

Formation Process of Silver–Polypyrrole Coaxial Nanocables Synthesized by Redox Reaction between AgNO_3 and Pyrrole in the Presence of Poly(vinylpyrrolidone)

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We have recently demonstrated a one-step process to fabricate silver–polypyrrole (PPy) coaxial nanocables (Chen, A.; Wang, H.; Li, X. *Chem. Commun.* 2005, 14, 1863). The formation process of silver–PPy coaxial nanocables is discussed in this article. It was found from the results of TEM and SEM images that large numbers of silver atoms were formed when AgNO_3 was added to a pyrrole solution. Then silver atoms transform to silver–PPy nanosheets with regular morphology, which will connect together to be more stable. Silver–PPy nanocables will be able to grow at the expense of the silver–PPy nanosheets. Poly(vinylpyrrolidone) (PVP) plays crucial roles in this process: as a capping agent to form silver nanowires, and as a dispersant of pyrrole monomers, which can influence the site at which pyrrole monomer exists. On the basis of experimental analysis, the possible mechanism was proposed. Because of the effect of PVP, silver ions and pyrrole monomers are apt to be adsorbed at the [111] and [100] facets of silver nanosheets, respectively. Obvious polymerization will take place on the boundary of the [111] and [100] facets. The PPy layer stays stable on the [100] facets. Meanwhile, newly formed silver atoms and silver nanosheets will further ripen and grow on the [111] facets. In a word, the morphology of final products and the formation process are determined by the reaction site between AgNO_3 and the pyrrole monomer, which is influenced by PVP.

Introduction

Recently, much effort has been focused on the preparation of noble metal nanowires, e.g. Au, Ag, and Cu, because of their superior performance as nanocircuits, nanodevices, and nanosensors.^{1–4} For instance, Ag nanowires can be synthesized by various methods, such as a templating method using porous alumina,⁵ polycarbonate membranes,⁶ block copolymers,⁷ or carbon nanotubes,⁸ and a solution-phase method based on capping reagents.^{9–12} In all of these methods, a modified polyol process is an excellent and simple route for synthesizing silver nanowires.^{9,10} Silver nitrate was reduced with ethylene glycol with or without exotic seeds, using poly(vinylpyrrolidone) (PVP) as a capping agent but not as a soft template. It is believed that PVP can control the growth rates of various faces of silver by coordinating to the surfaces.^{13–16} Xia and his group later proposed that each silver nanowire evolved from a multiply twinned nanoparticle of silver, with the assistance of PVP at the initial stage of the Ostwald ripening process.¹⁷ The anisotropic growth was maintained by selectively covering the [100] facets with PVP while leaving the [111] facets largely uncovered, and thus highly reactive. Xie et al. reported that the pyrrolidone ring might be tilted on the surface of the silver nanowires through Ag–O coordination.¹⁸

In addition, composite nanowires composed of Ag and other polymers have emerged recently. The representative structure of this composite nanowire is the coaxial nanocable, which is

generally defined as a multilayered structure with a core nanowire sheathed coaxially by one or more cylindrical layers of different materials. Ag–C coaxial nanocables¹⁹ have been fabricated under hydrothermal conditions using starch and silver nitrate as starting materials. During the formation process, limited pliability of the organized graphite platelets leads to a partially hollow structure in the carbonized graphite, which provides the place for silver nanoparticles to grow into nanowires. Ag–PVA coaxial nanocables were later fabricated by the same group.²⁰ They found that silver ions can make PVA cross-link together, and that PVA can be reduced to silver under hydrothermal conditions.

For the first time, we have developed a simple one-step method for the fabrication of silver–polypyrrole (PPy) coaxial nanocables in aqueous solution at room temperature.²¹ Silver–PPy coaxial nanocables can be obtained by the redox reaction between silver nitrate and pyrrole monomer in the presence of PVP. To some extent, the morphology and the aspect ratio of silver–PPy nanocables can be controlled by adjusting the molar concentration ratio of pyrrole to AgNO_3 .²²

In the present work, we have focused on the formation process of the silver–PPy coaxial nanocables and the influence of the capping agent on the morphology of silver–PPy nanostructures. The structural change during the growth process was observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). PVP plays a crucial role in the formation of silver–PPy nanocables. It was found that the silver–PPy nanocables grow at the expense of silver–PPy nanosheets. A low-pyrrole-concentration system was used as supporting evidence of this formation process. A possible mechanism has also been proposed in this article.

