

Fabrication of silver plated nylon 6 nanofibers using iodine

Takuya Tetsumoto^{*1,*2} and *Yasuo Gotoh*^{*1}

^{*1} Faculty of Textile Science and Technology, Shinshu University,
3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

^{*2} LINTEC Corporation, 5-14-42 Nishikicho, Warabi, Saitama 335-0005, Japan

Abstract: Silver (Ag) metal-plated nanofibers were prepared from nylon 6/silver iodide (AgI) composite nanofibers. Pristine nylon 6 nanofibers formed by electrospinning were iodinated with an iodine-potassium iodide aqueous solution and subsequently immersed in a silver nitrate solution to form AgI particles in the nanofiber matrix. After the reduction of AgI to Ag metal, electroless Ag plating was carried out on the composite nanofibers. Here, the Ag particles reduced from AgI function as autocatalyst particles as well as an anchor for the metal plated layer. SEM observations showed that a Ag plated layer formed on each nanofiber. The surface electrical conductivity of the Ag-plated nanofibers was determined to be ca. 1×10^{-1} ohm cm^{-2} . After sonication for 30 min, the Ag-plated layer remained intact and the conductivity of the samples was retained, indicating good interfacial adhesion between the nanofiber surface and metal plated layer.

(Received 28 April, 2010 ; Accepted 25 May, 2010)

1. Introduction

Morphological control of nanoparticles, particularly the shape and size, has attracted significant interest from researchers [1-10]. Nanoparticles with one-dimensional (1D) nanostructures, such as nanofibers, nanowires, nanotubes, and nanorods, have considerable potential due to their high aspect ratio in addition to the size. 1D nanoparticles are useful as fillers in electronic nanocomposite materials because the probability of contact between fillers is much higher in conjunction with the large particle numbers and specific surface areas, due to the nano-scale size. Thus, it is expected that nanocomposites can be fabricated with excellent electrical and thermal conductivities by incorporating 1D nanoparticles, even with low filler content. However, the construction of 1D nanostructures is difficult to reduce to the nanometer size compared to spherical nanoparticles.

Silver (Ag) is an attractive metal from the perspective of electrical and thermal conductivities. For Ag nanowires, researchers have reported wet chemical approaches including solvothermal methods with the help of various directing agents such as polyvinylpyrrolidone. These wet chemical approaches generally have associated problems such as difficulty in shape controllability, low reaction rate, and low yields due to low reagent concentrations [11-15]. Physical templating methods can also be utilized, for example, porous alumina prepared by

cathodic oxidation, and mesoporous silica have been used as a nanowire template [16, 17]. Although the use of templates can ensure a good shape of the 1D structure, the templates which are valuable need to be ultimately removed by dissolving them in a solvent to obtain the nanowires.

Electrospinning is a technique to form organic polymer nanofibers, and a useful method to fabricate 1D structures with dimensions between several tens of nanometers and several hundreds of nanometers [18-22]. Thus, if electroless plating is applied to the surfaces of nanofibers, metallic 1D nanostructures of continuous nanowires can be relatively easily obtained in higher volumes compared to other processes used to form neat metal nanowires. Electroless plating typically requires etching of polymer surfaces by oxidative agents with a strong acid, followed by a catalyst providing process including sensitization and activation steps [23-25]. In actuality, additional complicated processes are involved in electroless plating, and the kinds of polymers that can be plated are limited. Also, the etching process could cause decomposition of the nanofibers. Accordingly, surface modification using polymer grafting techniques has been carried out on polymer surfaces, including on nanofibers. This is a good method to make nanofiber surfaces suitable for electroless plating, however, expensive equipment such as plasma, electron and light sources are typically required [26-29].

We have previously reported a method to impart metal iodides into a polymer matrix by utilizing the affinity of iodine to various kinds of polymers to prepare organic/inorganic composites. For example, some polymers form complexes with polyiodide ions, and silver iodide and copper iodide can be precipitated *in situ* in polymer matrices by the reaction of polyiodide ions with metal ions [30,31]. The metal iodides thus introduced can be converted to metal particles in the composite by using a reducing agent.

