行政院國家科學委員會專題研究計畫 成果報告

使用多孔模板製作之高分子奈米材料及其應用 研究成果報告(精簡版)

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Introduction

The template method has been widely used to prepare on-dimensional nanomaterials.^[1-3] The template is only used as a scaffold, and the shapes of the nanomaterials is controlled by the geometry of the template. Various precursor materials, such as polymers, can be introduced into the nanopores of the templates by wetting or deposition on the walls of the template.^[11] The surface energy of the pore wall is usually high and the precursor materials can easily wet the surface of the walls to reduce the surface energy. The template method also enables the fabrication of nanomaterials made of multiple components.^[3] The nanomaterials made by template wetting can be released by selectively removing the template. These nanomaterials have been demonstrated in various applications, such as photovoltaics,^[4] photodetectors,^[5] and biosensors.^[6] Different materials have been applied as templates for the generation of nanomaterials, but ion-track-etched membranes and anodic aluminum oxide (AAO) templates are the most commonly used templates.^[7] Ion-tracked membranes are usually fabricated by polycarbonate or polyester films and are commercially available.^[8] But the porosity of the ion-tracked membranes is very low and the nanochannels are usually randomly distributed.^[1]

The AAO templates that contain cylindrical channels are produced electrochemically from aluminum, and the sizes of the pores can be controlled by the anodization conditions.^[9, 10] These templates have been widely used to prepare one-dimensional nanomaterials such as metallic and semiconductor nanowires,^[11] carbon nanotubes,^[12, 13] and polymer nanotubes.^[14] The major advantage of using the AAO templates is their well-controlled pore sizes. Additionly, the AAO templates can be easily removed after the preparation of the nanomaterials by using a selective etching solution such as a weak base or a weak acid. Using porous templates, freely standing polymer nanorods have been demonstrated to form on top of polymer films or even on top of polymer microspheres.^[15]

In this report, we study the fabrication of hierarchical polymer nanostructures by bring the electrospun polymer fibers into contact with the nanopores of the AAO templates followed by the wetting process. Although there have been many methods to generate hierarchical structures, it remains a challenge to precisely control the structures in both the micrometer and nanometer range. Such control helps us to know the structure-property relationship of hierarchical materials, enabling the rational design of novel materials for advanced devices and applications. Thus, it is necessary to develop fabrication methods in which the structures can be independently and precisely controlled in different length scales.

In this report, we prepare hierarchical polymer structures by combining the electrospinning technique and wetting of porous templates. The first length scale of ordering of these hierarchical structures is fabricated by the electrospinning process. Electrospinning is an efficient method to prepare polymer fibers from polymer solutions, with a diameter range from nanometers to a few micrometers.^[16] In the electrospinning method, a high potential difference is applied to create an electrically charged jet of polymer solution or melt, which dries or solidifies to produce polymer fibers. Electrospun polymer fibers have various applications such as sensors,^[17] filtration,^[18] drug delivery,^[19] tissue engineering,^[20, 21] catalysis,^[22] and wound dressing.^[23] In this work, the second length scale of ordering on the electrospun fibers is generated by wetting porous anodic aluminum oxide (AAO) templates.

In the past, electrospinning has been used to prepare hierarchical structures.^[24-27] For example, Hou and Reneker showed the preparation of carbon nanotubes on electrospun carbon fibers.^[25] The carbon fibers were generated by the carbonization of electrospun polyacrylonitrile fibers. Then the carbon nanotubes

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were formed by the catalysis of Fe nanoparticles embedded in the carbon fibers by exposing the fibers to hexane vapor.^[25] Ostermann *et al.* also synthesized single-crystal V₂O₅ nanorods grown on electrospun TiO₂ nanofibers by calcining composite nanofibers consisting of V₂O₅, TiO₂, and poly(vinylpyrrolidone).^[26] Even though hierarchical structures were generated by various methods, most methods to fabricate hierarchical structures using electrospun fibers still fail to generate the second length scale of ordering in a controlled way. Comparing to those materials, here we prepare hierarchical polymer structures, in which the sizes of the nanorods and the fibers can be well controlled.

