Evidence for the Monolayer Assembly of Poly(vinylpyrrolidone) on the Surfaces of Silver Nanowires

Y. Gao, P. Jiang, D. F. Liu, H. J. Yuan, X. Q. Yan, Z. P. Zhou, J. X. Wang, L. Song, L. F. Liu, W. Y. Zhou, G. Wang, C. Y. Wang, and S. S. Xie*

Institute of Physics, Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, China

J. M. Zhang and D. Y. Shen

State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

The well-defined silver (Ag) nanowires with five-twinned structure have been prepared by polyol reduction in the presence of poly(vinylpyrrolidone) (PVP K-30, 40 000). The obtained Ag nanowires are nearly monodispersed with an average diameter of 70 nm and length of 6 μm. It is confirmed from the results of thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and Fourier transform Raman spectra (FT-Raman) that one monolayer of the PVP molecules might be absorbed on the surface of the Ag nanowires through Ag−O coordination. On the basis of the experimental analysis, the probable spatial conformation of the PVP molecules is supposed to be that the CH skeleton chain of the PVP is close to the surface of the Ag nanowires. The pyrrolidone ring might be tilted on the surface of the Ag nanowires through Ag:O coordination. These results may provide direct evidence for the role of the PVP molecules in the formation of the Ag nanowires.

Introduction

One-dimensional nanomaterials such as nanotubes, nanowires, and nanorods have been widely investigated for their potential applications in the fields of nanocircuits, nanodevices, and nanosensors due to their extraordinary electronic and mechanical properties.[1−4] The properties of the nanomaterials are mainly dependent on their sizes and structures.[5,6] Therefore, it is of significant importance to control their morphologies in order to obtain desirable properties.[7−9] Recently, much effort has been focused on the preparation of noble metal nanowires, e.g., Au, Ag, and Cu, especially by solution phase methods in the presence of structure-directing agents with or without exotic seeds.[10−15] Some researchers have reported that thus-obtained metal nanowires possess the five-twinned crystal structure with a pentagonal cross-section.[16−18] However, it is not very clear how the structure is formed, though the preferential absorption of molecules to different crystal facets is now widely believed to direct the growth of nanoparticles into various morphologies by controlling the growth rates along different crystal axes.[19−22] Further investigation needs to be done into the routine to shed light on the phenomenon, especially the spatial conformation of the structure-directing agent on the surface of the metal nanowires and the interaction between the agent and the metal interface of the nanowires.[23] In this work, we prepared the silver (Ag) nanowires by polyol reduction of silver nitrate in the presence of poly(vinylpyrrolidone) (PVP, K-30, 40 000). As we reported previously, the obtained Ag nanowires are truncated decahedron with 5-fold symmetry.[24] To acquire more information about the interaction between the PVP and the Ag atoms

on the surface of the Ag nanowires, the Fourier transform Raman spectra (FT-Raman), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) have been employed to provide reasonable evidence.

Experimental Section

The Ag nanowires were synthesized by polyol reduction using PVP as the capping agent.[24] After the reaction finished, supernatant was decanted, and gray precipitate remained. The precipitate was further purified by washing and centrifuging using ethanol repeatedly, and then purified further by filtering through a PC membrane with 0.8 μm pore size. The samples for scanning electron microscopy (SEM) measurement were prepared by dipping a drop of ethanol suspension of the Ag nanowires on n-Si(100) wafer. The SEM images were observed using Hitachi S-5200. The X-ray powder diffraction (XRD) pattern was recorded using Rigaku D/max-2400 with Cu Kα radiation ($\lambda = 0.154056$ nm). The UV−vis absorption spectrum of the Ag nanowires dispersed in ethanol was measured using a Shimadu UV-1601 PC double beam spectrophotometer. FT-Raman experiments were performed using a Bruker IFS 100 FT-Raman spectrometer. X-ray photoelectron spectroscopy (XPS) data were recorded using a VG MK II spectrometer with Mg Kα source (1253.6 eV). The thermogravimetric analysis (TGA) was obtained using TGA 2050 (TA instruments) under nitrogen atmosphere at the heating rate of 10 K/min.