In the present study, we have applied this method to electrospun polymeric nanofibers to successfully carry out metal plating. Polyiodide ions were doped into polymer nanofibers and silver iodide (AgI) was generated by the reaction between the polyiodide ions and silver ions. The AgI component was then reduced to Ag metal. Electroless Ag plating was carried out by the autocatalytic action of the reduced Ag. The structure and electrical conductivity of the Ag-plated nanofibers were investigated.

2. Experimental

2.1 Materials

Nylon 6 (Ultrad[®] BS 700) was purchased from BASF. Formic acid, iodine (I₂), potassium iodine (KI), silver nitrate (AgNO₃), 28 % ammonia solution, D-glucose, sodium hydroxide (NaOH) and sodium borohydride (NaBH₄) were all purchased from Wako Pure Chemical Industries Ltd., Japan. All chemicals were used without further purification.

2.2 Preparation of nylon 6 nanofibers

Nylon 6 was dissolved in formic acid to make a solution with a concentration of 10wt%. The electrospinning process was carried out using a syringe and a 22 gauge needle with flat tip at an applied voltage of 15 kV. Nylon 6 nanofibers were collected as a mat form on a grounded copper plate covered with polyethylene mesh. The distance between needle tip and the grounded plate was 10 cm.

2.3 Pretreatment of electroless plating of nanofiber

The pretreatment of electroless plating of nylon 6 nanofibers was carried out as represented in Figure 1 ; nylon 6 nanofiber mat was immersed in I₂-KI (I₂ : 0.1 M, KI : 0.3 M) aqueous solution at room temperature for 3 min. Iodinated nylon 6 nanofibers were treated with 0.02 M AgNO₃ aqueous solution for 3 min, followed by reduction with 0.05wt% sodium borohydride aqueous solution for 3 min. After each process, the samples were

washed with distilled water for 1 min.

2.4 Ag electroless plating

Typical silver plating was carried out based on silver mirror reaction. Plating solution was prepared as follows ; 1 mL of 5wt% ammonia solution was dropped into 5 mL of 5wt% AgNO₃ aqueous solution until Ag₂O precipitation disappeared. Then, the solution of ammine complex of Ag⁺ was mixed with 5 mL of 10wt% glucose and 0.06 mL of 2wt% NaOH aqueous solutions. Silver mirror reaction was carried out by immersion of nylon 6 nanofiber mat (4 cm²) into the above mixture solution at room temperature for 15 min in a polypropylene vessel.

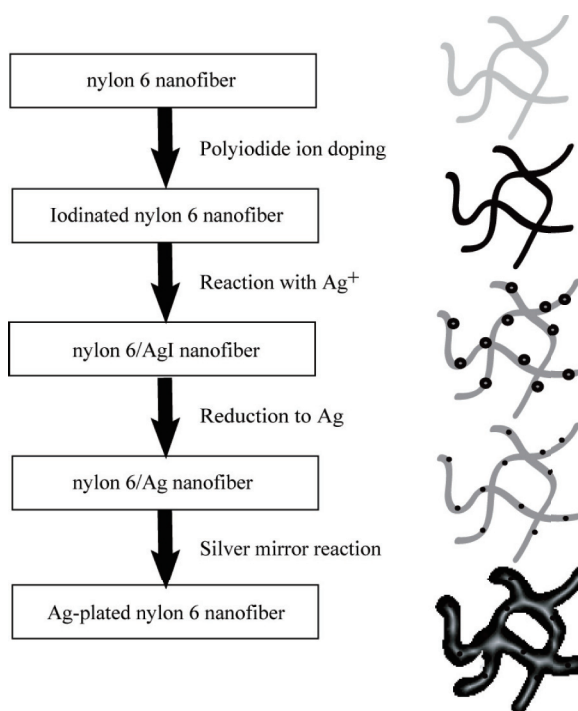


Fig. 1 Sample preparation procedure of Ag-plated nylon 6 nanofibers.