Experimental

Polystyrene (PS) (Mn: 22900; Mw: 166500; PDI: 7.27) and poly(methyl methacrylate) (PMMA) (M_n: 26600; M_w: 49300; PDI: 1.85) and were purchased from Sigma Aldrich. Benzyltriethylammonium chloride (BTEAC) was purchased from Alfa Aesar. N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from TEDIA. The commercial AAO membranes (pore diameter ca. 100–400 nm, thickness $\sim 60 \mu m$) were purchased from Whatman Ltd. The synthesized AAO templates were prepared according to the two-step anodization method developed by Masuda and co-workers.^[9, 28] First, a high-purity aluminum sheet (Sigma-Aldrich, 0.5 mm thick, 99.99 %) was degreased in acetone and rinsed in an ethanol solution. Later, the aluminum sheet was electropolished in a perchloric acid/ethanol mixture at 4 °C. The aluminum sheet was anodized at 40 V in 0.3 M oxalic acid at 17 °C for 12 hr. Followed by the resultant aluminum oxide film was chemically etched in a mixture of phosphochromic acid, a second anodization under the same conditions as for the first anodization was performed for different periods of time, depending on the required length of pores. The length of the pores is ~ 4 µm and the second anodization is carried out for 2 hr.

For a typical electrospinning experiment, 35 wt% PMMA (Mw: 49 kg/mol) solution in DMF was added into a syringe connected to a nozzle (inner diameter: 0.41 mm). The polymer solution was fed at a constant rate (1 mL/hr) through a syringe pump (brand: KD Scientific). The nozzle was connected to a high-voltage power supply (brand: SIMCO). The typical applied voltage range was 10-30 kV. The working distance range between the nozzle and the grounded collector was 10-20 cm. For most experiments, the organic salt BTEAC was added to control the smoothness and the size of the electrospun fibers. After the electrospun fibers were brought into contact with the AAO templates, the samples were heated at 135 or 150 °C for different times. The AAO templates were removed with 5 wt% NaOH_(aq) for 12 hr, and the samples were repeatedly washed with water, followed by dying in vacuum. The microscopic features of the samples were studied using a JEOL JSM-7401F scanning electron microscope (SEM) at an accelerating voltage of 10 kV. The samples were coated with 4 nm platinum before performing SEM measurements.

Results and Discussion

A schematic plot of our approach to prepare the hierarchical structure is presented in Figure 1. Polymer fibers are generated by electrospinning. First, the polymers are dissolved in a suitable solvent such as DMF and are ejected from a capillary nozzle. Under the electric field, the polymer solution is drawn into a polymer jet at the end of the nozzle followed by a whipping process due to electrostatic repulsion.^[29] The nanometer- or micrometer-sized polymer fibers are collected on the grounded collector after solvent evaporation. The fibers are then collected and are placed on top of an AAO membrane. Commercial AAO

templates or synthesized AAO templates are both used in the study. The nanochannels of the commercial AAO template are ~100-400 nm and are more irregular in shape. The home-made AAO templates prepared by the second anodization method have more regular and well-packed nanopores.^[10] The polymer fibers which are brought into contact with the AAO templates can wet the walls of the nanopores after thermal annealing. The polymer is going into the nanopores by capillary forces, forming nanorods whose length is governed by the time allowed for the polymer to be drawn into the nanopores. The hierarchical structures with nanorods on top of the polymer fibers are obtained after removing the AAO templates selectively using an NaOH solution.



Figure 1. Schematic plot of the approach to make hierarchical polymer structures based on electrospinning and wetting of porous templates.



Figure 2. The SEM images of electrospun PMMA fibers (M_w: 49k) under various electrospinning conditions. (a-c) Voltage: 15 kV; flow rate: 1mL/hr; working distance: 10 cm; different polymer concentrations in DMF: (a) 25 wt%; (b) 30 wt%; (c) 35 wt%. (d-f) Polymer concentration: 35 wt% in DMF; voltage: 10 kV; working distance: 10 cm; different flow rate: (d) 0.1 mL/hr; (e) 0.5 mL/hr; (f) 2.0 mL/hr.

