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Controlled growth of large-scale silver nanowires*

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Large-scale silver nanowires with controlled aspect ratio were synthesized via reducing silver nitrate with 1, 2-propanediol in the presence of poly (vinyl pyrrolidone) (PVP). Scanning electron microscopy, transmission electron microscopy and x-ray powder diffraction were employed to characterize these silver nanowires. The diameter of the silver nanowires can be readily controlled in the range of 100 to 400 nm by varying the experimental conditions. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy results show that there exists no chemical bond between the silver and the nitrogen atoms. The interaction between PVP and silver nanowires is mainly through the oxygen atom in the carbonyl group.

Keywords: silver nanowires, controlled growth, chemisorption
PACC: 6146, 8110D, 8715K

1. Introduction

In recent years, synthesis of one-dimensional metal nanostructures, such as nanowires, nanobelts, and nanotubes has attracted extensive attention due to their unique magnetic, optical, electronic and mechanical properties compared to zero-dimensional nanostructures.[1−10] Among these one-dimensional metal nanostructures, silver nanowires are particularly of interest because the bulk silver exhibits the highest electrical and thermoconductivity among all metals, and possesses the lowest contact resistance. Moreover, like other noble metal nanostructures, silver nanowires have many unique properties such as biological inertness,[6] surface plasmon resonance.[6,11] With these favourable properties, they can play an important role in the fabrication of nanoscale electronic and photonic devices. As far as the development of these nanodevices is concerned, systematic and precise size control of the components becomes more and more important for practical applications. In the past years, many research groups have synthesized silver nanowires using various methods.[12−19] However, they usually obtain nanowires with diameter smaller than 80 nm, and little work concerns with the controlled growth of silver nanowires. More recently, Xia *et al* reported an approach based on modified polyol process for synthesis of silver nanowires with diameters in the range of 40–70nm.[20−22] The polyol process has been widely used to produce many metal and bimetallic nanostructures.[23−26] In most cases, using a suitable surfactant or polymer is necessary to direct the growth of metal nanostructures and protect them from aggregation. For silver, poly (vinyl pyrrolidone) (PVP) is chosen because it has been experimentally proven that the selective interaction between PVP and various crystallographic planes lead to the anisotropic growth of silver nanowires. Previous work also reported that there existed a strong interaction between the surfaces of silver nanoparticles and PVP through coordination bonding with the pyrrolidone ring.[27−29] Despite of this, the exact bonding geometry and the nature of selectivity between different crystallographic planes are still not clear yet. Further research is needed to shed light on it and provide a more thorough understanding of what molecules in solution may generate a specific shape desired and a certain size of the nanostructures.

In this paper, we report the synthesis of large-

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scale silver nanowires with various aspect ratios by using 1, 2-propanediol as reducing agent and PVP as surfactant in the polyol process. These nanowires have a length ranging from 2 to 20 μm and an adjustable uniform diameter varying from 100 to 400 nm. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy have been employed to obtain more detailed information about the interaction between the polymer chain and silver nanowires.

2. Experiment

2.1. Materials

Anhydrous 1, 2-propandiol (99%), silver nitrate (99%), and poly (vinyl pyrrolidone) (PVP, MW ≈58000) were purchased from Acros. Acetone and anhydrous ethanol were obtained from Beijing Chemical Reagent Company. All the chemicals were used as-received without any further purification.

2.2. Synthesis of silver nanowires

In a typical experimental procedure, 10 ml 1, 2-propanediol was refluxed in a silicone oil bath at 170° C for 2h. Then 0.5 ml of 1, 2-propanediol solution of $AgNO_3$ (0.005M) was added into the 1, 2-propanediol under vigorous magnetic stirring to form seeds. Two minutes later, 3ml 1, 2-propanediol solution of $AgNO_3$ (0.1 M) and 3 ml 1, 2-propanediol solution of PVP (0.45 M) were added dropwise over a period of 5 min simultaneously. The reaction continued for 60 min and a grey suspension was obtained. After the reaction finished, the mixture was diluted by acetone (10 times by volume), centrifuged at 3000 rpm for 30 min and washed by deionized water to remove the byproducts. The final product was dominated by nanowires, with a small amount (<10%) of nanoparticles.