2.5 Measurements

Scanning electron microscope (SEM) was carried out with a Hitachi S-2380N at voltage of 25 kV. The specimens were sputtered with an ultra thin layer of Pt before imaging. Raman spectroscopy measurement was carried out on a HoloLab 5000 Raman spectroscope, equipped with an Mk II probe head using a Nd : YAG laser beam with 532 nm with 50 mW power. X-ray diffraction (XRD) measurement was performed by reflection method using a Rigaku Rotorflex RU-200B X-ray generator equipped with a goniometer. The X-ray source was Ni-filtered Cu-K_α radiation ($\lambda = 0.15418$ nm) generated at 40 kV and 150 mA. Surface resistance was measured by four-probe method using a Mitsubishi Chemical Analytech Loresta-GP.

3. Results and discussion

Figure 2 shows a SEM image of pristine nylon 6 nanofibers. The average diameter of the nanofibers was ca. 85 nm. After immersion in I₂-KI solution, the nylon 6 nanofibers immediately changed to a dense brown color, indicating successful sorption of polyiodide ions into the nylon 6 nanofibers. Figure 3 shows the Raman spectrum of the iodinated nylon 6 nanofibers. Raman spectroscopy is an effective method to study polyiodide ions. Two major scattering peaks were observed at 110 cm⁻¹ and 165 cm⁻¹, respectively assigned as I₃⁻ and I₅⁻, from the nylon 6-polyiodide complex [32-34]. This implies the formation of a nylon 6-polyiodide ion complex and the existence of at least two types of polyiodide ions in the sample.

Next, in the process of the reaction of polyiodide ions with Ag⁺, when the iodinated nanofibers were immersed in the AgNO₃ solution, the color changed to light yellow within one minute. This color is typical of AgI and thus indicates conversion to AgI. The morphology of the nylon 6/AgI sample is shown in Figure

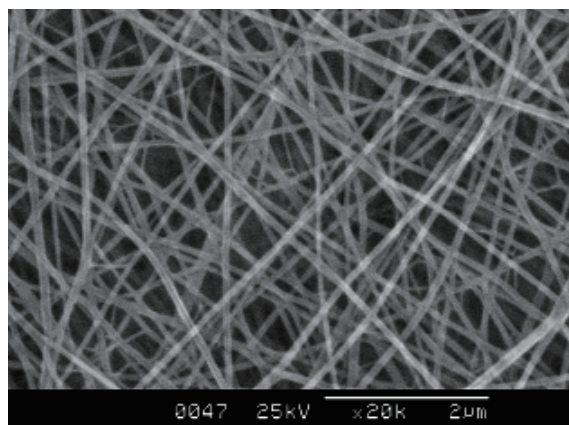


Fig. 2 SEM image of nylon 6 nanofibers prepared from 10 wt% nylon 6/ formic acid solution.

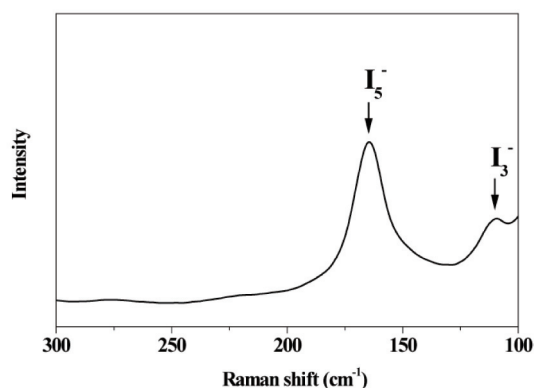


Fig. 3 Raman spectrum of nylon 6 nanofibers iodinated by immersion in an I₂-KI aqueous solution for 3 min.

4. AgI particles with size in the range of ca. 50-80 nm formed on the nanofibers. Consequently, the fiber diameter increased and the surface became scabrous. Thermogravimetric analysis revealed that the loaded AgI reached ca. 50wt% of the total composite weight. As shown in our previous work [31], AgI easily forms in the bulk nylon 6 matrix. Thus, the AgI component is considered to exist both on the surface and inside the nanofiber.