The electrospinning method is a useful technique to make polymer fibers. If suitable solvents are available, almost all kinds of polymers can be made as fibers by the electrospinning method. The size and morphology of the electrospun polymer fibers are controlled by different experimental factors such as polymer molecular weight, solution concentration, solvent, flow rate, voltage, nozzle size, or working distance.^[30] Figure 2 displays the SEM images of electrospun fibers under different conditions. The concentration of the polymer solution is one of the most common ways to control the size and morphology of the electrospun fibers. When the polymer concentration is lower than a critical value, the viscosity of the solution is not high enough to maintain a stable polymer jet. The polymer liquid jet might break into droplets caused by the Rayleigh instability, and polymer fibers are unable to be formed.^[31] For low solution viscosity, beads-on-string structures are also observed caused by the entanglement of polymer chains and the contraction of the jet,^[32] as shown in Figure 2a. When the viscosity of the solution is larger, both the size of the beads and the distance between beads increase.^[32] If the polymer concentration is higher than a critical value, polymer fibers without beaded defects are formed. In general, the diameter of the electrospun polymer fiber increases with the concentration of the polymer solution. Figure 2a-c show the polymer fibers generated from different concentrations while keeping all other experimental factors constant. Poly(methyl methacrylate) (PMMA) (M_w: 49k) was dissolved in DMF at different concentrations (Fig. 2a: 25 wt%; Fig. 2b: 30 wt%; Fig. 2c: 35 wt%) with the flow rate of 1 mL/hr and working distance of 10 cm under the voltage of 15 kV. The diameters of the electrospun PMMA fibers increase from ~ 1 μ m for 25 wt% to ~ 4 μ m for 35 wt%. It has to be noted that the polymer solution might be difficult to be ejected from the nozzle when the concentration is too high because of the increased viscosity. In addition to the polymer concentration, the solution viscosity is also determined by the molecular weight and molecular weight distribution of the polymers.^[33] It has been reported that the onset of uniform fiber formation in relative broader molecular weight distribution polymers occurs at a higher concentration comparing with that in the narrow molecular weight distribution polymers. These results are because a relatively broad molecular distribution polymer has a wide distribution of the hydrodynamic radii and relaxation times of the chains in solution.^[33]

The second method to control the diameters of the electrospun fibers is by varying the flow rate. The amount of the produced polymer fibers is proportional to the flow rate, and the diameter of the polymer fibers increases as the flow rate increases. Fridrikh *et al.* showed that varying the flow rate yields a $10^{2/3}$ (~6) fold variation in the fiber diameter when the flow rate is over a certain range.^[34] But if the flow rate is too fast, beaded fibers are formed. The electrospun fibers might also be partially dissolved by the residual solvent if the flow rate is too fast, and the morphology of the fiber can be affected. Figure 2d-f show the SEM images of electrospun fibers (49 k PMMA; 35 wt% in DMF; voltage: 10 kV; working distance: 15 cm) at different flow rates ((d) 0.1 mL/hr; (e) 0.5 mL/hr; (f) 2.0 mL/hr). The average diameters of the fibers are larger when the flow rates are higher, and the relationship between the fiber diameters and the flow rate is plotted in the Supporting Information. The diameters and morphology of the electrospun fibers can also be controlled by other experimental conditions such as the applied voltage. When the applied voltage is higher, the electric field and the electrostatic force are stronger, resulting in the smaller diameters of the electrospun fibers.^[35]

The anodic aluminum oxide (AAO) membranes are used to control the second length scale of ordering on the electrospun polymer fibers. AAO templates are made by anodization of aluminum plates, and the pore density can be as high as 10^{11} pores/cm².^[36] In this work, we used two different kinds of AAO membranes as the templates, including the commercial AAO templates and the synthesized AAO templates.

SEM images of the commercial and synthesized AAO templates are shown in Figure 3a and 3b, respectively. Figure 3a shows the SEM image of a commercial AAO template whose pore diameters are \sim 100-400 nm, and the pores are packed irregularly compared with those of the synthesized AAO templates. The pore sizes of the synthesized AAO templates shown in Figure 3b are more regular and are controlled by the anodization condition. Pore sizes ranging from 5 to 250 nm can be prepared by changing the type and the concentration of the electrolyte solution, the temperature, and the voltage of the anodization process.^[10] The AAO membrane shown in Figure 3b was synthesized in 0.3 M oxalic acid at 40 V, and the pore size is \sim 30-40 nm with the pore-to-pore distance \sim 100 nm. The pore sizes can be increased by either increasing the voltage or by a pore-widening process using phosphoric acid (5 wt%) at 40 °C. The AAO templates can be easily removed by a selective etching solution. In this study, an NaOH solution was used to selectively remove the AAO templates without dissolving the polymer fibers.