2.3. Characterization of silver nanowires

Scanning electron microscopy (SEM) images were taken using a field-emission scanning electron microscope (XL-SFEG, FEI Corp.) operated at an acceleration voltage of 5 kV or 10 kV. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were taken using JEOL 200CX microscope at 120 kV. A high-resolution transmission electron microscope (Tecnai F20, FEI Corp.) was used to provide high-resolution images of silver nanowires. The specimens were prepared by placing one drop of the aqueous solution of silver nanowires on a silicon wafer or carbon-coated copper grid, and letting the solvent evaporate naturally. The structure of the nanowires was examined using Rigaku D/MAX 2400 x-ray diffractometer with Cu Kα radiation (λ=0.15405nm). XPS spectra were recorded using an ESCA LAB5 x-ray photoelectron spectrometer with Mg Kα radiation, and the FT-IR spectra were measured on Vector22 FT-IR spectrometer.

3. Results and discussion

3.1. Controlled growth of silver nanowires

In the modified polyol process, the introduction of the capping reagent with a suitable concentration is the key to the growth of anisotropic nanostructures. The morphologies and aspect ratios of these silver nanowires are highly dependent on the molar ratio between the repeating unit of PVP and $AgNO_3$. Only when this ratio was kept in a proper range, can large scale silver nanowires be easily achieved. In addition, the injection rate of precursors, size and morphology of seeds and reaction temperature are also important factors for controlling the morphologies and the yield of silver nanowires. Figure 1 shows the SEM images of several typical products obtained through tuning the molar ratio of PVP/$AgNO_3$ and the injection rate. When the molar ratio between the repeating unit of PVP and $AgNO_3$ was 6:1 and injection rate was 0.3 ml/min, the sample contained a mixture of relatively thick nanowires (∼250 nm in diameter and 2–5 μm in length). Increasing the injection rate from 0.3 ml/min to 0.6 ml/min while the molar ratio was maintained at 6:1, nanowires with larger aspect ratio (∼400 nm in diameter and 10–20 μm) can be obtained (Fig.1(c) and 1(d)). When the molar ratio of PVP repeating unit and $AgNO_3$ decreases to 4.5:1, the diameter of nanowires decreases to ∼100 nm and the length increases to ∼20 μm (Fig.1(e) and 1(f)). These results clearly indicate that the morphology of silver nanowires can be controlled by the relative concentration of the precursors and the injection rate.

