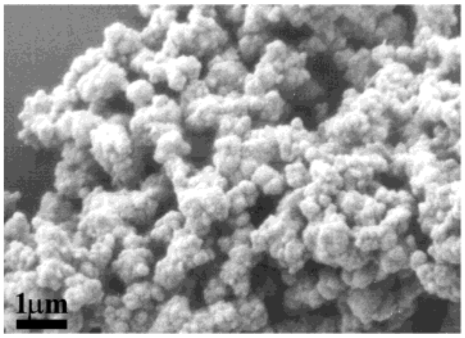

Figure 6. SEM image of silver products obtained in a plastic tube.

formed on the glass wall, as shown in Figure 2. It is worth mentioning that a static condition without stirring is required for the formation of ideal silver nanowire films on the glass wall. If stirring was conducted throughout the aging process, only irregular silver nanowires as well as their aggregates were obtained (Figure 5), suggesting that the convection induced by stirring would considerably disturb the heterogeneous nucleation and growth of bundles of silver nanowires on the glass wall, leading to the peeling of primary nanowire nuclei from the glass wall or the homogeneous nucleation and growth of individual nanowires in solution.

When the reaction was conducted in plastic tubes instead of glass tubes under otherwise similar conditions, no films formed on the plastic wall and only spherical silver particles precipitated (Figure 6), indicating that the silver nanowire bundles grew from a single starting point where the glass wall provided the necessary heterogeneous nucleation sites. It is noted that the isoelectric point of the silicate glass surface is about 2−3 and the glass wall would be negatively charged under the synthesis conditions (pH ∼ 3.6). Therefore, some negatively charged sites or defects on the glass wall could preferentially adsorb cationic Ag^+ ions and so acted as the heterogeneous nucleation sites for the growth of bundles of silver nanowires whereas the surface of the plastic wall essentially carried no charges and could not provide effective heterogeneous nucleation sites.

The effect of pH on the formation of silver nanowire films on glass wall was investigated, which supported the proposed role of the glass wall as nucleation sites. It was observed that as the pH of the solution was decreased by adding HNO_3, the nanowire films became more sparse and more and more silver nanowires precipitated on the bottom. When the pH was decreased to 2.0, just below the isoelectric point of the glass wall, only individual Ag nanowires with a diameter of 25−100 nm were obtained (Figure 7a). This result indicated that the negatively charged glass surface was protonated and lost its role as heterogeneous nucleation sites gradually as the pH was decreased from 3.6, a suitable pH for the nanowire film formation. However, if the pH was increased to larger than 4.3, i.e., the dissociation constant pK_a for PMAA, by adding NaOH, many individual spherical particles precipitated in addition to some irregular nanowires. When the pH was increased to 6.0, only spherical silver particles of about 0.5−0.6 μm were obtained (Figure 7b). At pH above the pK_a, the PMAA molecules were mainly in the form of polyanionic chains, which could result in a strong interaction with all of the silver crystal surfaces rather than specific crystal surfaces, leading to the formation of spherical particles rather than anisotropic nanowires. Therefore, a suitable pH was crucial for the formation of dense silver nanowire films on the glass wall.

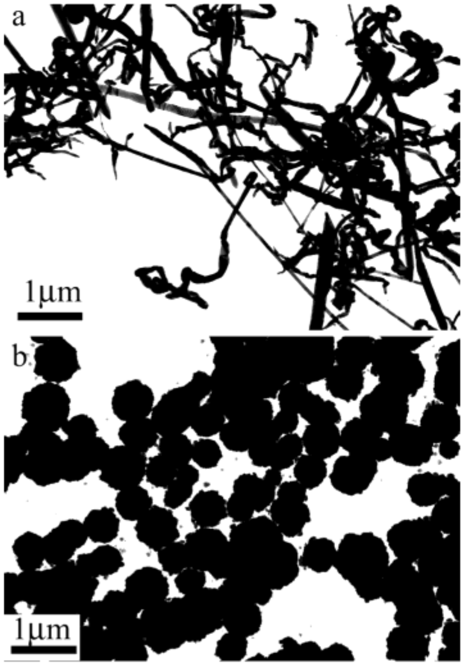

Figure 7. TEM images of silver products obtained in glass tubes at adjusted pH values. pH: (a) 2.0; (b) 6.0.

Furthermore, it was found that a suitable PMAA concentration (e.g., 3 g L^{-1}) was essential for the formation of silver nanowire films in glass tubes. As shown in Figure 8, spherical silver particles precipitated at a lower PMAA concentration (0.3 g L^{-1}) whereas individual short silver nanowires precipitated at a higher PMAA concentration (6 g L^{-1}). It indicated that enough PMAA was required for the heterogeneous nucleation and 1D growth of silver nanowires but excessive PMAA would considerably inhibit heterogeneous nucleation of silver on the glass wall, which is consistent with the result obtained from the polymer-mediated growth of bundles of $BaSO_4$[16]and $BaCrO_4$[17] nanofibers on glass substrates. It might be rationalized by considering that, at a high polymer concentration, the glass wall was largely covered by the adsorbed polymer molecules, impairing the direct adsorption of Ag^+ ions on the glass surface, which could lead to poor heterogeneous nucleation sites.