Results and Discussion

Figure 1a gives the molecular formula of the PVP we used, and Figure 1b shows the spatial morphology of optimal conformation of PVP with four repeating units. It is supposed

* To whom correspondence should be addressed. E-mail: ssxie@aphy.iphy.ac.cn.
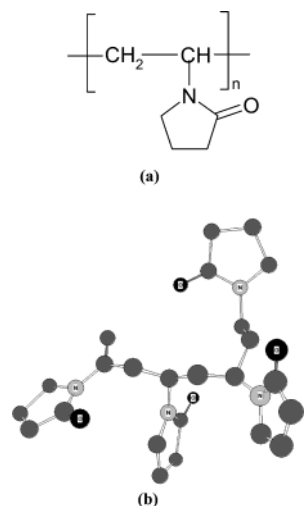
Figure 1. (a) Molecular formula of PVP. (b) Three-dimensional illustration of four repeating units of PVP.
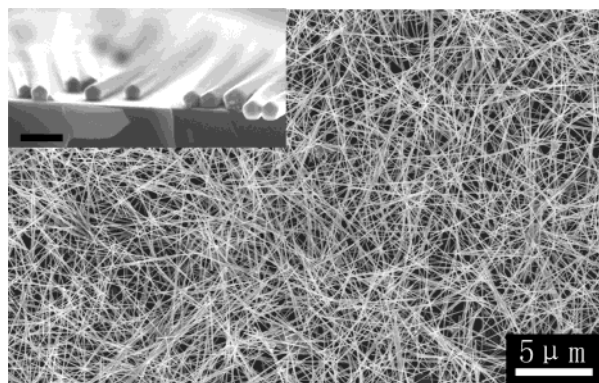

Figure 2. SEM image of Ag nanowires. Inset is the typical pentagon shape of the cross section of Ag nanowires. The scale bar in the inset is 200 nm.

Figure 3. XRD pattern of the Ag nanowires.

Figure 4. UV−vis absorption spectra of the Ag nanowires.