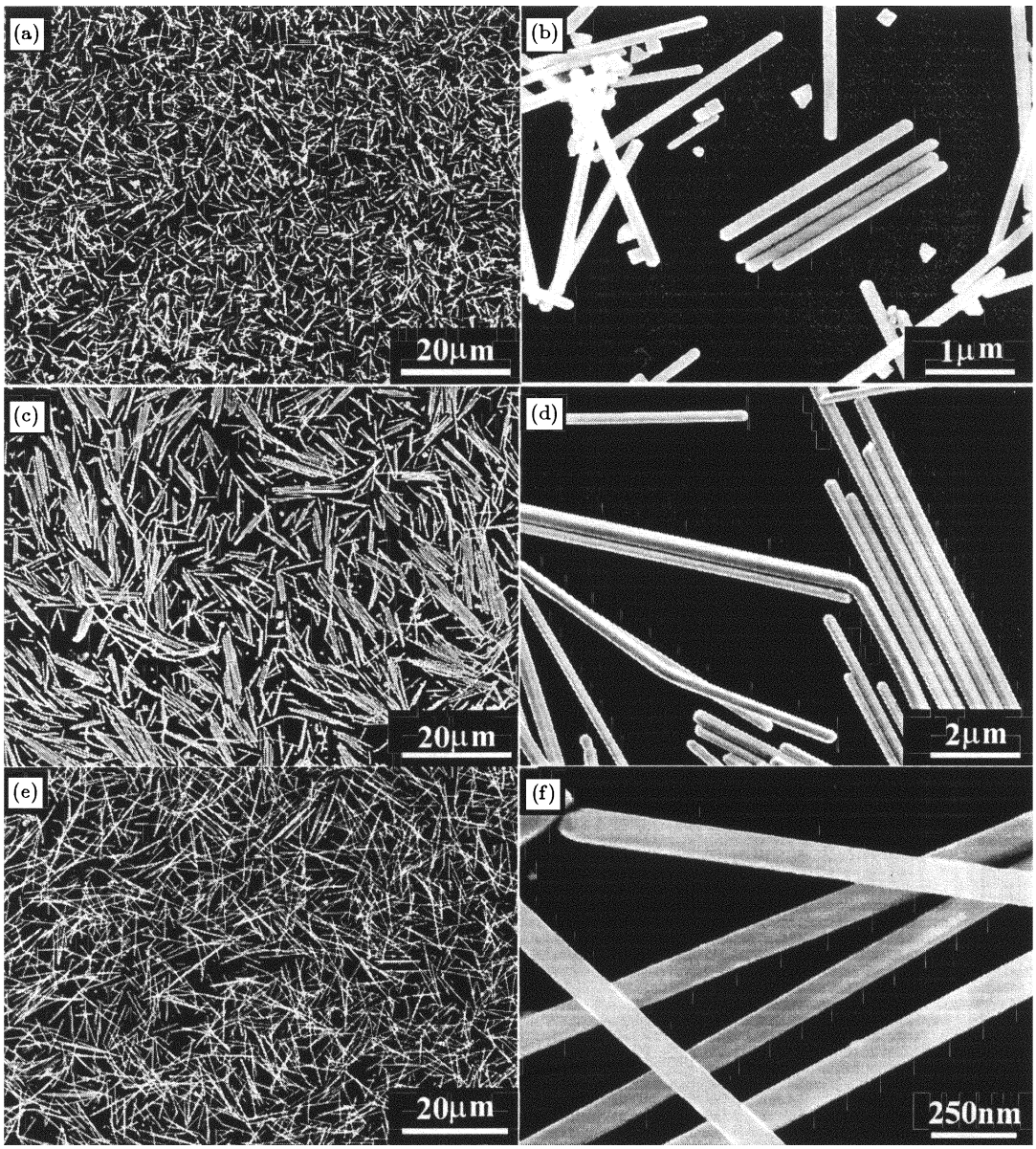


Fig.1. SEM images of several typical products with different aspect ratios, showing the variation of morphology when reaction condition changed. (a) and (b) n_{PVP}/n_{AgNO3}=6:1, injection rate=0.3ml/min; (c) and (d) n_{PVP}/n_{AgNO3}=6:1, injection rate=0.6ml/min; (e) and (f) n_{PVP}/n_{AgNO3}=4.5:1, injection rate=0.6ml/min.

It is well known that the number and size of nuclei depend strongly on the concentration of reactants and surfactants. Once the nuclei form, the surfactants in the solution are adsorbed reversibly by the surfaces of these particles, providing a dynamic capping layer that stabilizes the particles in the solution and mediating their growth through preferential binding to some specific facets.[30−34] Here, the influence of injection rate on the morphology of nanowires can also be attributed to the change of concentration of reactants and surfactants during nucleation. The variation in injection rate leads to different concentrations of reactants and surfactants, and thus influences the diffusion direction and rate of silver atoms toward the seeds. Moreover, although we use a seeding step to separate the nucleation and growth process, new clusters will inevitably form due to the local supersaturated solution in the injection process. Rapid injection causes the formation of more new clusters. Compared with the seeds already formed, these clusters are so small that they cannot grow into larger ones, but dissolve into the solution and grow onto the large nanoparticles via Ostwald ripening process. As a result, more silver atoms will participate in the following growth process. All these factors will contribute to the growth of thicker nanowires by rapid injection.