Upon immersing the nylon 6/AgI in an NaBH₄ solution, the sample immediately turned gray, indicating that AgI was reduced to Ag metal. Figure 5 shows the XRD patterns of pristine nylon 6, nylon 6/AgI and nylon 6/Ag. For nylon 6/AgI, diffraction peaks at ca. 2θ = 22.3°, 23.7°, 39.2° and 46.4° were assigned to (100), (002), (110) and (112) planes of the β form of the AgI crystal, respectively.

Nylon 6/Ag shows diffraction peaks of the Ag metal at 2θ = 38.5° and 2θ = 44.7° in Figure 5, though a part of the AgI remained after the reduction treatment. The formed Ag metal particles were at least partially on the fiber surface. Therefore, these surface Ag particles can act as an autocatalyst for electroless plating.

Figure 6 shows SEM images of the electroless-plated nanofibers prepared from (a) pristine nylon 6 (electrospinning time : 1 min, nylon 6 nanofiber amount : 0.02 mg cm⁻²), (b) pristine nylon 6 (electrospinning time : 30 min, nylon 6 nanofiber amount : 0.85 mg cm⁻²), (c) nylon 6/Ag (electrospinning time : 1 min, nylon 6 nanofiber amount : 0.02 mg cm⁻²) and (d) nylon 6/Ag (electrospinning time : 30 min, nylon 6 nanofiber amount : 0.85 mg cm⁻²) nanofibers. For the pristine nylon 6 nanofibers shown in Figure 6 (a), the nanofiber surfaces were inhomogeneously covered with Ag particles of between around 100 to 400 nm in diameter. In Figure 6 (b), isolated Ag particles of ca.100-150 nm were primarily formed, and a small amount of large Ag

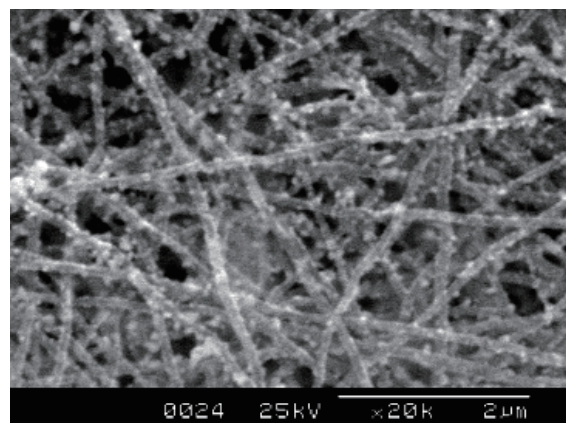


Fig. 4 SEM image of nylon 6/AgI nanofibers.

aggregates of 1-2 μm are also observed. These results suggest that an Ag layer can not be uniformly generated on the fiber surface without the pretreatment. In contrast, smooth but thicker Ag plated fibers are observed in Figure 6 (c). In Figure 6 (d), a thinner plated layer consisting of Ag nanoparticles is uniformly formed on the nanofibers surface. High resolution SEM observations (not shown here) revealed that the plated layer is constructed with densely deposited Ag particles of about 50 nm in diameter. These results indicate that pretreatment using iodine is effective to form a silver plating layer. Comparing Figures 6 (c) and 6 (d), it is concluded that when the fiber amount is smaller, the thickness of the plated layer is larger.

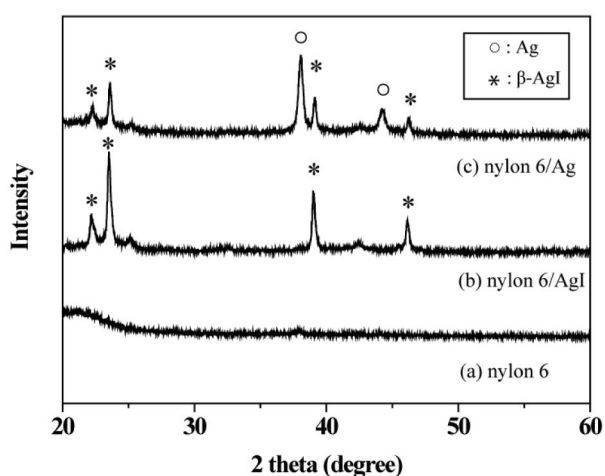


Fig. 5 XRD patterns of (a) pristine nylon 6, (b) nylon 6 /AgI, and (c) nylon 6/Ag nanofibers.