Following the electrospun polymer fibers are prepared, the polymer fibers are brought into contact with the AAO template by two different ways. The first way is to directly place the fibers on top of the AAO template. The second way is to collect the fibers on a substrate, and then place the AAO template on top of the fibers. Both ways are feasible, and it is critical to ensure good contact between the polymer fibers and the AAO template for the wetting process to occur. The fibers can also be redispered into nonsolvents such as ethylene glycol for good dispersion before being placed on top of the AAO template. The wetting process is critical in making the hierarchical structures, and there are two popular methods for wetting porous templates with polymers. The first method involves the wetting of porous templates using polymer solutions, and polymer nanotubes can be formed after the drying of solvents.^[37] In the first method, annealing is not required because the solvent already provides enough mobility for the polymers to go into the nanopores. The second method to wet the nanopores is by heating a polymer film above the glass transition temperature or even the melting temperature for the wetting to occur.^[14] In this work, we use the second method of wetting by thermally annealing the sample above the glass transition temperature of the polymers (T_g of PMMA: 105 °C) for different periods of time.

The rate of the polymer drawn into the nanopres of the templates can be estimated by the following equation:^[38]

$$dz/dt = R\gamma \cos\theta/(4\eta z) \tag{1}$$

where *t* is the time, *z* is the rod height, γ is the surface tension, θ is the contact angle, η is the viscosity, and *R* is the hydraulic radius (the ratio between the volume of the polymer in the pore and the area of solid/liquid interface). Therefore, the length of the polymer rods in the nanopores can be increased by using longer annealing time or lower polymer viscosity. The wetting behavior of polymer melts in cylindrical nanochannels was also studied by Zhang *et al.* that the polymer can be formed as nanorods or nanotubes depending on whether the polymer is in the partial wetting state or in the complete wetting state.^[39] The wetting transition from the partial wetting state to the complete wetting state depends on the molecular weight and molecular weight distribution of the polymers. For higher molecular weight polymers, the temperature of wetting transition is also higher. The difference in the wetting rate between partial and complete wetting can be used to fractionate polymers with different molecular weights.^[39]



Figure 4. Four SEM images of electrospun PMMA fibers with nanorods. (a-b) Electrospun PMMA fibers wetting into the nanopores of commercial AAO templates. The PMMA fibers were annealed at 150 $^{\circ}$ C for 30 min. The lengths of the nanorods are ~ 100 nm. (c-d). Electrospun PMMA fibers wetting into the nanopores of synthesized AAO templates.

We note that there are only limited surfaces of the polymer fibers that are in contact with the nanopores of the AAO template before thermal annealing because of the cylindrical shape of the fibers. When the sample is heated above the glass transition temperature of the polymer, only polymers in these regions are initially drawn into the nanopores. At longer annealing time, larger surfaces of the polymer fibers are in contact with the template, and more polymers are drawn into the nanopores. Thus, there is a distribution in the length of the nanorods on the polymer fibers. The idea case is that the height of the

nanorods near the center of the fiber should be higher than that of the nanorods near the edge of the fiber. Figure 4 shows the results of the SEM images of the electrospun PMMA fibers with nanorods. Figure 4a and 4b are from the fibers wetting with commercial AAO templates. The sizes of the electrospun polymer fibers are \sim 3-4 µm, and the pore sizes of the commercial AAO are \sim 100-400 nm. Some electrospun fibers are overlapping and melt together before or during the wetting process, as shown in Figure 4b. Figure 4c and 4d show the electrospun fibers wetting with the synthesized AAO templates. The diameters of the electrospun polymer fibers are \sim 600-800 nm, and the pore sizes of the synthesized AAO templates are \sim 30-40 nm. In Figure 4c, the meniscus shapes on the top of the polymer nanorods can be seen, which are the signatures of the capillary rising of the polymer melts into the nanopores. Fibers are also observed to overlap and melt together before or during the wetting process, as show in Figure 4d. The fibers with nanorods shown in Figure 4c and 4d are from samples with short annealing time (135 °C for 10 min).