that when the EG solutions of silver nitrate and PVP are added, the coordination bond between the Ag^+ ion and the lone pair electron of the oxygen atom on the carbonyl is formed, which will decrease the chemical potential of Ag^+ ion and make it easier to be reduced during the nucleation period.[25] Once the multiple-twinned nuclei are formed,[26−27] PVP molecules are preferentially absorbed to [100] planes of the Ag nanoparticles, leading to the growth along the [110] direction and further resulting in the formation of five-twinned nanowires due to limited growth along the [100] direction.[28] A representative SEM image of the Ag nanowires is shown in Figure 2. Several Ag nanowires can be observed lying on the silicon substrate, as shown in the inset in Figure 2. They are nearly monodispersed with pentagonal cross-sections. The average length and diameter of the Ag nanowires are about 6 μm and 70 nm, respectively. The XRD pattern of the Ag nanowires is shown in Figure 3, the peaks occurring at 38.1°, 44.3°, 64.4°, and 77.8° are indexed as [111], [200], [220], and [311] facets, being consistent with the bulk FCC Ag single crystal. The ratio of the intensity between the [111] and [220] or [311] peak is 19 and 25, respectively, far higher than the theoretical ratio (4 and 3.8, respectively). The fact indicates the preferential orientation of [111] and [100] planes in the Ag nanowires on the silicon wafer, which provides indirect evidence of the Ag nanowires bounded by five [100] planes and capped by [111] planes with [110] growth direction. The obvious split of the [200] peak might be attributed to be the deformation of five-twinned structure.
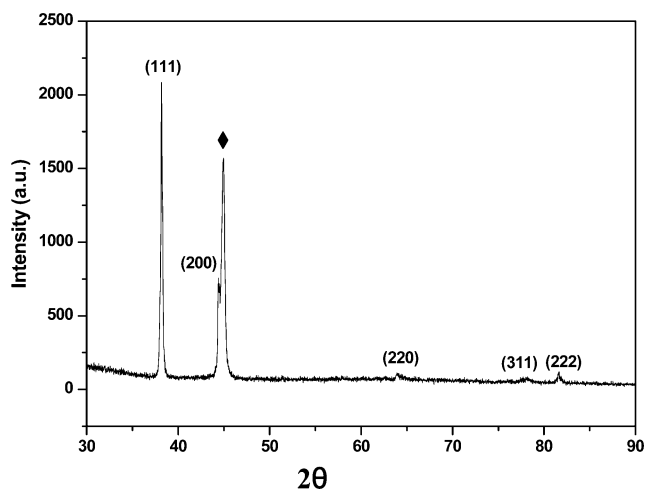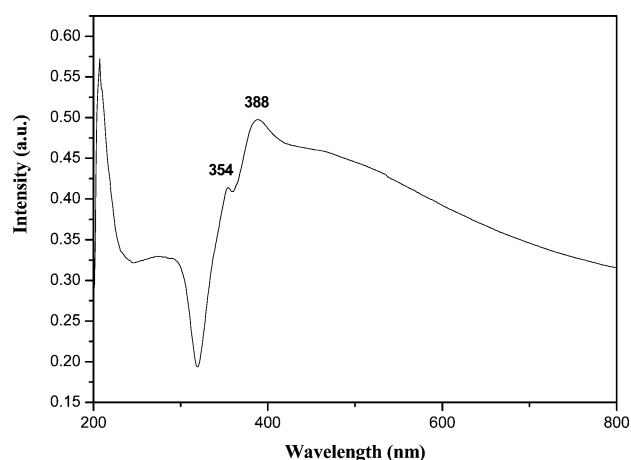
Figure 4 shows a typical UV−vis spectrum of the Ag nanowires in ethanol solution. The spectrum exhibits two relatively sharp surface plasma resonance peaks (SPR) at about 354 and 388 nm positions. Both of them belong to the tranversal SPR modes of the Ag nanowires with pentagonal cross-section, basically agreeing with the simulation result calculated by Martin.[29] It is concluded that the number of transversal resonances of Ag nanowires with different cross sections ranging from triangular to pentagonal and spherical increases when the section symmetry decreases. The longitudinal mode has not been found in the UV−vis absorption spectrum probably due to the much larger aspect ratio of the Ag nanowires. Absence of the peak assigned to Ag nanoparticles indicates the purity of the Ag nanowires because of the effective removal of Ag nano-particles.

To further investigate the interaction between PVP molecules and the Ag atoms on the surface of the Ag nanowires, FT-Raman, XPS, and TGA were conducted to elucidate the spatial conformation of the PVP molecules and the chemical state of the Ag atoms on the surfaces. Figure 5a shows a three-dimensional schematic illustration of the truncated decahedron bounded by [100] planes and capped by [111] planes with [110] growth direction. Figure 5b shows the cross section of a truncated decahedron in Figure 5a with two adjacent {110} planes of five subunits. The basic unit cell of [100] plane is shown by a white square in Figure 5a, in which *a* represents the lattice constant of the FCC Ag crystal. To roughly estimate the ratio of the surface Ag atoms to the whole Ag atoms, we
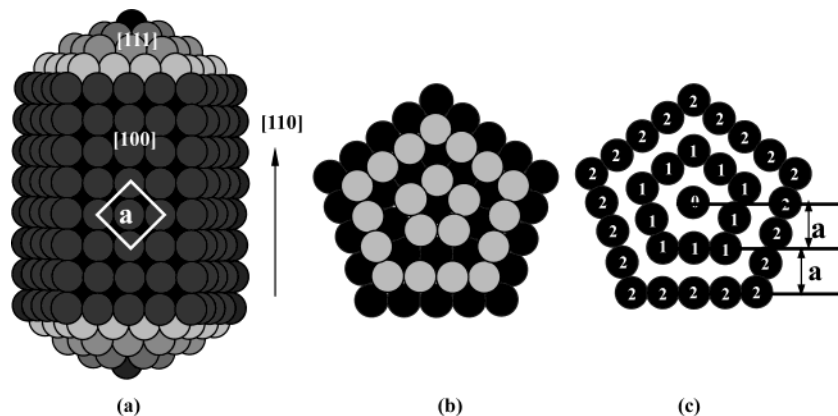
Figure 5. (a) Illustration of three-dimensional truncated decahedron. (b) Pentagonal cross section of part a with five [110] subunits. It contains two layers, which form the repeating unit of the cross-section to form the truncated decahedron. (c) Bottom layer of the pentagon in part b for clarity. The vertical distance between the adjacent pentagons is a.
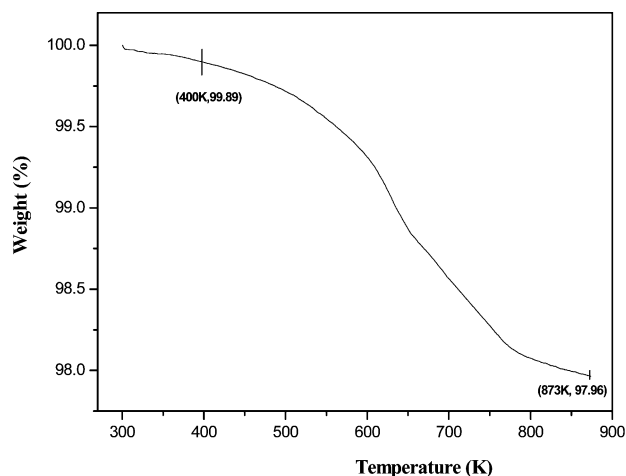