This trend is further clarified in Figure 7, which shows the dependence of the Ag-plated layer thickness on the amount of nanofibers. The thickness was determined from the change of the fiber diameters in SEM images. The thickness of the plating clearly decreased with increasing nanofiber amount. This is caused by a decrease in the amount of attached Ag on the fiber, because the quantity of Ag^+ ions in the solution for the silver mirror reaction is constant and thus the share of Ag^+ ions for each fiber decreases with increasing nanofiber amount. This result indicates that the morphology of the plating can be varied by changing the ratio of the amount of nanofibers and Ag^+ ions.

The Ag-plated nylon 6/Ag nanofiber mat samples showed low surface resistance on the order of $10^{-1} \sim 10^0 \text{ ohm cm}^{-2}$. As shown in Figure 8, the surface resistance depended on the amount of nylon 6 nanofibers. The surface resistance increased from $1.12 \times 10^{-1} \text{ ohm cm}^{-2}$ to $7.82 \times 10^0 \text{ ohm cm}^{-2}$ by increasing the amount of nanofibers from 0.02 mg cm^{-2} to 1.08 mg cm^{-2} . The

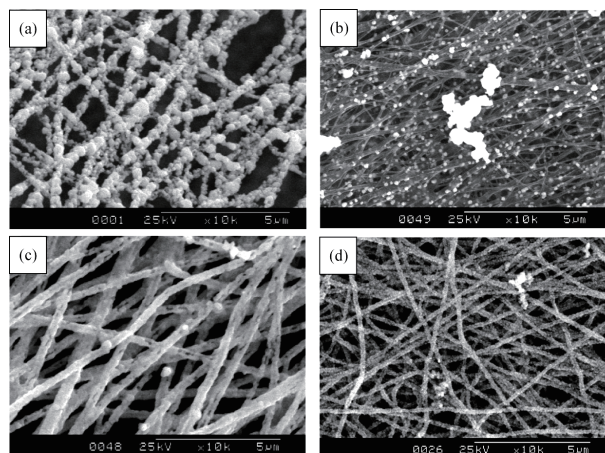


Fig. 6 SEM images of electroless Ag-plated nylon 6 nanofibers prepared from (a) pristine nylon 6 (electrospinning time : 1 min, nylon 6 nanofiber amount : 0.02 mg cm^{-2}), (b) pristine nylon 6 (electrospinning time : 30 min, nylon 6 nanofiber amount : 0.85 mg cm^{-2}), (c) nylon 6/Ag (electrospinning time : 1 min, nylon 6 nanofiber amount : 0.02 mg cm^{-2}) and (d) nylon 6/Ag (electrospinning time : 30 min, nylon 6 nanofiber amount : 0.85 mg cm^{-2}) nanofibers.

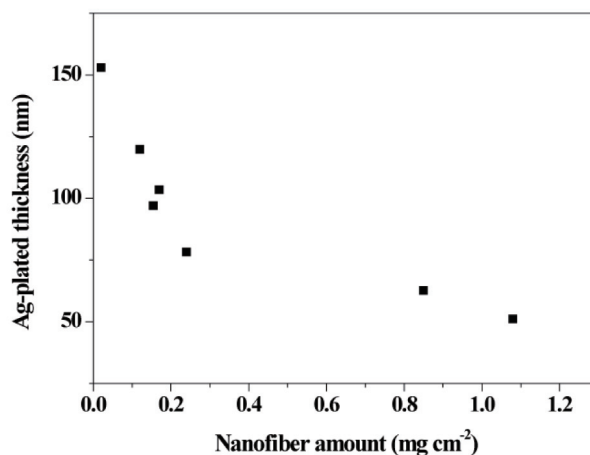


Fig. 7 Diameter of plated nylon 6 nanofibers as a function of nanofibers amount.

reason for this may be related to the state of the Ag in the plated layer. That is, the Ag layer in a sample with a small nanofiber amount is smooth as shown in Figure 6 (c), implying that a dense Ag layer will be formed by higher extent of contact between individual Ag particles. In actuality, the appearance of the bulk sample is white and smooth. In contrast, a sample with a larger nanofiber amount consists of distinct Ag nanoparticles with a rough plated layer, and is muddy gray in color. Thus, just the contact state of each particle is not sufficient to enhance the conductivity of the Ag plating.

Figure 9 shows SEM images of electroless-plated nylon 6 nanofibers after sonication for 30 min without

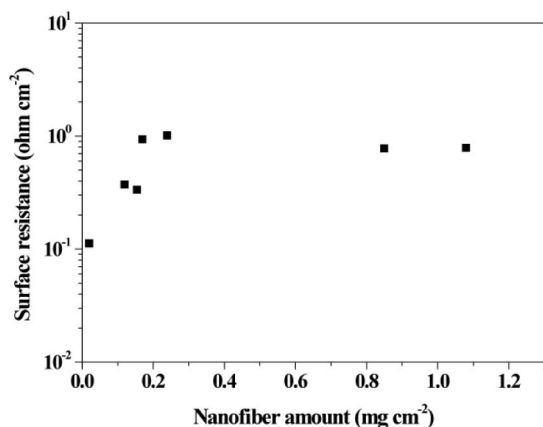


Fig. 8 Surface resistance of Ag-plated nylon 6 nanofibers as a function of the nanofibers amount.

pretreatment (a) and with pretreatment (b). The samples shown in these micrographs were prepared from nylon 6 nanofibers with a nanofiber amount of 0.85 mg cm^{-2} . Figure 9 (a) indicates that Ag particles were removed from the nylon 6 nanofibers due to low adhesion. On the other hand, as shown in Figure 9 (b), the metal-plated layer on the nanofibers subjected to pretreatment was retained even after sonication. The conductivity of the samples was also retained after the sonication. This indicates good interfacial adhesion between the nanofibers surface and metal plating layer, and the effectiveness of the iodine utilization technique for electroless Ag plating on the nanofibers.

4. Conclusions

Ag-plated nylon 6 nanofibers were prepared from nylon 6/AgI composite nanofibers by electroless plating without the need for an etching process or other complicated procedures. The Ag plating layer formed smoothly on each fiber, and remained intact due to the presence of the anchoring effect of the autocatalyst silver particles formed from AgI that were loaded previously in the composite. The morphology of the plating could be

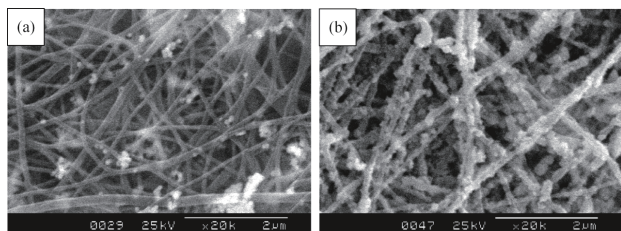


Fig. 9 SEM images of electroless Ag-plated nylon 6 nanofibers after sonication for 30 min (nanofiber amount is 0.85 mg cm^{-2}); (a) without pretreatment and (b) with pretreatment.

controlled by adjusting the ratio of the amount of nanofiber and Ag^+ ions. The plated nanofibers possess high surface conductivity and a high aspect ratio (in principle, infinity). Various potential applications of these materials are anticipated, including as conductive thin materials and as anisotropic fillers for conductive composites.

Acknowledgement

This paper is dedicated to the first principal, Chotaro Harizuka, on the occasion of 100th anniversary of Faculty of Textile Science and Technology, Shinshu University.

References

1. Q. Lu, F. Gao and S. Komarneni, *Langmuir*, **21**, 6005 (2005).
2. N. R. Jana, *small*, **1**, 875 (2005).
3. Y. Zhou, S. H. Yu, C. Y. Wang, X. G. Li, Y. R. Zhu and Z. Y. Chen, *Adv. Mater.*, **11**, 850 (1999).
4. Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem. Int. Ed.*, **48**, 60 (2009).
5. Z. L. Wang, *J. Phys. Chem. B*, **104**, 1153 (2000).
6. Y. Sun and Y. Xia, *Science*, **298**, 2176 (2002).
7. M. Tsuji, N. Miyamae, M. Hashimoto, M. Nishio, S. Hikino, N. Ishigami and I. Tanaka, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **302**, 587 (2007).
8. M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa and T. Tsuji, *Chem. Eur. J.*, **11**, 440 (2005).
9. C. Chen, L. Wang, H. Yu, G. Jiang, Q. Yang, J. Zhou, W. Xiang and J. Zhang, *Mater. Chem. Phys.*, **107**, 1317 (2008).
10. C. J. Johnson, E. Dujardin, S. A. Davis, C. J. Murphy and S. Mann, *J. Mater. Chem.*, **12**, 1765 (2002).
11. B. Wiley, Y. Sun, B. Mayers and Y. Xia, *Chem. Eur. J.*, **11**, 454 (2005).
12. P. Jiang, S. Y. Li, S. S. Xie, Y. Gao and Li Song, *Chem. Eur. J.*, **10**, 4817 (2004).
13. S. H. Im, Y. T. Lee, B. Wiley and Y. Xia, *Angew. Chem. Int. Ed.*, **44**, 2154 (2005).
14. Y. Sun, Y. Xia, *Adv. Mater.*, **14**, 833 (2002).
15. X. Sun and Y. Li, *Adv. Mater.*, **17**, 2626 (2005).
16. X. Niu, S. Liu, R. X. Wang, B. Zhang, J. Chen and L. Yang, *Mater. Lett.*, **61**, 5098 (2007).
17. S. Lee, Y. Jeong, H.J. Oh, J.H. Lee, O. Y. Lee and C. S. Chi, *Met. Mater. Int.*, **15**, 631 (2009).

18. J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong and C. M. Whitehouse, *Science*, **246**, 64 (1989).
19. H. Fong, I. Chun and D.H. Reneker, *Polymer*, **40**, 4585 (1999).
20. J.M. Deitzel, J. Kleinmeyer, D. Harris and N.C. Beck Tan, *Polymer*, **42**, 261 (2001).
21. S.V. Fridrikh, J. H. Yu, M. P. Brenner and G. C. Rutledge, *Phys. Rev. Lett.*, **90**, 144502-1 (2003).
22. D. Li, Y. Xia, *Adv. Mater.*, **16**, 1151 (2004).
23. K. D. Bruyn, M. V. Stappen, H. D. Deurwaerder, L. Rouxhet and J. P. Celisand, *Surf. Coat. Technol.*, **163-164**, 710 (2003).
24. A. Shojaei, R. Fathi, N. Sheikh, *Surf. Coat. Technol.*, **201**, 7519 (2007).
25. M. Charbonnier, M. Romand, *Int. J. Adhes. Adhes.*, **23**, 277 (2003).
26. A. E. Alia and A. A. Aal, *Polym. Adv. Technol.*, **20**, 729 (2009).
27. X. Hu, Q. He, H. Lu and H. Chen, *J. Electroanal. Chem.*, **638**, 21 (2010).
28. D. Tao, Q. Wei, Y. Cai, Q. Xu and L. Sun, *J. Coat. Technol. Res.*, **5**, 399 (2008).
29. M. Okubo, M. Tahara, T. Kuroki, T. Hibimo and N. Saeki, *J. Photopolym. Sci. Technol.*, **21**, 219 (2008).
30. Y. Fujimori, Y. Gotoh, N. Tamaki, Y. Ohkoshi and M. Nagura, *J. Mater. Chem.*, **15**, 4816 (2005).
31. Y. Fujimori, Y. Gotoh, A. Kawaguchi, Y. Ohkoshi and M. Nagura, *J. Appl. Polym. Sci.*, **108**, 2814 (2008).
32. S. Hayashi, T. Hirai, S. Shimomichi and N. Hojo, *J. Polym. Sci. Polym. Lett. Ed.*, **20**, 69 (1982).
33. Y-S. Choi and Miyasaka, *J. Appl. Polym. Sci.*, **51**, 613 (1994).
34. A. Kawaguchi, *Polymer*, **35**, 2665 (1994).