Figure 5. Four SEM images of electrospun PMMA fibers with collapsed nanorods. (a-b) Electrospun PMMA fibers (fiber diameter $\sim 1 \ \mu m$) wetting into the nanopores of synthesized AAO templates (pore diameters \sim 30-40 nm) at different magnifications. (c-d). Electrospun PMMA fibers (fiber diameter $\sim 4 \ \mu m$) wetting into the nanopores of synthesized AAO templates (pore diameters \sim 30-40 nm) at different magnifications.

The nanorods collapsed with longer annealing time, mainly caused by the high aspect ratio of nanorods and the capillary force driven by the removal of the etching solution, as shown in Figure 5. To further understand the thermal annealing effect on the electrospun polymer fibers, we also annealed the fibers at 150 °C for 10 min without the presence of the AAO templates. The roughness of the fiber surfaces is decreased after the annealing process, as shown in Figure 6. The reduction of surface roughness is attributed to the decrease of surface energy at the polymer-air interface. Another possible outcome of the

polymer fibers after thermal annealing is that the fibers may undergo surface undulation and break into spheres, the so-called Rayleigh-instability.^[40] But this kind of instability was not observed in this work, which might be explained by the high viscosity and the strong polymer chain-chain interaction.



Figure 6. Two SEM images of electrospun PMMA fibers before and after thermal annealing. The electrospun fibers were prepared from PMMA (M_w : 49k) and were annealed at 150 °C for 10 min.

To show the universality of this work, we also study the fabrication of hierarchical structures by using polystyrene (PS), another commonly used polymer. As shown in Figure 7a, electrospun PS fibers are first obtained by electrospinning 20 wt% PS (M_w: 166k) in DMF under a voltage of 15 kV at a flow rate of 1mL/hr with a working distance of 15 cm. The diameters of the as-spun fibers are ~ 2-3 μ m. After the PS fibers are brought into contact with a synthesized AAO template (pore diameters ~ 50 nm) followed by an annealing process at 135 °C for 15 min, hierarchical PS structures are obtained (see Figure 7b).



Figure 7. (a) A SEM image of electrospun PS fibers. PS (M_w : 166k) fibers were fabricated by electrospinning 20 wt% PS in DMF under a voltage of 15 kV at a flow rate of 1mL/hr with a working distance of 15 cm. The fiber diameters are ~ 2-3 µm. (b) A SEM image of an electrospun PS fiber with nanorods. The PS fiber was wetted into the synthesized AAO templates (pore diameters ~ 50 nm) at 135 °C for 15 min.

Conclusions and Suggestions

In this report, we demonstrate a simple approach to fabricate hierarchical structures by placing electrospun polymer fibers in contact with the nanopores of AAO templates. The advantage of this technique is that the two size scales of ordering can be independently controlled. The first length scale is controlled by the diameters of the electrospun fibers, which can be controlled by changing the electrospinning conditions

such as the polymer concentration or the flow rate. The second length scale is varied by the pore sizes of the AAO templates, which can be changed by changing the anodization conditions. For the suggestions for the future work, we would like to apply this concept to other functional materials such as conjugated polymers and to study their electronic, mechanical, and surface properties for potential applications.^[41]