Figure 6. TG curve of the silver nanowires. The weight loss from 400 to 873 K was assigned to the presence of PVP covered on the surface of Ag nanowires.

consider the two adjacent {110} planes in Figure 5b. We define the total number of the pentagons in the bottom layer as n, where n is only dependent on the diameter of the Ag nanowires, as shown in Figure 5c. The vertical distance between the adjacent pentagons is to be a (see Figure 5c). It is calculated from Figure 5b that the percentage of Ag atoms on the outer surface of the Ag nanowires is to be $1/n$,[30] which is independent of the length of the Ag nanowires, provided the Ag atoms at the both ends of the Ag nanowires are negligible. It is known from the results above that the average diameter of the Ag nanowires is about 70 nm, from which the n value of the Ag nanowires is deduced to be 72.[31] The amount of PVP covered on the surface of the Ag nanowires is shown in the TGA (see Figure 6). It can be seen from Figure 6 that the weight loss from 400 to 873 K is to be 1.93%, which is attributed to the PVP covered on the surface of the Ag nanowires. Compared with pure PVP, we found that it started to lose weight at 640 K and was near zero at 760 K in the TGA test under the same condition (the TGA curve is not shown here). The molar ratio of repeating units of the PVP molecules to the Ag atoms on the surface of Ag nanowires is to be 1.38.[32] Considering the Ag atoms at both ends, we think that one monolayer of PVP molecules might be formed on the outer surfaces of the Ag nanowires with about three repeating units of the PVP molecule on the one unit cell of the [100] facet.

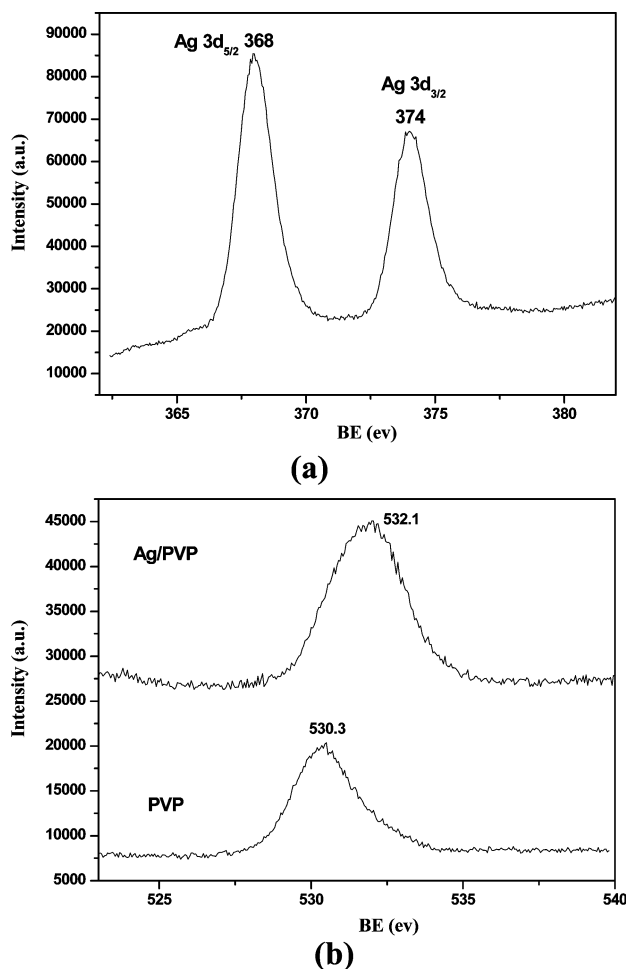To further investigate the interaction between PVP and the Ag nanowires, XPS was performed on the purified Ag nano-

