

# Fabrication of Au/PVP Nanofiber Composites by Electrospinning

Yongzhi Wang,<sup>1,2</sup> Yaoxian Li,<sup>1</sup> Guoen Sun,<sup>3</sup> Guangliang Zhang,<sup>1</sup> Hui Liu,<sup>2</sup> Jianshi Du,<sup>1</sup> Songtao Yang,<sup>1</sup> Jie Bai,<sup>1</sup> Qingbiao Yang<sup>1</sup>

<sup>1</sup>Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

<sup>2</sup>Environmental Monitoring Center, Environment Protection Bureau of Changchun City, Changchun 130012, People's Republic of China

<sup>3</sup>Department of Material Science and Engineering, Jilin University, Changchun 130023, People's Republic of China

Received 3 December 2005; accepted 12 June 2006

DOI 10.1002/app.25003

Published online 9 June 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Gold nanoparticles prepared by trisodium citrate reduction of HAuCl<sub>4</sub> in poly(vinylpyrrolidone) (PVP) ethanol solution were dispersed into PVP nanofibers by electrospinning. The optical property of Au nanoparticles before and after electrospinning was measured by UV-Vis. The morphology and distribution of gold nanoparticles in PVP nanofibers were observed by transmission electron micros-

copy (TEM). The influence of the amount of Au added to and the concentration of PVP in electrospinning solution over the morphology of Au/PVP nanofibers were studied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3618–3622, 2007

**Key words:** gold nanoparticle; PVP nanofiber; electrospinning

## INTRODUCTION

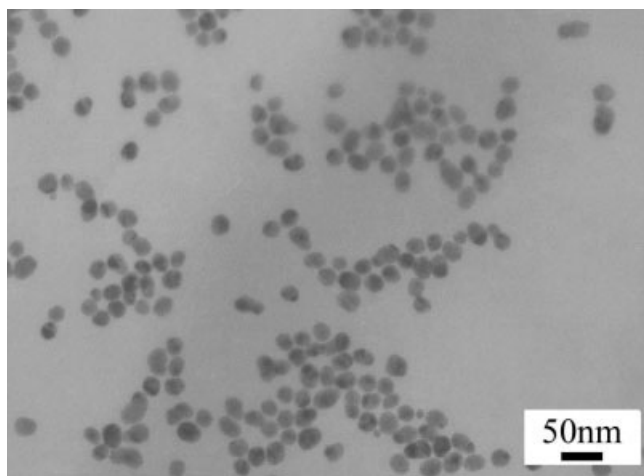
The dispersion of metal nanoparticles into polymer nanofibers are of great interest in recent years, because of not only the novel properties of the nanocomposite materials but also continuously growing demand for further miniaturization of electronic components, optical detectors, chemical and biochemical sensors, and devices.

Within the past decade, dispersion of gold nanoparticles in polymer matrix have particularly received extensive attention due to the possibility of fabricating suitable materials for applications such as catalysts, drug and wound dressings, information storage, and surface enhanced Raman scattering, etc.<sup>1–5</sup> Many different approaches have been used to prepare Au/polymer nanocomposite. Generally gold nanoparticles are collected in the form of either colloids or powders.<sup>6,7</sup> It is extremely difficult to disperse gold nanoparticles homogeneously on solid substrates by conventional casting methods,<sup>8</sup> which hinder the practical application of gold nanoparticles in many aspects. Therefore, convenient and effective ways to disperse gold nanoparticles into suitable solid materials are strongly demanded.