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Experimental Section

Chemicals. Pyrrole (98%) monomer was purchased from Aldrich and was vacuum-distilled before use. Silver nitrate (AgNO_3 , $\geq 99\%$) and poly(vinylpyrrolidone) (PVP, MW $\approx 55\,000$) were also purchased from Aldrich and used without further purification.

Synthesis of Silver-PPy Nanocables. The experimental method has been reported in our previous papers. In a typical procedure for the preparation of silver-PPy nanocables, 4 mL of pyrrole monomer was added to a round-bottom flask. AgNO_3 aqueous solution (50 mL, 0.3 M) and 50 mL of PVP aqueous solution (0.45 M) were added dropwise to the flask. Magnetic stirring was used throughout the entire process. The reaction was continued for 48 h at room temperature.

Characterization. The morphology of the sample was observed by transmission electron microscopy (TEM, HITACHI 7000) operating at 100 kV. To investigate the real state of the solution at different reaction stages, the TEM images were obtained from the solution without any purification or centrifugation. For the TEM observation, samples were obtained by dropping two drops of solution onto carbon-coated copper grids placed on a filter paper for rapid removal of the liquid. Scanning electron microscopy (SEM) images were obtained on an FEI XL-30 ESEM-FEG microscope. High-resolution TEM images were taken by a JEOL JEM-2010 with an accelerating voltage of 200 kV. The UV-vis-NIR spectra of the colloidal solutions were recorded on a Shimadzu UV-3100 spectrometer in the range of 200–1300 nm. AFM images were collected by a Digital Instruments NanoScope III microscope, operated in tapping mode in ambient air using a SiO_2 -Si wafer as substrate.

Results

1. Microscopic Studies on the Formation of Silver-PPy Nanocables. The silver-PPy nanostructures at various stages of the growth process were observed by TEM and SEM. Figure 1 shows TEM and SEM images of the samples that were taken from the reaction mixture at different stages. Before PVP and AgNO_3 were dropped into the flask, the pyrrole monomer was transparent. The reaction was very fast, and the system turned a pale grass-green color as soon as PVP and AgNO_3 were dropped into the flask simultaneously. A mixture of silver-PPy nanoparticles with different morphologies and sizes was formed at a reaction time of 10 min (Figure 1A). In addition to silver nanorods and silver spherical nanoparticles, two-dimensional crystal materials with regular shapes, such as triangular, pentagonal, and hexagonal, were observed (highlighted by dark arrows in Figure 1A). However, it is interesting to note that in addition to these smaller-sized silver nanosheets, we have also observed larger ones, as shown in Figure 1B. The selected-area electron diffraction (SAED) pattern (Figure 1C) taken from an individual nanosheet by directing the electron beam perpendicular to one of its faces indicates that the sheet is single crystalline. The hexagonal nature of the diffraction spots is a clear indication that the silver-PPy nanosheets are highly [111] oriented with the top normal to the electron beam. The spots could be indexed based on the face-centered-cubic (fcc) structure of silver. Figure 1D is the HRTEM image of a silver-PPy nanosheet. The interplanar spacing is about 2.4 Å, which corresponds to the [111] plane of silver. As the reaction continued, the small, unstable nanoparticles of silver spontaneously and slowly dissolved into the solution and recrystallized onto the larger particles (Ostwald ripening).²³ After ~ 30 min, the color of the reaction system gradually turned to pale brown, and the shape of the silver-PPy nanosheets had begun to