References

- [1] C. R. Martin, Science 1994, 266, 1961.
- [2] M. Steinhart, J. H. Wendorff, A. Greiner, R. B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, U. Gosele, *Science* 2002, 296, 1997.
- [3] M. Steinhart, R. B. Wehrspohn, U. Gosele, J. H. Wendorff, Angew. Chem.-Int. Edit. 2004, 43, 1334.
- [4] J. S. Kim, Y. Park, D. Y. Lee, J. H. Lee, J. H. Park, J. K. Kim, K. Cho, Adv. Funct. Mater. 2010, 20, 540.
- [5] G. A. O'Brien, A. J. Quinn, D. A. Tanner, G. Redmond, Adv. Mater. 2006, 18, 2379.
- [6] P. Kohli, M. Wirtz, C. R. Martin, *Electroanalysis* 2004, 16, 9.
- [7] A. Huczko, Appl. Phys. A-Mater. Sci. Process. 2000, 70, 365.
- [8] P. Apel, Radiat. Meas. 2001, 34, 559.
- [9] H. Masuda, K. Fukuda, Science 1995, 268, 1466.
- [10] A. P. Li, F. Muller, A. Birner, K. Nielsch, U. Gosele, J. Appl. Phys. 1998, 84, 6023.
- [11] J. M. Moon, A. Wei, J. Phys. Chem. B 2005, 109, 23336.
- [12] S. H. Jeong, H. Y. Hwang, K. H. Lee, Y. Jeong, Appl. Phys. Lett. 2001, 78, 2052.
- [13] J. T. Chen, K. Shin, J. M. Leiston-Belanger, M. F. Zhang, T. P. Russell, Adv. Funct. Mater. 2006, 16, 1476.
- [14] M. Steinhart, "Supramolecular Organization of Polymeric Materials in Nanoporous Hard Templates", in Self-Assembled Nanomaterials Ii: Nanotubes, Springer-Verlag Berlin, Berlin, 2008, p. 123.
- [15] J. T. Chen, D. Chen, T. P. Russell, Langmuir 2009, 25, 4331.
- [16] Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, Compos. Sci. Technol. 2003, 63, 2223.
- [17] B. Ding, M. R. Wang, J. Y. Yu, G. Sun, Sensors 2009, 9, 1609.
- [18] D. R. Nisbet, A. E. Rodda, D. I. Finkelstein, M. K. Horne, J. S. Forsythe, W. Shen, Colloid Surf. B-Biointerfaces 2009, 71, CP1.
- [19] W. J. Li, R. L. Mauck, R. S. Tuan, J. Biomed. Nanotechnol. 2005, 1, 259.
- [20] Q. P. Pham, U. Sharma, A. G. Mikos, *Tissue Eng.* 2006, 12, 1197.
- [21] L. S. Nair, S. Bhattacharyya, C. T. Laurencin, Expert Opin. Biol. Ther. 2004, 4, 659.
- [22] S. Agarwal, J. H. Wendorff, A. Greiner, Macromol. Rapid Commun. 2010, 31, 1317.
- [23] P. Zahedi, I. Rezaeian, S. O. Ranaei-Siadat, S. H. Jafari, P. Supaphol, Polym. Adv. Technol. 2010, 21, 77.
- [24] J. Y. Yang, S. H. Zhan, N. Wang, X. M. Wang, Y. Li, W. Y. Ma, H. B. Yu, J. Dispersion Sci. Technol. 2010, 31, 760.
- [25] H. Q. Hou, D. H. Reneker, Adv. Mater. 2004, 16, 69.
- [26] R. Ostermann, D. Li, Y. D. Yin, J. T. McCann, Y. N. Xia, Nano Lett. 2006, 6, 1297.
- [27] Y. Q. Dai, X. F. Lu, M. McKiernan, E. P. Lee, Y. M. Sun, Y. N. Xia, J. Mater. Chem. 2010, 20, 3157.

- [28] H. Masuda, M. Satoh, Jpn. J. Appl. Phys. Part 2 Lett. 1996, 35, L126.
- [29] Y. M. Shin, M. M. Hohman, M. P. Brenner, G. C. Rutledge, Polymer 2001, 42, 9955.
- [30] A. Greiner, J. H. Wendorff, Angew. Chem.-Int. Edit. 2007, 46, 5670.
- [31] M. M. Hohman, M. Shin, G. Rutledge, M. P. Brenner, Phys. Fluids 2001, 13, 2201.
- [32] H. Fong, I. Chun, D. H. Reneker, Polymer 1999, 40, 4585.
- [33] P. Gupta, C. Elkins, T. E. Long, G. L. Wilkes, Polymer 2005, 46, 4799.
- [34] S. V. Fridrikh, J. H. Yu, M. P. Brenner, G. C. Rutledge, Phys. Rev. Lett. 2003, 90, 4.
- [35] C. Wang, C. H. Hsu, J. H. Lin, *Macromolecules* 2006, 39, 7662.
- [36] D. Almawlawi, N. Coombs, M. Moskovits, J. Appl. Phys. 1991, 70, 4421.
- [37] V. M. Cepak, C. R. Martin, Chem. Mat. 1999, 11, 1363.
- [38] E. Kim, Y. N. Xia, G. M. Whitesides, Nature 1995, 376, 581.
- [39] M. F. Zhang, P. Dobriyal, J. T. Chen, T. P. Russell, J. Olmo, A. Merry, Nano Lett. 2006, 6, 1075.
- [40] M. E. Toimil-Molares, A. G. Balogh, T. W. Cornelius, R. Neumann, C. Trautmann, Appl. Phys. Lett. 2004, 85, 5337.
- [41] N. Tian, Q. H. Xu, Adv. Mater. 2007, 19, 1988.