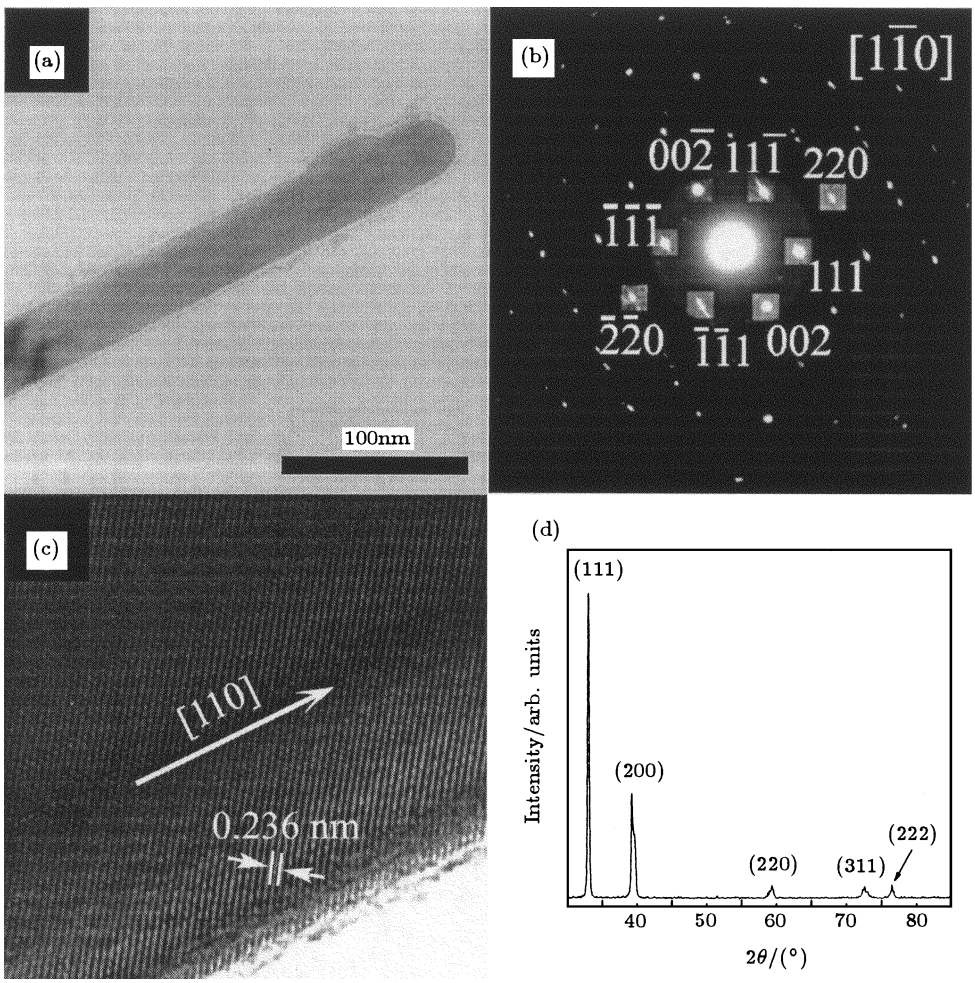


Fig.2. (a) TEM image of an individual silver nanowire, indicating the coverage of PVP on the surface of nanowires (b) SAED pattern of the same nanowire. (c) HRTEM image taken from the edge of a silver nanowire. (d) XRD pattern from the same batch of silver nanowires in Fig.1(e).

Figure 2(a) shows the TEM image of an individual silver nanowire. An organic layer can be clearly seen round the silver nanowire, implying the formation of PVP layer on the surface of nanowire. As shown in Fig.2(b) the SAED pattern of the nanowire demonstrates that the growth direction is along the [110] axis. The high resolution TEM (HRTEM) image shown in Fig.2(c) was taken from the edge of a nanowire. The lattice spacing of this nanowire could be resolved and indexed to a faced-centred cubic (fcc) phase of silver. The x-ray diffraction (XRD) pattern taken from the same batch of sample shown in Fig.1(c) is displayed in Fig.2(d). The peaks can be assigned to diffractions from the (111), (200), and (220) planes of fcc silver, respectively. It is worth noting that the intensity ratios of the (111) and (220) peaks and of the (200) and (220) peaks are 25.0 and 8.6, much higher than the conventional values, 4.0 and 1.6, respectively. This result indicates that the silver nanowires have relatively abundant (111) and (200) facets on the surfaces. From this pattern the lattice constant is calculated to be 0.4093nm, which is in agreement with the value of 0.4086nm in the literature.