In recent years, electrospinning process has regained great attention<sup>9,10</sup> as it is a simple and low

cost method for fabricating polymer ultra-fine fibers with diameter ranging from a few micrometer to a few nanometer. The novel nanofiber spinning technique has been explored mainly to prepare pure polymer nanofibers in past years. In our lab, we first prepared ultra-fine polyacrylonitrile (PAN) fibers containing silver nanoparticles by the method.<sup>11</sup> The experiments show that it is a convenient way to disperse silver nanoparticles homogeneously into polymer matrix. The properties of the nanocomposite were studied by surface enhanced Raman scattering spectroscopy (SERS).<sup>12</sup> It was recently reported that this kind of nanocomposite, polymer nanofiber embedded silver nanoparticles prepared by electrospinning, had a high antimicrobial activity.<sup>13</sup> Demir prepared Palladium nanoparticles dispersed in poly(acrylonitrile-co-acrylic acid) nanofibers and studied their catalytic activity.<sup>14</sup> Kim et al. fabricated one-dimensional arrays of Au nanoparticles within a semicrystalline polymer poly(ethylene oxide) (PEO).<sup>15</sup> They found that average diameter of PEO nanofiber increased from 500 to 550 nm after adding gold nanoparticles, whose surface was capped with dodecanethiol. Here, we disperse gold nanoparticles by electrospinning without other capping molecule into polymer poly(vinylpyrrolidone) (PVP). It is known that PVP is one of the attractive polymers to immobilize metal nanoparticles due to its strong affinity of pyridyl group to metals and its ability to undergo hydrogen bonding with polar species. Some metal and semiconductor nanoparticles have been successfully prepared under the existence of PVP in

Correspondence to: Q. Yang (yangqb@mail.jlu.edu.cn).



**Figure 1** TEM images of gold nanoparticles in PVP ethanol solution before electrospinning.

solution.<sup>7</sup> Since PVP has high solubility in most organic solvents and metal nanoparticles can be prepared in PVP solution, nanoparticles could be easily dispersed into PVP matrix by electrospinning. Previously, Xia et al. synthesized nanocomposites of TiO<sub>2</sub>/PVP, SnO<sub>2</sub>/PVP, and NiFe<sub>2</sub>O<sub>4</sub>/PVP.<sup>16–18</sup> As so far, however, few convenient approaches can homogeneously disperse gold nanoparticles in solid PVP substrates.

In this study, we present a convenient method to disperse gold nanoparticles homogeneously in PVP nanofibers, which includes two main steps. In the first one, gold nanoparticles are prepared by trisodium citrate reduction of HAuCl<sub>4</sub>. In the following one, the gold nanoparticles are added to PVP ethanol solution and then the solution is electrospun to prepare PVP nanofiber dispersed gold nanoparticles.

## EXPERIMENTAL SECTION

### Materials

Poly(vinylpyrrolidone) (PVP, K-90) is provided by Xiamen Sanland Chemicals Company (China) and tetrachloroauric acid was purchased from Aldrich. Sodium citrate and ethanol are supplied by Beijing Chemicals Co. (China). All reagents were used without further purification.

### Preparation of gold nanoparticles

Au nanoparticles: Aqueous tetrachloroauric (III) acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O, 1.0 wt %, 10 mL)<sup>19</sup> was mixed with 200 mL triple distilled water in a 500 mL round-bottom flask and the solution was heated to boiling. Then aqueous trisodium citrate (1.0 wt %, 20 mL) was injected quickly. The mixed solution had been

kept boiling and stirring for 10 min followed by cooling to room temperature and high speed centrifugal settling.

### Preparation of electrospinning solution

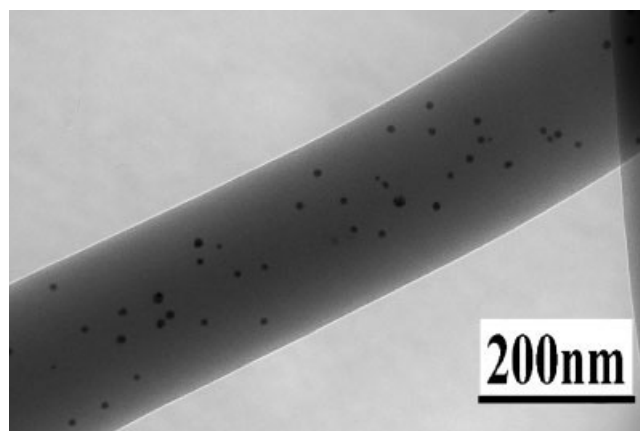
Different amounts of PVP was dissolved in ethanol to make solutions with concentration of 8, 6, and 4 wt %, respectively. Au nanoparticles were added to the above solutions to make solutions with molar ratio of repeat unit of PVP to Au of 10 : 1, 20 : 1, and 30 : 1, respectively. The solutions were kept under ultra-sonic dispersion for 30 min and then kept in stirring 24 h for electrospinning.

### Preparation of Au/PVP nanofiber by electrospinning

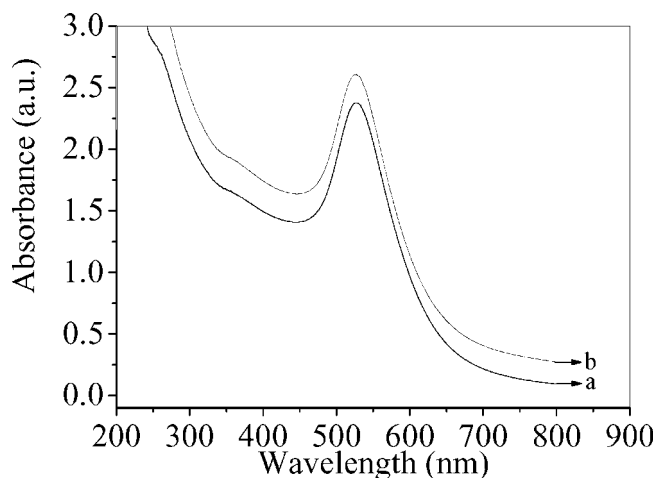
We used home-made electrospinning setup that contains basically three components: a high voltage supplier, a glass tube with a tip diameter of 0.8 mm, and an Al-foil collector to fabricate Au/PVP nanofiber. The process is that the Au/PVP solution was loaded in the glass tube connected to anode that is 15 cm far away from Al-foil collector as a cathode. The Au/PVP solution was electrospun at 13 kV positive voltage and 0.5 mL/h solution flow rate.

### Characterization of Au nanoparticles and Au/PVP nanofiber

A copper grid was stuck on to the cathode of electrospinning setup to collect nanofiber for observing the morphology of PVP nanofiber and distribution of Au nanoparticles in PVP nanofiber by high-resolution transmission electron microscopy (TEM). TEM images were recorded on a Hitachi S-570 Trans-



**Figure 2** TEM images of Au/PVP nanofibers electrospun from 8 wt % PVP ethanol solution containing gold nanoparticles (molar ratios of repeat unit of PVP to Au was 10 : 1).



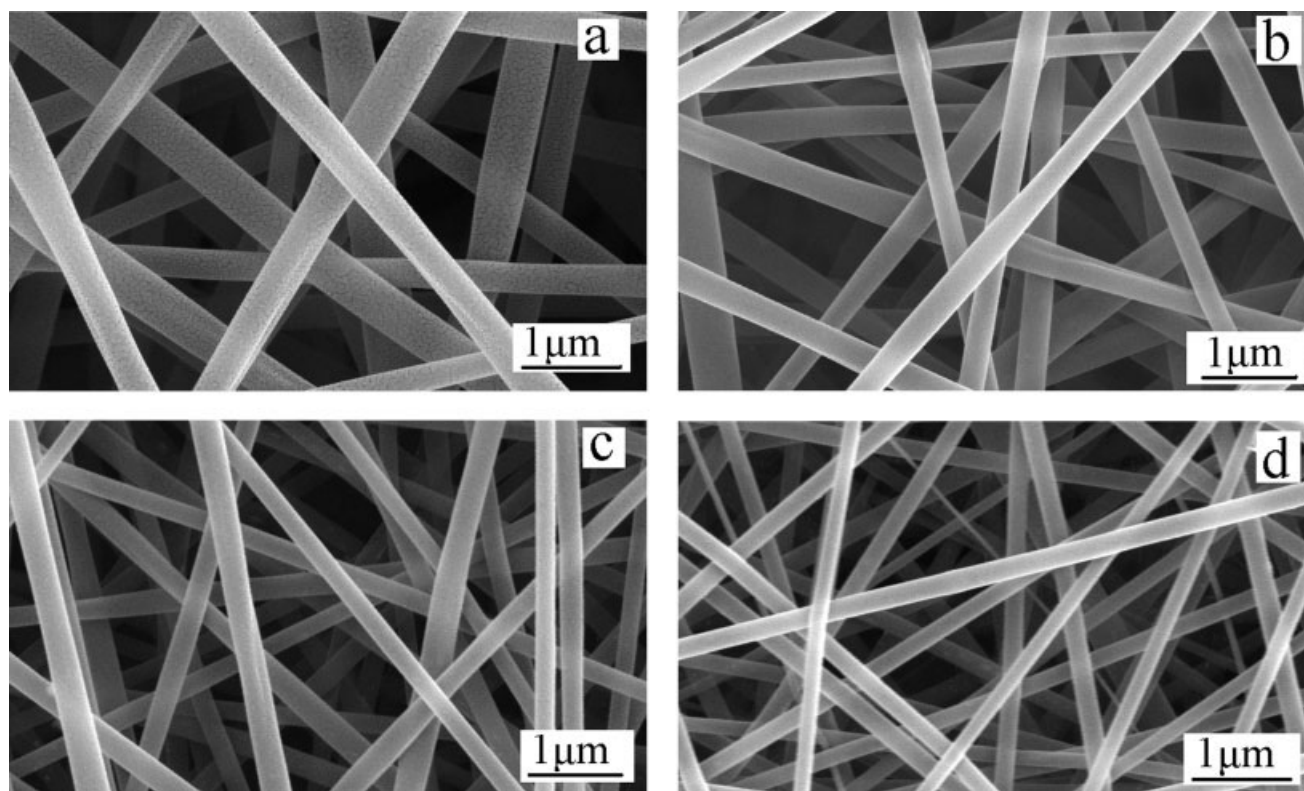
**Figure 3** UV-Vis spectra of Au nanoparticles in PVP ethanol solution before (a) and after (b) electrospinning.

mission Electron Microscopy. UV-Vis absorption spectra were measured by a Cary 100 spectrophotometer (Varian Corp.) with a 10 mm quartz cell. The conductivities was measured by a conductivity meter (DDS-11, Shanghai, China). All SEM images were obtained by a FEI XL30 scanning electron microscopy.

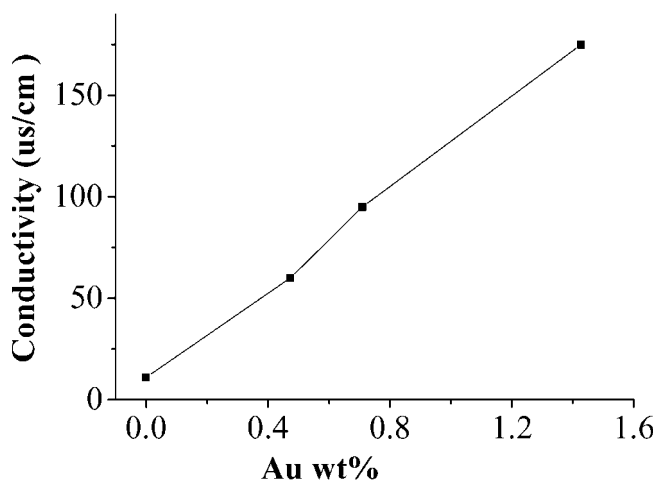
## RESULTS AND DISCUSSION

The gold nanoparticles in PVP ethanol solution before electrospinning were examined by TEM. Small amount of PVP solution containing Au nanoparticles (molar ratio of repeat unit of PVP to Au was 10 : 1) was painted on a copper grid for observing TEM image. Figure 1 is the TEM image of the gold nanoparticles. It shows that gold nanoparticles have a spherical form and exhibit a narrow size distribution and that the average diameter of gold nanoparticles is 20 nm.

According to our previous study,<sup>20</sup> we chose 8 wt % of PVP with Au nanoparticles in ethanol solution for a series of experiments. Figure 2 shows magnified TEM images of the Au/PVP nanofiber. It reveals that the morphologies and diameter distribution of gold nanoparticles are not changed through electrospinning and that the gold nanoparticles are very well dispersed in PVP nanofiber. The result could be attributed to the structural features of PVP, which is a polymer with a long and soft polyvinyl chain, and polar groups. PVP prohibits gold nanoparticles agglomeration as a result of its steric effect and the coordinative chemical bonding of C—N and C=O to Au atom. Further investigation on interaction between the gold atoms and the PVP are currently in progress.



**Figure 4** SEM images of PVP and Au/PVP nanofibers electrospun from 8% PVP solution (a) with different molar ratio of Au to PVP (b) 30 : 1; (c) 20 : 1; (d) 10 : 1.

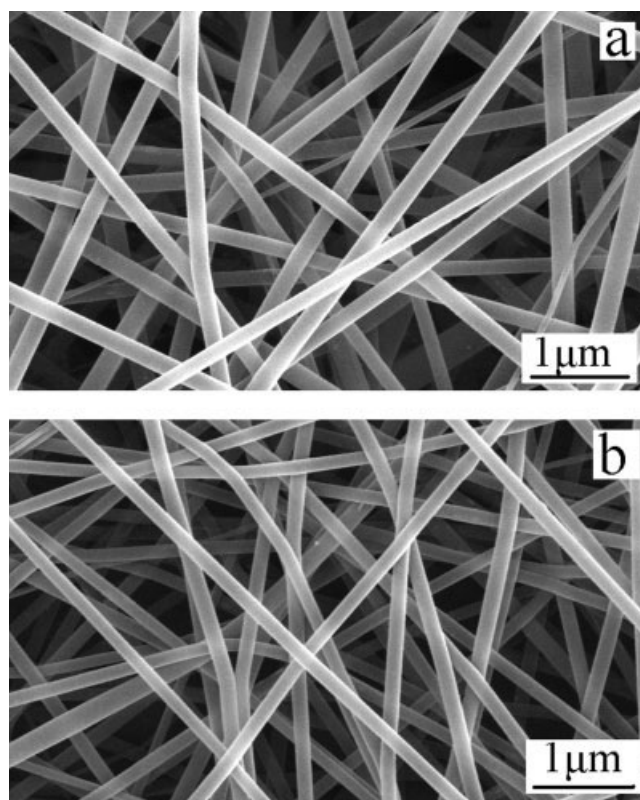


**Figure 5** Changes in conductivity of 8 wt % PVP alcohol solutions according to the amount of Au nanoparticles added.

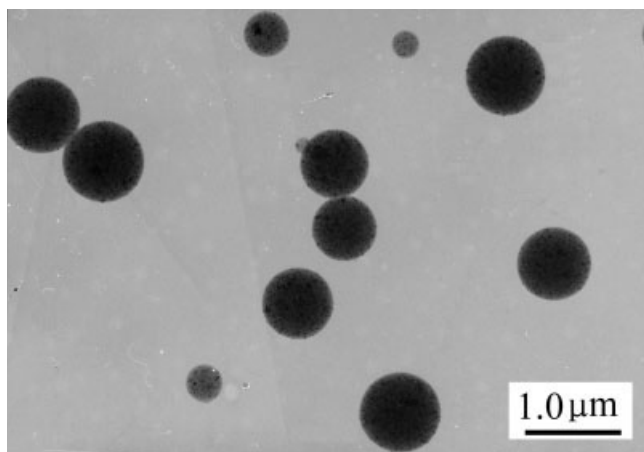
UV-Vis spectroscopy is a very useful technique for characterization of metal nanoparticles. Small metallic particles exhibit a high optical absorbance due to the existence of discrete energy levels of electron and particularly of specific states. Gold particles with diameters about 20 nm exhibit absorption bands at 520–540 nm depending on their chemical environment.<sup>21</sup> This band is broadened and shifted towards higher wave lengths with increasing particle diameter. To investigate the stability of Au nanoparticles in the process of electrospinning, the UV-Vis spectra of Au nanoparticles in PVP ethanol solution before and after electrospinning were measured. The latter was obtained by collecting the Au/PVP nanofiber on the collector and then redissolving it into ethanol. Figure 3(a) is the absorption spectrum of Au nanoparticles in PVP ethanol solution before electrospinning. It can be seen that an absorption band with a sharp maximum at 520 nm arises. The result corresponds very well with the spectral behavior of gold nanoparticles. Figure 3(b) is the spectrum of Au nanoparticles after electrospinning. It is observed that absorption peak of Au nanoparticles are also located at 520 nm without any shifting. This suggests that the morphology and size of Au nanoparticles are not changed in the process of electrospinning.

The effects of Au nanoparticles on the morphology of Au/PVP nanofiber are studied. The concentration of PVP solution was 8% and the molar ratio of Au to PVP is 1 : 30, 1 : 20, and 1 : 10, respectively. Figure 4 are SEM images of pure PVP nanofiber and Au/PVP nanofiber. By comparison, it is found that the diameter of pure PVP nanofiber (420 nm) was thicker than that of Au/PVP nanofiber. The average diameters of the Au/PVP nanofiber electrospun from solutions of molar ratio of Au to PVP 1 : 30, 1 : 20, and 1 : 10 are 330, 290, and 245 nm, respectively. Many parameters

have influence on diameter of polymer nanofibers in the process of electrospinning. When dopant is added to polymer solution for electrospinning, interaction between dopant and polymer will make the nanofiber thicker.<sup>11</sup> If the dopant increases the conductivity of the polymer solution, it will make nanofiber thinner.<sup>13</sup> In our investigation, gold nanoparticle was added to PVP solution and the conductivity of the solution was increased. Figure 5 shows changes in conductivity of PVP alcohol solution according to the amounts of gold nanoparticles added. The conductivities of PVP solutions were linearly increased with the amount of gold nanoparticles added. It increases the charge density in PVP ethanol solution and thus stronger elongating forces are imposed on the ejected jets under the electrical field, resulting in thinner PVP fiber. It is true that there is an interaction between Au atoms and PVP molecular chain, but conductivity increased by Au nanoparticles plays a predominant role in diameter of PVP nanofiber in the process of electrospinning. In the experiment of Kim et al.,<sup>15</sup> they reported that diameter of pure PEO nanofibers was thinner than that of Au/PEO nanofibers. The reason was that the conductivity of the gold nanoparticles was greatly reduced after the surface of gold nanoparticles was capped with dodecanethiol. The interaction between gold nanoparticles



**Figure 6** SEM images of Au/PVP nanofibers electrospun from 6 wt % (a) and 4 wt % (b) PVP solution with 1/10M ratio of Au to PVP.



**Figure 7** TEM image of Au/PVP nanoparticles electrospun from low concentration PVP solution containing Au nanoparticles.

and PEO molecules played predominant role and made PEO/Au nanofibers thicker. Therefore, the result of our experiment is not inconsistent with Kim's conclusion.

The influence of the concentration of PVP over the morphology of Au/PVP nanofiber is also investigated. Figure 6 is the SEM images of Au/PVP nanofiber electrospun from 6 wt % and 4 wt % of PVP solution containing Au nanoparticles (the molar ratio of Au to PVP kept 1 : 10 in both solutions). The diameters of Au/PVP nanofiber are decreased with the concentration decreasing of PVP. The average diameters of the Au/PVP nanofiber electrospun from 8, 6, and 4 wt % of PVP solution with 1/10M ratio of Au to PVP are 250, 190, and 140 nm, respectively. The result is in agreement with that reported by Son and Youk.<sup>22</sup>

In addition, it is noteworthy that Au/PVP nanoparticles with core-shell structure are obtained when the concentration of PVP solution further decreases. Figure 7 is the TEM image of the nanoparticles. Diameters of the nanoparticles are ranging from 900 to 420 nm. The novel composite nanoparticles are under investigation in our lab.

## CONCLUSIONS

Gold nanoparticles with narrow size distribution were dispersed very homogeneously in PVP nanofiber by electrospinning process. The structure and optical property of the Au nanoparticles were not changed through a high voltage pressure. The average diameter of PVP and Au/PVP nanofiber electrospun from 8% PVP ethanol solution and 8% PVP solution with 1/30, 1/20, and 1/10M ratio of Au to PVP were 420, 330, 290, and 245 nm, respectively. The average diameter of Au/PVP nanofiber decreased with the decreasing concentration of PVP in electrospinning solution.

## References

1. Lee, T. M.; Cai, H. *Electroanalysis* 2004, 161, 628.
2. Pustovalov, V. K.; Babenko, V. A. *Laser Phys Lett* 2004, 1, 516.
3. Larsson, M.; Lu, J.; Lindgron, J. *J Raman Spectrosc* 2004, 35, 826.
4. Shlyahovsky, B.; Katz, E.; Xia, Y. *Small* 2005, 1, 213.
5. Diniel, M. C.; Astruc, D. *Chem Rev* 2002, 104, 293.
6. Sun, Y.; Xia, Y. *Science* 2002, 298, 2176.
7. Kim, F.; Song, J. H.; Yang, P. *J Am Chem Soc* 124 2002, 14316.
8. Yonezawa, T.; Kunitake, T. *Colloids Surf A* 1999, 149, 193.
9. Loscertales, I. G.; Barrero, A.; Guerrero, I. *Science* 2002, 295, 1695.
10. Dzenis, Y. *Science* 2004, 304, 1917.
11. Yang, Q. B.; Li, D. M.; Hong, Y. L. *Synth Met* 2003, 137, 973.
12. Wang, Y. Z.; Yang, Q. B.; Shan, G. Y. *Mater Lett* 2005, 59, 3046.
13. Son, W. K.; Youk, J. H.; Lee, T. S. *Macromol Rapid Commun* 2004, 25, 1632.
14. Demir, M. M.; Gulgun, M. A.; Menciloglu, Y. Z. *Macromolecules* 2004, 37, 1787.
15. Kim, G. M.; Wutzler, A.; Radusch, H. *J Chem Mater* 2005, 17, 4949.
16. Li, D.; Wang, Y.; Xia, Y. *Nano Lett* 2003, 3, 1167.
17. Li, D.; Xia, Y. *Nano Lett* 2003, 3, 555.
18. Li, D.; Herricks, T.; Xia, Y. *Appl Phys Lett* 2003, 83, 4586.
19. Tsai, C. Y.; Chien, H. T.; Ding, P. P. *Mater Lett* 2004, 58, 1461.
20. Yang, Q. B.; Li, Z. Y. *J Polym Phys B* 2004, 42, 3721.
21. Calandra, P.; Giordano, C. *Mater Chem Phys* 2006, 98, 494.
22. Son, W. K.; Youk, J. H. *Macromol Rapid Commun* 2004, 25, 1632.