國科會補助專題研究計畫項下出席國際學術會議心得報告

日期:<u>100</u>年<u>10</u>月<u>28</u>日

計畫編號	NSC 99-2218-E-009-028-						
計畫名稱	使用多孔模板製作之高分子奈米材料及其應用						
出國人員 姓名	陳俊太 服務機構 交通大學應用化學系助理教授						
會議時間	100年5月8日至 100年5月11日	會議地點	北京				
人举力的	(中文)第二屆亞洲高分子學會聯合會高分子大會						
曾诫名柟	(英文)The 2nd FAPS Polymer Congress (FAPS-PC2011)						
	(中文)利用模板潤濕法製備之高分子奈米材料						
發表論文 題目	(英文)Fabrication of Polymer Nanomaterials via Template						
	Wetting						

一、參加會議經過

這次參加的會議為第二屆亞洲高分子學會聯合會高分子大會,地點在北京的國際會議中心。這個會議的地點在著名的2008年奧運場地附近,因此從旅館至會場的路上就可以看到著名的水立方與鳥巢體體育館。

5/8 (日)

這一天到達會議的現場辦理註冊事宜,拿到會議相關的摘要報告等資料。之後 參考會議的手冊研究了一些跟自己研究相關領域學者的報告時間以便之後聽取報 告。晚上參加大會所舉辦的 Welcome Reception。

5/9 (-)

這是大會正式的第一天,一開始有 Chi Wu 教授等人的 Plenary Lecture, Chi Wu

教授的演講是會議幾天當中聽到最好的報告之一。他的題目是: How a Star Chain (Nanooctopus) Crawls Through a Nanopores? 一開始從理論開始講起,最後再以 實驗的結果來印證其理論,最後提出了他之後的可能工作。這個工作雖然是高分子 物理方面比較基礎的工作,但是對於生物高分子等的應用會很有幫助。印象非常深 刻的是有一張投影片, Chi Wu 教授特地放了非常多的公式,告訴大家高分子科學不 只是漂亮的圖片而已,也是有很深的科學在裡面,這一點讓人印象非常深刻。

在其他學術專題演講方面,主要參加高分子以及奈米材料領域學者的報告。其 中特別去聽了南京大學 Yong Wang 教授的演講, Young Wang 教授的研究領域跟我作 的研究題目比較接近,之前常在期刊上看到他的研究成果。這一次藉此機會跟他討 論了一些可能的研究方向。

5/10 (ニ)

早上聽取學術專題報告,並在早上10:50 報告關於 "Fabrication of Polymer Nanomaterials via Template Wetting "的題目, 並回答相關問題。其中來自 University of Akron 的 Ali Dhinojwala 教授根據我的報告內容問了一個非常深入 的問題,是有關於高分子薄膜之間的吸引力對高分子不穩定狀態的影響。這是一個 非常好的問題,我除了就我所知道的回答他外,在演講結束後也跟他請教了一些關 於高分子介面方面的問題。

5/11 (三)

會議的最後一天,只有在早上的時間有演講報告,主要是聽了比較多高分子在 能源方面的應用,例如導電高分子在太陽能電池、有機發光二極體、以及紅外線感 測上的應用。

2

二、與會心得

這次參加這個會議遇到了相當多從事高分子領域的學者。與這些學者交流中學 到了許多高分子領域最新的進展,覺得很有收穫。我這次參加會議所報告的內容是 關於奈米高分子材料的製備與應用,探討利用模板法來製備高分子奈米材料,在參 加完這次會議後也獲得了一些不錯的想法,希望可以應用在相關的研究工作上。

另外在聽取的報告部份,主要發現在高分子奈米材料的方面有相當多的進展,例 如共聚高分子與無機奈米材料的互相混摻可以幫助無機奈米材料的有效排列,是一 個很有趣的領域。另外在導電高分子方面,有較多的研究團隊集中在研發導電高分 子於太陽能電池的應用上面,現在的新合成的導電高分子,已可達到9%以上的太陽 能量子效率,對未來有機太陽能電池的商業化應用應該是很有前景。這次與會收穫 非常豐富,與世界各國的高分子領域專家探討研究是很令人興奮的事情,希望之後 能有機會多參加類似的會議。

三、攜回資料名稱及內容

The 2nd FAPS Polymer Congress (FAPS-PC2011) Program Book

Fabrication of Polymer Nanomaterials via Template Wetting

Jiun-Tai Chen

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050,

Recently, one-dimensional (1-D) polymer nanomaterials have attracted great interests because of their unique properties and potential applications. However, there have been relatively few studies on the generation of one-dimensional polymer nanomaterials. Here, we study the fabrication and characterization of different polymer-related nanomaterials by using a simple template method. The templates we chose were anodic aluminum oxide (AAO) templates because of the regular pore distribution, high pore density, and high aspect ratio of the pores. Different nanomaterials such as amorphous carbon nanotubes, amphiphilic block copolymer nanotubes, and porous inorganic materials were fabricated by using AAO templates. We also studied the instabilities of polymer nanomaterials under confinement within the cylindrical pores. Moreover, the AAO template is used to generate hierarchical structures by the wetting of polymer microspheres.

國科會補助計畫衍生研發成果推廣資料表

日期:2011/10/27

	計畫名稱:使用多孔模板製作之高分:	子奈米材料及其應用				
國科會補助計畫	計畫主持人:陳俊太					
	計畫編號: 99-2218-E-009-028-	學門領域: 高分子物理				
	無研發成果推廣	資料				

99年度專題研究計畫研究成果彙整表

計畫主持人:陳俊太 計畫編號:99-2218-E-009-028-							
計畫名稱: 使用多孔模板製作之高分子奈米材料及其應用							
成果項目			實際已達成 數(被接受 或已發表)	量化 預期總達成 數(含實際已 達成數)	本計畫實 際貢獻百 分比	單位	備註(質化說 明:如數個計畫 时同成果、成果 列為該期刊之 封面故事 等)
		期刊論文	0	0	100%	篇	
		研究報告/技術報告	1	1	100%		
	·····································	研討會論文	3	3	100%		
		專書	0	0	100%		
	重利	申請中件數	0	0	100%	供	
		已獲得件數	0	0	100%	14	
國內	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
		碩士生	4	4	100%	人次	
	參與計畫人力 (本國籍)	博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		
	論文著作	期刊論文	2	2	80%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%	章/本	
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
國外	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
		碩士生	0	0	100%		
	參與計畫人力 (外國籍)	博士生	0	0	100%	人次	
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		

無	
其他成果	
(無法以量化表達之成	
果如辦理學術活動、獲	
得獎項、重要國際合	
作、研究成果國際影響	
力及其他協助產業技	
術發展之具體效益事	
項等,請以文字敘述填	
列。)	

	成果項目	量化	名稱或內容性質簡述
科	測驗工具(含質性與量性)	0	
教	課程/模組	0	
處	電腦及網路系統或工具	0	
計	教材	0	
重加	舉辦之活動/競賽	0	
填	研討會/工作坊	0	
項	電子報、網站	0	
目	計畫成果推廣之參與(閱聽)人數	0	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值(簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性)、是否適 合在學術期刊發表或申請專利、主要發現或其他有關價值等,作一綜合評估。

1	·請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估
	■達成目標
	□未達成目標(請說明,以100字為限)
	□實驗失敗
	□因故實驗中斷
	□其他原因
	說明:
2	研究成果在學術期刊發表或申請專利等情形:
	論文:■已發表 □未發表之文稿 □撰寫中 □無
	專利:□已獲得 □申請中 ■無
	技轉:□已技轉 □洽談中 ■無
	其他:(以100字為限)
3	 請依學術成就、技術創新、社會影響等方面,評估研究成果之學術或應用價
	值 (簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性) (以
	500 字為限)
	高分子奈米材料有許多學術上與工業上的應用。不同於一般的高分子材料,高分子在奈米
	尺度會展現出一些不同的特性。本研究探討的是以多孔模板製作高分子奈米材料,除了探
	討其性質外,也將應用於太陽能電池等應用領域。