3.2. Interaction of silver nanowires with PVP

Figure 3 shows FT-IR spectra of the pure PVP and PVP absorbed on the silver nanowires. In high wavenumber side, a strong peak at 2956 cm^{-1} is found which corresponds to the C–H bond vibration. In low wavenumber side, several other peaks are found. Three peaks at 1463, 1423 and 1495 cm^{-1} are produced due to the pyrrollidone ring of PVP bond absorption and the peak at 1373 cm^{-1} corresponds to the symmetrical terminal methylene group. Here, we concentrate on the evolution of C=O absorption peaks at 1664cm^{-1} and the two C–N absorption peaks at 1074 and 1018 cm^{-1}. It is found that C=O absorption peak shifts slightly to low wavenumber side for silver nanowires covered with PVP. This decrease in wavenumber is caused by partial donation of oxygen lone pair electrons of PVP to the vacant orbitals at the silver surface. As for the C–N bond, the two absorption peaks at 1074 and 1018 cm^{-1} merge into one broad and weak peak. There are two possible explanations for this phenomenon: 1) formation of the bond between silver and nitrogen atoms, and 2) constrained motion of atoms due to the relatively close-packed polymer chain on the nanowire surface. In this case, we believe that the latter mechanism may play a more important role than the former one, because the nitrogen atom is almost surrounded by three carbon atoms and less likely to form chemical bond with silver atoms for the steric constraint effect. To further support the above statement, we have performed XPS spectra analysis. The XPS spectra for pure PVP and PVP-coated nanowires are shown in Figs.4 and 5, respectively. We can see clearly that the peak of O1s shifts from 530.55 to 531.75eV, which is in good agreement with the results of FT-IR analysis. The adsorption of oxygen atom on silver nanowire will induce partially positive charges on the surface of the nanowires. In Fig.5(c), the XPS spectrum of PVP-coated Ag nanowires shows double peaks with the binding energies of 367.96 and 373.8eV, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. Compared with the standard spectrum of metal Ag^0, 368.3 eV ($3d_{5/2}$) and 374.8 eV ($3d_{3/2}$),[35] the binding energy of PVP-coated silver nanowires is found to be decreased. In contrast, for N1s peak no obvious shift can be found in the PVP-coated silver nanowires, indicating that the chemical environment around nitrogen atoms does not change. This fact provides an indirect evidence to support our hypothesis that nitrogen atoms do not interact with silver atoms directly. The evolution of FT-IR spectra might be caused by constrained motion of PVP molecules on silver nanowires.

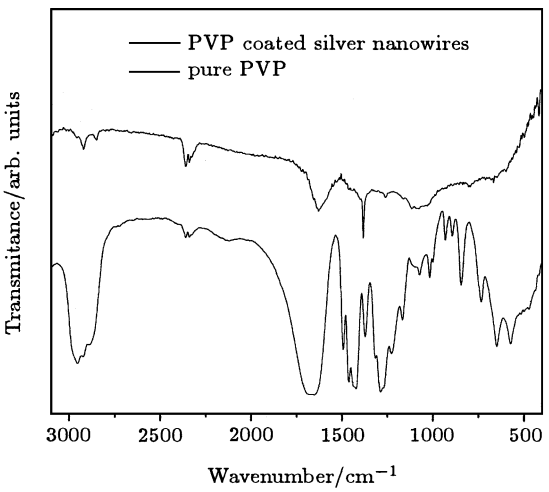


Fig.3. FT-IR spectra of the pure PVP and PVP coated silver nanowires, showing the evolution of C–N and C=O absorption peaks.