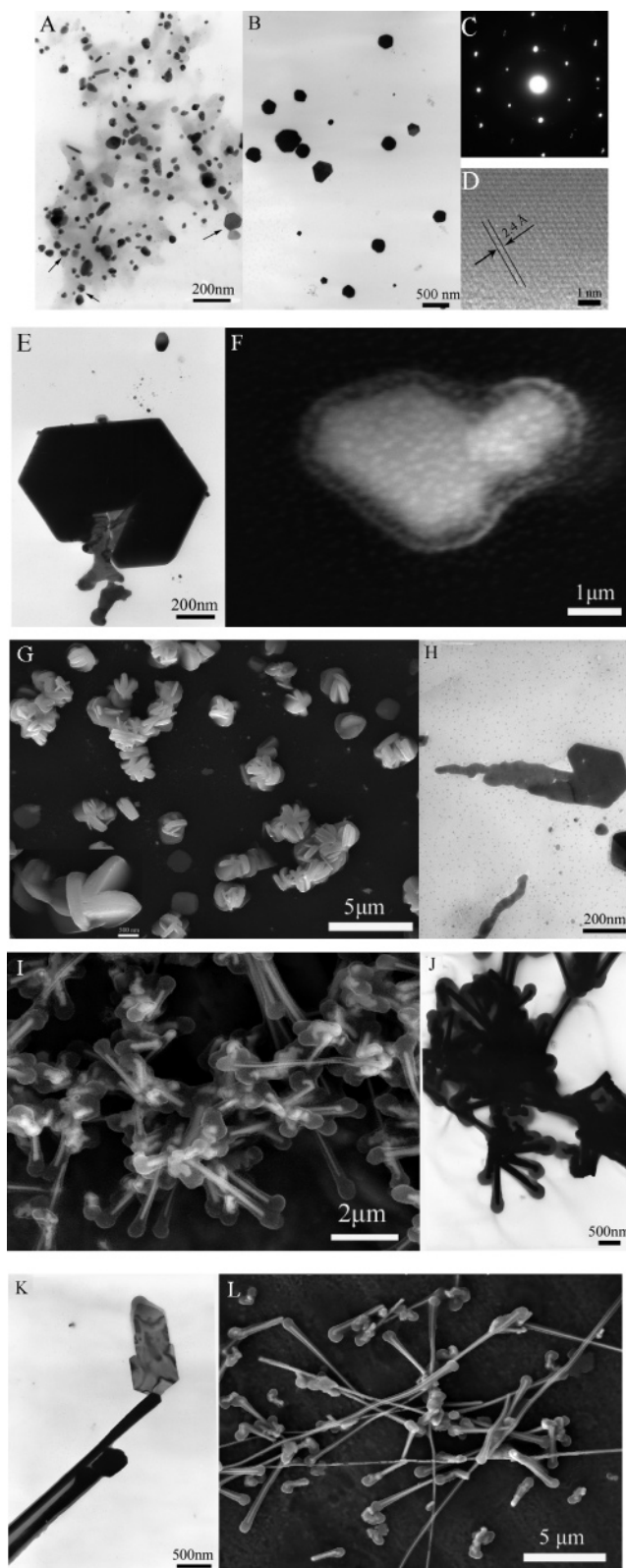


Figure 1. TEM and SEM images mapping the morphology conversions. These samples were prepared by taking a small portion from the reaction mixture at 10 min (A and B). (C) SAED pattern of a silver-PPy nanosheet. (D) HRTEM image of a silver-PPy nanosheet. Samples taken from the reaction mixture after 30 min (E and F), 4 h (G and H), 8 h (I and J), 36 h (K), and 48 h (L).

change. As shown in Figure 1E (30 min), it seems that the samples began to form one-dimensional structures at the one edge of the silver nanosheet. Figure 1F is the SEM image of the resulting sample obtained at this time. It can be seen that

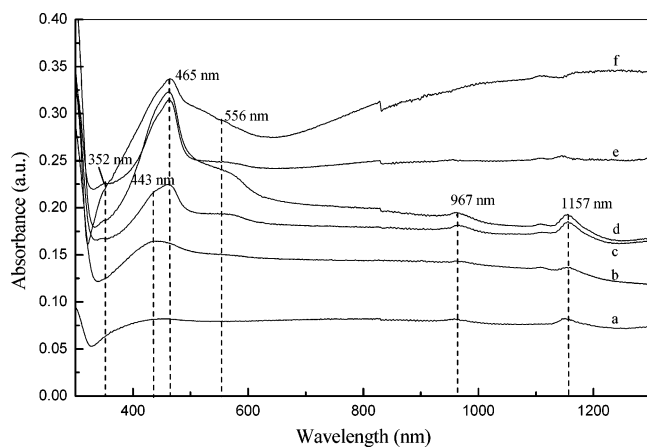


Figure 2. UV-vis-NIR spectra of the reaction mixture at various reaction times. Curves a–e corresponds to spectra recorded after 10 min and 8, 9, 12, 36, and 48 h.

the two Ag-PPy nanosheets are connected together and growing in different planes. As the reaction continued, more silver-PPy nanosheets connected together to form larger silver-PPy congeries, as shown in Figure 1G (after 4 h of reacting). The inset is a typical SEM image with high magnification of the sample in this case. Furthermore, rodlike anisotropic nanostructures were also observed in this case (Figure 1H).

When the reaction time reached 8 h, the shape of the samples changed greatly, as shown in Figure 1I. A large number of silver-PPy cables had formed. The PPy layer on the surface of the silver wires can obviously be observed. At one of its termini, the PPy layer looks like a half-sphere, whereas at another terminal, these Ag-PPy cables connected together, which can be observed clearly in Figure 1J. According to this, we can presume that these silver-PPy nanocables convert from the silver particles with special morphology, as shown in Figure 1G. In other words, silver-PPy nanocables are growing at the expense of silver-PPy nanosheets. Figure 1K is the TEM image of the sample obtained at 36 h. Note that a silver-PPy nanocable is still connected with a silver-PPy sheet, which can further prove that silver-PPy nanocables are converted from silver-PPy nanosheets. These silver-PPy nanocables will become longer until the silver nanosheets are used up. As shown in Figure 1L, silver-PPy nanocables several tens of micrometers in length were obtained as the final products (48 h). At this time, these silver-PPy nanocables had divorced from each other, and had their own separated two termini.

2. Spectroscopic Monitoring of the Silver-PPy Nanocable Growth Process. The UV-vis-NIR spectroscopic method can also be used to track the morphological evolution involved in the growth process because silver nanostructures with different shapes exhibit surface plasmon resonance (SPR) bands at different frequencies.²⁴ Meanwhile, the π - π^* transition of the PPy chain is located in the region of 400–500 nm.²⁵ Figure 2 compares the UV-vis-NIR absorption spectra obtained from solutions sampled at different reaction times (after the addition of AgNO₃ and PVP). At the initial stage (curve a), the absorbance maximum of the sample appeared at \sim 443 nm. This broad absorbance peak potentially results from two contributions: the polymerized PPy with short conjugation length and the formed silver nanoparticles. It was reported that peaks at \sim 410 and \sim 440 nm were consistent with the formation of silver spherical nanoparticles and triangular nanosheets.^{26–28} According to the theoretical calculations by Schatz et al. for the triangular prisms with the discrete dipole approximation (DDA) method,²⁹ the 446-nm peak is the out-of-plane dipole. The

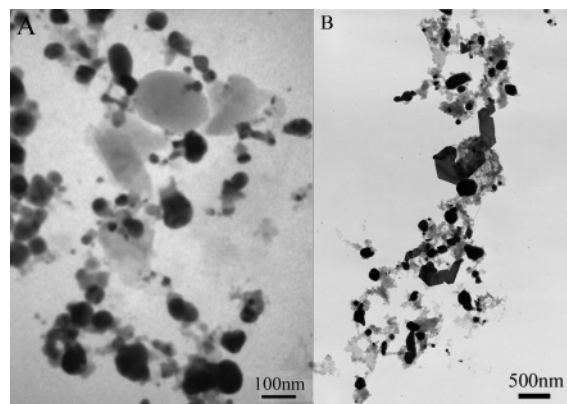


Figure 3. TEM images of the as-synthesized silver-PPy composites either (A) without the use of PVP or (B) with the replacement of PVP with other coordination reagents (PEG, MW \approx 4000).

distinct peak in the near-infrared (NIR) region (\sim 967 and \sim 1157 nm) might also arise from the in-plane dipole resonance mode associated with silver nanosheets whose edge lengths exceeded 100 nm.³⁰ As the reaction proceeded to 8 h (curve b), the peak at \sim 443 nm became sharp and increased in intensity. At the same time, a new peak appeared at \sim 540 nm. This implies the formation of rodlike structures. When the reaction had proceeded for 9 h (curve c), more silver nitrate was reduced, more pyrrole monomer was polymerized in situ on the surface of the silver nanostructures, and the silver-PPy nanorods continued to grow in length. A new peak appeared at 465 nm, and the intensity is larger than that of the 443-nm peak, indicating that the conjugation length of PPy began to increase. Furthermore, the peak at \sim 540 nm shifted to \sim 550 nm and increased in energy. This results from the fact that the longitudinal SPR band (λ_L) should be red-shifted as the aspect ratio increases.³¹ As the reaction continued to 12 h (curve d), the peak at \sim 443 nm completely red-shifted to 465 nm and increased in intensity, because of the increased conjugation length and amount of PPy in this system. At this point, optical signatures similar to those of bulk silver began to appear, as indicated by the shoulder peak around 352 nm. Once the reaction continued to 36 h (curve e), the peak at \sim 967 and \sim 1157 nm almost disappeared, indicating that most of the silver nanosheets were consumed, and that a large number of silver-PPy nanorods were formed whose absorbance peak red-shifted to \sim 570 nm. When the reaction stopped (48 h), the PPy was in a doped state, as the sample showed a broad absorption peak in the near-IR region (curve f). The SPR peak was still positioned around 570 nm, although a significant increase in intensity was observed. This result revealed that the silver-PPy nanocables increased in number without apparent growth in length, and the aspect ratio of the most final product is no more than five.³²

3. Influence of the Coordination Reagent. The influence of the coordination reagent PVP was discussed. Panels A and B of Figure 3 show TEM images of silver-PPy composite obtained without any agent, and with PEG, respectively. Neither silver nanowires nor silver-PPy composites with regular core-shell structure were obtained. This indicated that PVP plays a critical role in the formation of silver nanowires, and can influence the polymerization site of pyrrole monomer.

Discussion

In a solution-based polyol method, PVP can be used as an assistant agent to form Ag nanowires.^{9,10} In the chemical route, AgNO₃ can initiate polymerization of pyrrole monomers to yield PPy and Ag. Herein, these two rules were used together to

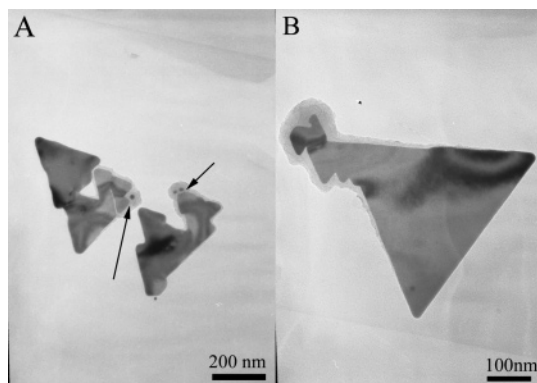


Figure 4. TEM images of the as-synthesized silver-PPy nanosheets for $R = 0.1$ (R is the molar concentration ratio of pyrrole monomer to AgNO_3).

fabricate Ag-PPy coaxial nanocables by a one-step process. There are three requirements for preparing silver-PPy coaxial nanocables through this one-step method. First, polymerization of pyrrole into PPy and the reduction AgNO_3 to silver should occur simultaneously. Then, silver one-dimensional structures can be formed in this system. Last, pyrrole monomer can stably polymerize in situ on the surface of silver nanowires. In our system, PPy and silver can be obtained concurrently because of the redox reaction between pyrrole monomer and silver nitrate. On the basis of what we discussed above, it can be seen that PVP not only helps in the formation of silver nanowires but also helps pyrrole monomer polymerize in situ on the surface of silver nanowires.

In the polyol route, Ag nanowires were fabricated with the help of PVP, which can control the growth rates of various faces of silver.^{9,10} However, in our system, there is a PPy sheath layer on the surface of the silver nanowire, which can render the growth process and the formation mechanism of silver-PPy nanocables different from those of naked silver nanowires. In our system, according to all mentioned above, the following growth process of silver-PPy nanocables could be concluded: tiny silver particles were formed when the AgNO_3 aqueous solution was added to pyrrole monomer. Then, through Ostwald ripening, these silver particles transformed to silver-PPy nanosheets, which connected together for stability. Lastly, these silver-PPy sheets transformed into silver-PPy nanocables. In other words, silver-PPy nanocables are able to grow at the expense of silver-PPy nanosheets. The following low-pyrrole-concentration systems can be used as supporting evidence of this.

In our previous work, we observed that the morphology of silver-PPy nanostructures was seriously influenced by the pyrrole-monomer concentration.²² Few silver-PPy nanocables with a high aspect ratio would be obtained under relatively low pyrrole concentrations. Only small quantities of silver-PPy nanosheets with nonregular morphology were obtained if the pyrrole concentration was too low. Panels A and B of Figure 4 are the TEM images of the silver-PPy nanostructure prepared with a low concentration of pyrrole ($R = [\text{pyrrole}]/[\text{AgNO}_3] = 0.1$). Obviously, the PPy layer covered the surface of the silver-PPy nanosheets on one corner of the triangle, as shown especially in Figure 4B. In this case, the reaction will stop before further transformation of the triangular silver-PPy nanosheets, because the reducing agent is entirely consumed. Otherwise, the reaction continues, and the obvious transformation takes place at one corner of the triangular silver-PPy nanosheet, as shown in Figure 5 ($R = 0.25$). Figure 6 is the AFM image of one typical silver-PPy nanosheet obtained at this R -value. It

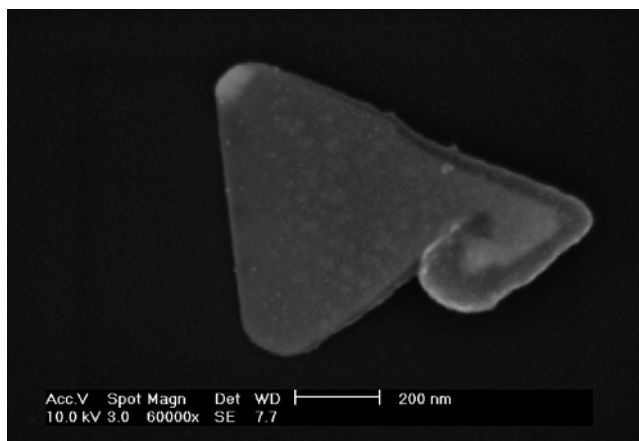


Figure 5. SEM image of the as-synthesized silver-PPy nanosheet for $R = 0.25$.

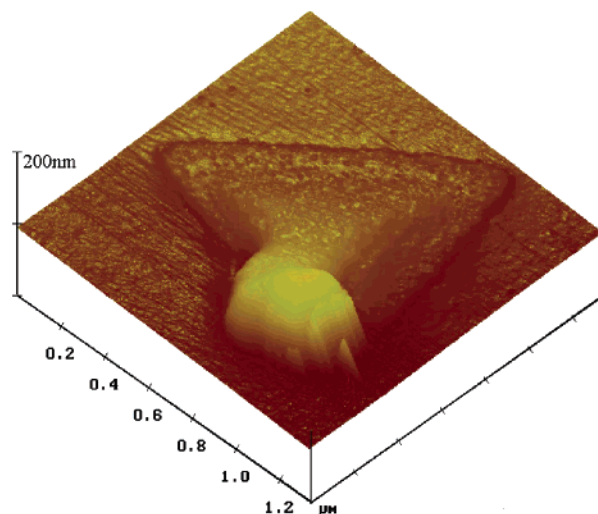


Figure 6. AFM image of the as-synthesized silver-PPy nanosheet for $R = 0.25$.

can clearly be seen that the transformed silver-PPy nanosheet is not in only one plane. With the increase of pyrrole concentration, the above reaction will continue. These silver-PPy nanosheets will grow in a one-dimensional way, as shown in panels A and B of Figure 7, obtained at $R = 0.5$. Especially in Figure 7B, a typical silver-PPy nanocable has been formed that is still connected with a silver-PPy nanosheet.

Although the exact transformation mechanism from silver-PPy nanosheets to silver-PPy nanocables is still not completely understood at this point, a plausible one is described below. Large numbers of tiny silver particles would be formed if silver nitrate were added to pyrrole monomer. These tiny silver particles will transform to silver-PPy nanosheets with regular morphology due to Ostwald ripening. If the pyrrole concentration is high enough, a lot of silver-PPy nanosheets will be formed. They are apt to connect together and stabilize by further ripening.

According to the above discussion, each silver nanosheet is highly [111] oriented. It is reported that the newly formed side surfaces are [100] facets.^{10,18} Scheme 1 depicts the proposed structure of the silver nanosheets. It is believed that the interaction between PVP and the [111] facets is much weaker than that between PVP and the [100] facets.^{10,18} Therefore, PVP is strongly adsorbed on the [100] facets, and pyrrole monomers are apt to be distributed on a surface where a large amount of PVP exists. At the same time, silver atoms easily diffuse on

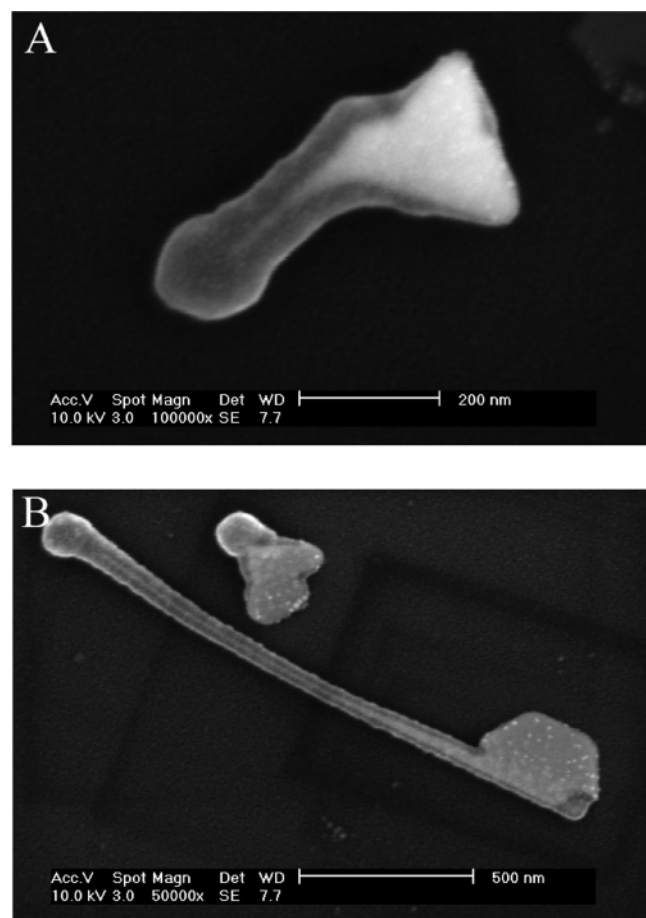
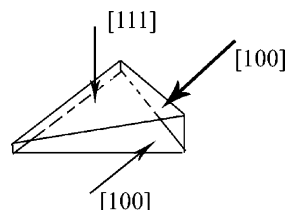


Figure 7. SEM images of the as-synthesized silver-PPy nanosheets for $R = 0.5$.

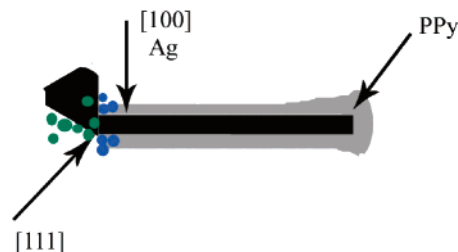
SCHEME 1: Structure of a Silver Nanosheet



the [111] facets, and thus, according to the ion adsorption effect,^{33–35} large numbers of silver ions will be adsorbed on the [111] facets. Polymerization will easily take place on the boundary of the [111] and [100] facets. Polymerized PPy will stay stable on the [100] facets.

Meanwhile, the newly formed silver atoms and the silver nanosheets will diffuse together by Ostwald ripening to grow on the [111] facets. At the early stage of the reaction, the silver nanosheet is large enough to adsorb a large number of silver ions, which will initiate a lot of pyrrole monomers, so the PPy layer at the one terminal is very thick. As the reaction continues, silver ion and pyrrole concentration will both decrease, and the silver nanosheets will become smaller and smaller. All of these induce the PPy layer on the silver nanowires to become thin. Scheme 2 depicts the structure of the growing silver-PPy nanocable from a silver-PPy nanosheet. If pyrrole concentration is low, the reaction will stop at an early stage once all the pyrrole monomer is consumed. In this case, silver-PPy nanocables connected with silver-PPy nanosheets could be observed. If pyrrole concentration is high enough to consume the silver

SCHEME 2: Growing Silver-PPy Nanocable from a Silver-PPy Nanosheet^a



^a The blue dots represent pyrrole monomers, and the green dots represent silver ions.

nanosheet, the last polymerized PPy will envelop the newly formed silver atoms, which diffused on the [111] facets.

Conclusions

In conclusion, silver-PPy nanocables can be fabricated through the redox reaction between AgNO_3 and pyrrole monomer in the presence of PVP. The following growth process was observed: a large number of silver atoms were formed when AgNO_3 was added to pyrrole solution. Through Ostwald ripening, silver atoms transformed to silver-PPy nanosheets with regular morphology, which will connect together for stability. Silver-PPy nanocables will be able to grow at the expense of the silver-PPy nanosheets. This formation process was further proved by the resulting products obtained in low-pyrrole-concentration systems. In this process, PVP plays two roles in the formation process: as a capping agent to form silver nanowires and as a dispersant of pyrrole monomer. A possible mechanism was proposed to explain this growth process. Because of the effect of PVP, silver ions and pyrrole monomer are apt to be adsorbed at [111] and [100] facets of silver nanosheets, respectively. Obvious polymerization will take place on the boundary of [111] and [100] facets. With the help of PVP, the PPy layer stays stable on the [100] facets. Meanwhile, newly formed silver atoms and silver nanosheets will further ripen to grow on the [111] facets. In this polymerizing system, PVP influenced the site of pyrrole monomer existence, and then affected the polymerization sites. In a word, the final product morphology and the formation process are decided by the reaction site between AgNO_3 and pyrrole monomer, which is influenced by PVP.

References and Notes

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- (35) In a typical synthesis, silver nanowires were fabricated according to the method demonstrated in ref 9. Then, the as-synthesized silver nanowires were disposed with 20 mL of 5% (wt) AgNO₃ aqueous solution. After 10 min, the excess AgNO₃ solution was removed by centrifugation at high speed. The solid part was added to a flask with 20 mL of deionized water. Pyrrole monomer (0.5 mL) was added to this system. The reaction mixture was stirred for 48 h. The resulting sample was characterized by TEM, showing that silver nanowires were sheathed by a PPy layer. This indicated that after being disposed with AgNO₃, silver ions were absorbed on the surface of silver nanowires, which initiates polymerization of the pyrrole monomers.