Figure 7. X-ray photoelectron spectra of silver nanowires and pure PVP.

wires. Figure 7a shows the XPS spectrum in the region of Ag 3d of the Ag nanowires. It can be seen from the spectrum that two peaks occur at 367.7 and 373.8 eV, corresponding to Ag $3d_{5/2}$ and $3d_{3/2}$ binding energy, respectively. In comparison with Ag^0 (368.3 and 374.3 eV), the peaks shift down to lower binding energy, indicating that the chemical environment around Ag atoms is changed. Figure 7b shows the XPS spectra of O1s of the Ag nanowires and pure PVP. It is observed from Figure 7b that, in the case of PVP-capped Ag nanowires, the peak attributed to O1s is shifted toward to higher binding energy compared with pure PVP. The large shift (1.8 eV) of the O1s
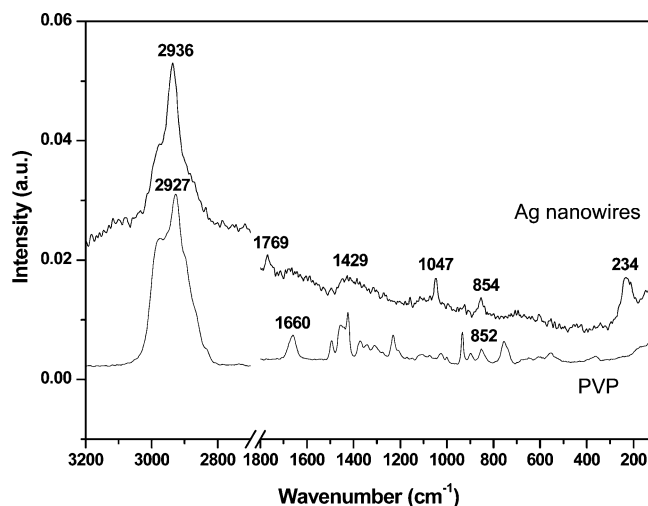
Figure 8. FT-Raman spectra of Ag nanowires covered by PVP and the pure PVP.
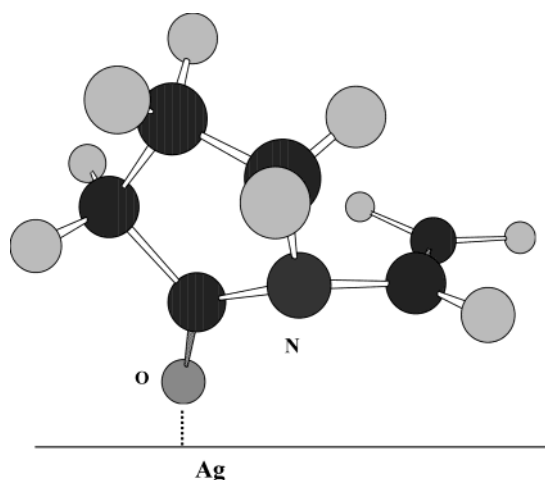

Figure 9. Schematic illustration of PVP conformation on the surface of Ag nanowires.

binding energy originates from the weakness of electron density around O atoms in the carbonyl group of PVP, implying that the surface Ag atoms strongly coordinate with O atoms in PVP.[33] Thus, it is probably the strong Ag:O coordination that restricts the radial growth of the Ag nanowires along the ⟨100⟩ direction.