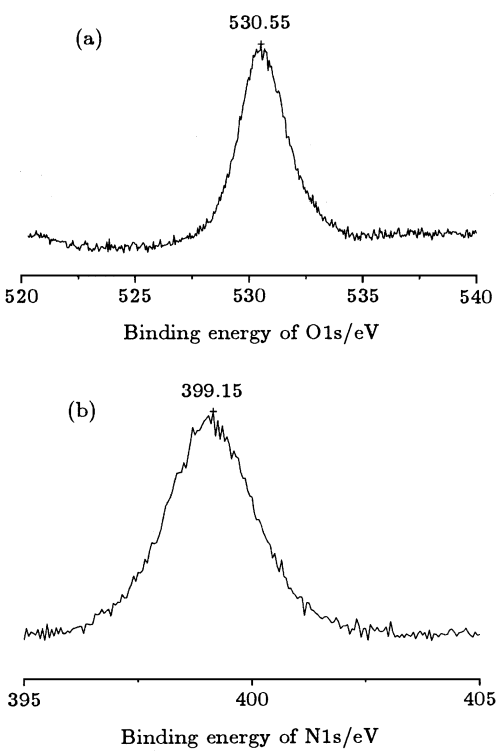


Fig.4. X-ray photoelectron spectra of pure PVP. (a) Binding energy of O1s; (b) Binding energy of N1s.

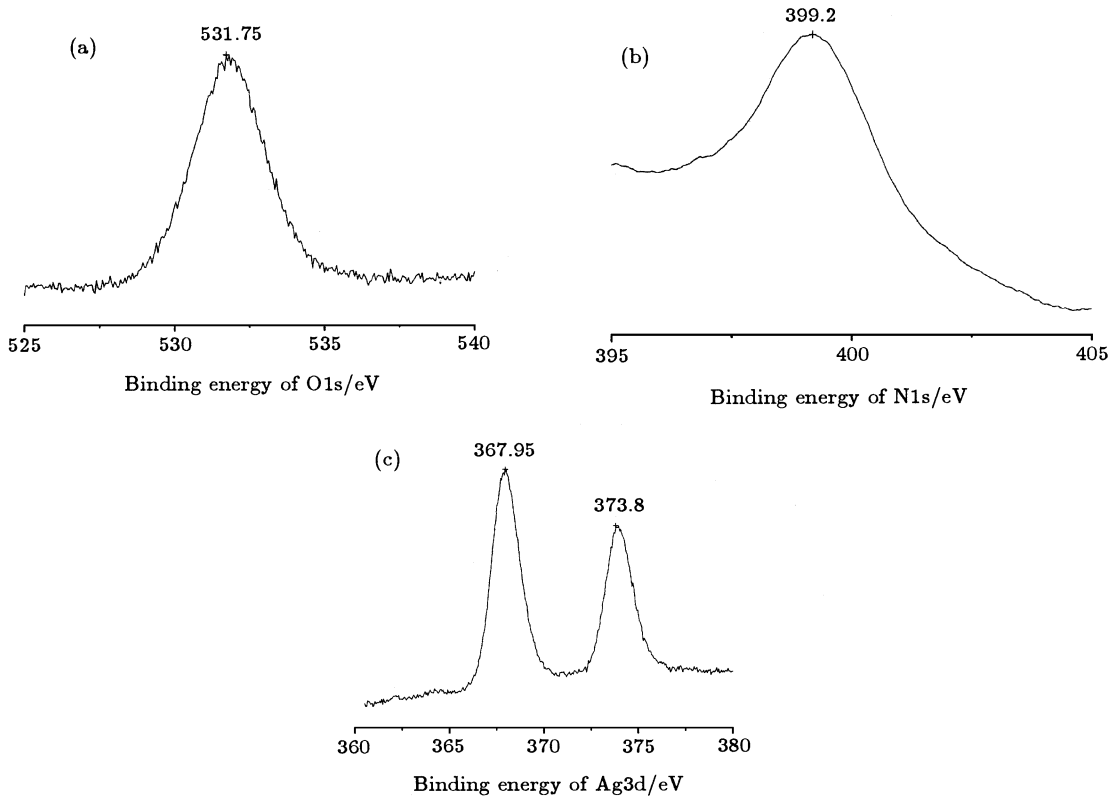


Fig.5. X-ray photoelectron spectra of silver nanowires. (a) Binding energy of O1s; (b) Binding energy of N1s; (c) Binding energy of Ag3d.

4. Conclusions

We have successfully synthesized large-scale silver nanowires with controlled aspect ratios by varying the experimental conditions. These nanowires are adjustable in length ranging from 2 to 20 μm and with a uniform diameter varying from 100 to 400nm. The combination of XPS and FT-IR analyses shows that there exists no chemical bond formed between silver and nitrogen atoms, and PVP interacts with silver nanowires mainly through the oxygen atom in carbonyl group.