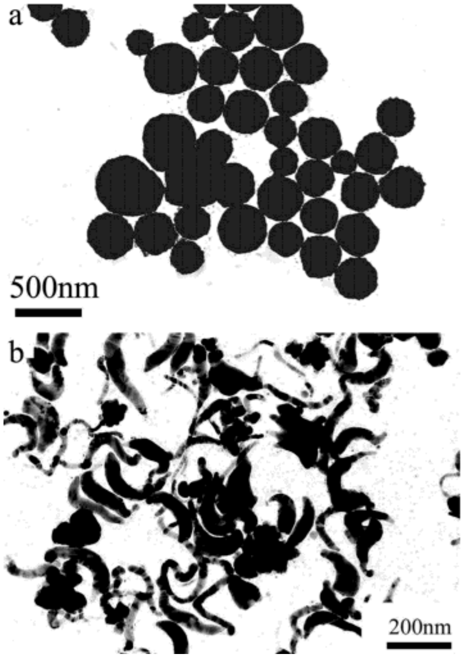

Figure 8. TEM images of silver products obtained in glass tubes at different polymer concentrations. [PMAA]: (a) 0.3 g L^{-1}; (b) 6 g L^{-1}.

The obtained results indicated that the bundles of silver nanowires formed through a polymer-mediated heterogeneous nucleation and growth process, which has been demonstrated previously for the growth of bundles of $BaSO_4$[16]and $BaCrO_4$[17] nanofibers on glass substrates directed by functional polymers. In the current case, PMAA could play multiple roles in the formation of silver nanowires. The PMAA molecules could considerably inhibit the nucleation and growth of silver crystals in the solution, thereby favoring heterogeneous nucleation of silver crystals on the glass wall. When the crystal growth from the nuclei proceeded through directed diffusion of primary silver particles/clusters as well as Ag^+–PMAA aggregates, the PMAA molecules could act as an efficient capping reagent to kinetically control the growth rates of various faces of the silver seed, leading to highly anisotropic growth of silver nanocrystals. It is noted that in the current situation relatively dense silver nanowire films resulted from the intergrowth of silver nanowire bundles whereas no nanowire films were obtained in the cases of barium salts, which could be partly attributed to the higher nucleation density of silver on the glass wall and the better elasticity of silver nanowires compared with the $BaSO_4$ or $BaCrO_4$ nanofibers. The current formation of silver nanowire films represents a unique example of higher order organization by mesoscale transformation of hybrid nanostructures.[18]

It is noteworthy that the treelike morphology of the bundles of silver nanowires that constituted the thin films is apparently similar to the dense parallel copper filaments grown by nonequilibrium electrochemical deposition.[19,20] It has been revealed that the electrodeposition process that involves oscillatory nucleation and growth usually generates highly branched dendrites consisting of polycrystalline metallic filaments in the dendritic growth regime. It can be noted that the bundles of silver nanowire obtained by the current heterogeneous nucleation and growth process showed a rather low branching rate and consisted of single-crystalline silver nanowires, indicating different growth mechanisms between the electrochemical and electroless deposition of metallic wires. Moreover, the classical diffusion theory that has been successfully used to explain the electrodeposition process may not be directly applied to explain the growth of the silver nanowires on the glass wall since the electroless deposition involved complex chemical processes. For instance, in the present synthesis, there existed a competition between precipitation of spherical particles, homogeneous nucleation and growth of individual nanowires in the solution, and heterogeneous nucleation and growth of nanowires on the glass wall, which resulted in the formation of silver nanowire films. It has been shown that the precipitation of spherical particles was favored at a low polymer concentration or a high pH; otherwise, the nucleation and growth of nanowires were favored. Then, the heterogeneous nucleation and growth of nanowires on the glass wall would be favored at an appropriate polymer concentration and an appropriate pH, leading to the formation of dense nanowire films. Finally, the homogeneous nucleation and growth of individual nanowires in the solution would be favored at a high polymer concentration or a low pH where the glass wall cannot act as effective heterogeneous nucleation sites. These observations may have important implications for the selective synthesis of inorganic nanoparticles, individual nanowires, and nanowire films.

In summary, we have demonstrated a novel polymer-mediated synthesis of silver nanowire thin films on glass wall by chemical reduction in aqueous solutions at room temperature. This synthetic process is remarkably simple and mild, and it provides a facile method for low-temperature solution growth of metal nanowires and their assembly into thin-film superstructures.

Acknowledgment. This work was supported by NSFC (20003001, 20325312, 20233010), the Special Fund of MOE, China (200020), and the Doctoral Program Foundation of MOE, China (2000000155).

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