Surfaced-enhanced Raman scattering (SERS) is a powerful technique used to characterize the chemical state of bonds formed on the metal surfaces and the molecular conformation on the specific metal films.[34,35] On the basis of the selection rules of SERS for molecules absorbed on metal surfaces, molecular vibrations perpendicular to the surface should be enhanced in the spectra, while those parallel to the surface should be weakened. Therefore, to further investigate the spatial orientation and conformation of PVP molecules on the outer surface of the Ag nanowires, we explore the Fourier transform Raman spectrum (FT-Raman) to detect the PVP-covered Ag nanowires. Figure 8 shows FT-Raman spectra of the Ag nanowires and the pure PVP. Compared with the pure PVP, the appearance of Ag—O stretching vibrations at 233 cm^{-1} confirms that the PVP molecule is coordinated to the Ag surface through the nonbonding electrons of the oxygen atom in carbonyl, which is consistent with the results of XPS. The peak at 854 cm^{-1}, which can be referred to the breathing vibration of the pyrrolidone ring, exhibits a moderate enhancement. It is suggested that the pyrrolidone ring might be tilted on the

surfaces of Ag nanowires. The significant enhancement of the signal at 2936 cm^{-1} (asymmetric stretching vibration of CH$_2$ in the skeletal chain of PVP) reveals that the CH$_2$ chain is close to the surface of Ag nanowires. Figure 9 schematically illustrates the conformation of one repeating unit in PVP absorbed on the [100] surface of the Ag nanowires.

Conclusions

In summary, the five-twinned Ag nanowires with an average length of 6 μm and diameter of about 70 nm have been synthesized by polyol reduction of silver nitrate using PVP as structure-directing agent. It is confirmed that the molar ratio of the repeating unit of the PVP to the Ag atoms on the surface of the Ag nanowires is close to 1.5. Thus, one monolayer of PVP is probably absorbed on the surface of the Ag nanowires through Ag—O coordination. The results from SERS indicate the skeleton chain of the PVP molecules is almost lying on the surface of the Ag nanowire, and the pyrrolidone ring might be tilted on the surface of Ag nanowires.

Note Added After ASAP Posting. This article was released ASAP on 7/9/2004. Figure 1 has been replaced and the corresponding author e-mail address has been added. The correct version was posted on 08/02/2004.

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(30) This is a simple number sequence. When $n = 1$, the percentage of the silver atoms on the outer surface is to be $10/(1 + 10 + 5)$. When $n = 2$, it is to be $20/(1 + 10 + 20 + 15 + 5)$. When $n = 3$, it is to be $30/(1 + 10 + 20 + 30 + 25 + 15 + 5)$. When $n = n$, it is to be $10n/(1 + 10 + 20 + 30 + ... + 10n + 5 + 15 + 25 + ... + 5(2n - 1))$, $=10n/(1 + 5n(n + 1) + 5n^2)$, $\approx 1/n$. Therefore, it is concluded that the percentage of silver atoms on the outer surfaces of the Ag nanowires is to be $1/n$, which is independent of the length of silver nanowires assuming that the silver atoms at both ends can be ignored when the Ag nanowires are much longer.

(31) Under SEM measurement, we have found that the Ag nanowires with the pentagonal cross-section usually lie on the substrate with one side plane. The 70 nm diameter of the Ag nanowires is estimated on the basis of the diagonal of the pentagonal cross-section. It is calculated that the edge length of the outer pentagon of the Ag nanowires is about 43 nm. Therefore, n is equal to $n = (0.5dc \tan(36))/a = (0.5 \times 43 \times c \tan(36))/0.409 \approx 72$.

(32) The actual amount of PVP covering the surfaces of Ag nanowires takes up 1.93% of the whole Ag nanowires capped by PVP. Also, the percentage of silver atoms on the surfaces of Ag nanowires is to be $2/(1 + 101) = 1/51$. Therefore, it is calculated that the molar ratio between repeating units of PVP to the silver atoms on the surfaces of Ag nanowires is equal to $[(1.93/111)/(97.96/108)] \times 72/1 \approx 1.38$.

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