References

[1] Xia Y N, Yang P D, Sun Y G, Wu Y Y, Mayers B, Gates B, Yin Y D, Kim F and Yan H Q 2003 *Adv. Mater.* **15** 353
[2] Wang Z L 2000 *Adv. Mater.* **12** 1295
[3] Hu J, Odom T W and Lieber C M 1999 *Acc. Chem. Res.* **32** 435
[4] Cao P J, Gu Y S, Liu H W, Sheng F, Wang Y G, Zhang Q F, Wu J L and Gao H J 2003 *J. Mater. Res.* **18** 1686
[5] Liu F, Cao P J, Zhang H R, Wang Z, Li J Q and Gao H J 2005 *J. Crys. Growth* **274** 126
[6] Sun Y G and Xia Y N 2004 *Adv. Mater.* **16** 264
[7] He S T, Yao J N, Jiang P, Shi D X, Zhang H X, Xie S S, Pang S J and Gao H J 2001 *Langmuir* **17** 1571
[8] He S T, Xie S S, Yao J N, Gao H J and Pang S J 2002 *Appl. Phys. Lett.* **81** 150
[9] Xing Y J, Yu D P, Xi Z H and Xue Z Q 2002 *Chin. Phys.* **11** 1047
[10] Chen L, Zhang G M, Wang M S and Zhang Q F 2005 *Chin. Phys.* **14** 181
[11] Tao A, Kim F, Hess C, Goldberger J, He R, Sun Y G, Xia Y N and Yang P D 2003 *Nano Lett.* **3** 1229
[12] Zhou Y, Yu S H, Wang C Y, Li X G, Zhu Y R and Chen Z Y 1999 *Adv. Mater.* **11** 850
[13] Zhou Y, Yu S H, Cui X P, Wang C Y and Chen Z Y 1999 *Chem. Mater.* **11** 545
[14] Zhu J, Liu S, Palchik O, Koltypin Y and Gedanken A 2000 *Langmuir* **16** 6396
[15] Braun E, Eichen Y, Sivan U and Ben-Yoseph G 1998 *Nature* **391** 775
[16] Jana N R, Gearheart L and Murphy C J 2001 *Chem. Commun.* 617
[17] Huang M H, Choudrey A and Yang P 2000 *Chem. Commun.* 1063
[18] Bhattacharrya S, Saha S K and Chakravorty D 2000 *Appl. Phys. Lett.* **76** 3896

[19] Choi J, Sauer G, Nielsch K, Wehrspohn R B and Gosele U 2003 *Chem. Mater.* **15** 776
[20] Sun Y G, Gates B, Mayers B and Xia Y N 2002 *Nano Lett.* **2** 165
[21] Sun Y G and Xia Y N 2002 *Adv. Mater.* **14** 833
[22] Sun Y G, Mayers B, Herricks T and Xia Y N 2003 *Nano Lett.* **3** 955
[23] Fievet F, Lagier J P and Figlarz M 1989 *MRS Bull.* **14** 29
[24] Kurihara L K, Chow G M and Schoen P E 1995 *Nanostruct. Mater.* **5** 607
[25] Sun S H, Murray C B, Weller D, Folks L and Moser A 2000 *Science* **287** 1989
[26] Feldmann C 2003 *Adv. Func. Mater.* **13** 101
[27] Zhang Z T, Zhao B and Hu L M 1996 *J. Solid State Chem.* **121** 105
[28] Huang H H, Ni X P, Loy G I, Chew C H, Tan K L, Loh F C, Deng J F and Xu G Q 1996 *Langmuir* **12** 909
[29] Bonet F, Tekaia-Elhsissen K and Sarathy K V 2000 *Bull. Mater. Sci.* **23** 165
[30] Goia D V 2004 *J. Mater. Chem.* **14** 451
[31] Wang Z L 2000 *J. Phys. Chem.* B **104** 1153
[32] Chen S H and Carroll D L 2002 *Nano Lett.* **2** 1003
[33] Peng X G 2003 *Adv. Mater.* **15** 459
[34] Murphy C J 2002 *Science* **298** 2139
[35] Moudler J F, Stickle W F, Sobol P E and Bomben K D 1992 *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN