

Electrospun Nanoporous Microspheres for Nanotechnology

Lan Xu, Ji-Huan He*, Jian-Yong Yu

Modern Textile Institute, Donghua University, 1882 Yan'an Xilu Road
Shanghai 200051, China

Abstract: Nanoporous microspheres were formed from electrospinning Poly(butylene succinate) (PBS) solutions with an additive of 'Yunnan Baiyao', a kind of Chinese traditional drugs, and a mixed solvent of chloroform and iso-propylalcohol in a single processing step. The numbers and sizes of electrospun nanoporous microspheres could be controlled by tunable voltage and flow rate applied in the electrospinning process. With the increase of voltage and the decrease of flow rate, there had appeared ever-increasing numbers and ever-decreasing sizes of the nanoporous microspheres. The electrospun nanoporous microspheres offer the potential for direct fabrication of biologically based, high-surface-area porous materials without the use of multiple synthetic steps, or postprocessing surface treatments.

Keywords: Electrospinning, electrospun nanoporous microsphere, Chinese Drug

1. INTRODUCTION

Seventy years after the discovery of the principle of electrospinning by A Formhals in 1937, we are only just beginning to understand the depth and complexity of how nanofibers behave unusually well in many aspects, for example remarkable strength, high surface energy and surface reactivity, excellent thermal and electric conductivity, and to consider their roles in the scientific and economical revival, especially of the developing world.

Although there are many methods of fabricating nanofibers, electrospinning is perhaps the simplest, the cheapest, the most straightforward way to produce nanofibers by forcing a polymer melt or solution through a spinnerette with an electric field. Due to its ultra high specific surface, electrospun nanofibers have caught much attention as the most promising material in nanotechnology, and served as a highly versatile platform for a broad range of applications in widely different areas such as photonic structures, microfluid channels (nanofluidics), catalysis, sensors, medicine, pharmacy, drug delivery, radioprotection, and tissue engineering, just to name a few.

In this paper we will discuss a new approach to producing nanoporous microspheres by electrospinning. Because of ultra high specific surface, nanoporous structures [1-6], which are potentially of great technological interest for the development of electronic,

* corresponding author: E-mail: jhhe@dhu.edu.cn

catalytic and hydrogen-storage systems, invisibility device (e.g. stealth plane, stealth clothes), and others, have been caught much attention recently [7]. Pore structure and connectivity determine how microstructured materials perform in applications such as adsorption, separation, filtering, catalysis, fluid storage and transport, electrode materials or as reactors [8]. Far-reaching implications are emerging for applications including medical implants, cell supports, materials that can be used as instructive three-dimensional environments for tissue regeneration [9-12] and others.

Nanoporous materials can be prepared by leaching the purified montmorillonite clay with sulfuric acid (H_2SO_4) solution with varying concentrations[13] and other methods[1-6], nanoporous membranes can also be widely produced by electrospinning[14-16]. In this paper we will apply electrospinning to prepare for nanoporous microspheres.

Electrospinning has been recognized as an efficient technique for the fabrication of polymer nanofibers, and has received much attention in recent years[14-18]. We recently developed vibration-electrospinning [19,20], magneto-electrospinning[21] and Siro-electrospinning[17], respectively, to control electrospun fiber morphology and fiber diameter, to control instability of the electrospinning process, and to mock the spider-spinning.

Electrospun nanofiber technology actually bridges the gap between deterministic laws (Newton mechanics) and probabilistic laws (quantum mechanics)[17]. The nano-effect[17] has been demonstrated for unusual strength, high surface energy, surface reactivity, high thermal and electric conductivity.

In this paper we use a kind of Chinese traditional drugs called '*Yunnan Baiyo*' [22] as an additive for possible application in drug carrier. Similar experiments were done by other some researchers who studied the electrospinning of poly (vinyl alcohol) with acetylsalicylic acid (Aspirin) [23-25].

The chosen drug '*Yunnan Baiyo*' is a highly valued and important traditional Chinese drug. It is a kind of fawn powder mixture composed of several kinds of drugs. There are a wide variety of therapeutic uses of '*Yunnan Baiyo*', including promotion of blood circulation, removal of blood stasis, anti-inflammatory action, hemostasis, induction of blood clotting, relief of swelling and alleviation of pain. And it can also be used for the treatment of traumatic injury, spitting blood, hemoptysis, surgical bleeding, suppurative and pyogenic infections, soft tissue bruise, closed fracture and infective diseases on skin etc. It has potential applications in wound dressings, i.e., hemostatic bandages. In the field of tissue engineering, '*Yunnan Baiyo*' can be added to scaffolding materials so that the material can restrain an inflammatory response. The base material for electrospun fibrous is poly(butylenes succinate) (PBS), a kind of biodegradable materials.

PBS solutions with additive of '*Yunnan Baiyo*' and mixed solvent of CHCl_3 (CF) and iso-propylalcohol were electrospun under different voltages and flow rates. Figures 3-9 show scanning electron microscope (SEM) images of electrospun nanoporous microspheres that were formed from various different conditions. IR spectra analysis (see supporting material) revealed that '*Yunnan Baiyo*' was electrospun into the electrospun fibers or microspheres.

3. EXPERIMENTAL SET-UP

Experimental set-up is illustrated in Fig.1.

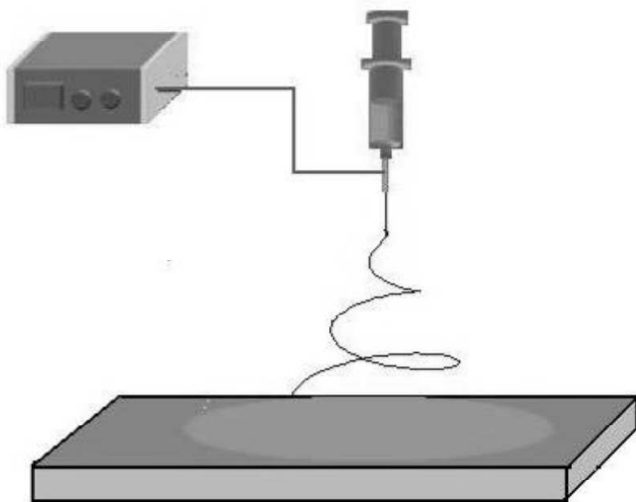


Figure 1: Scheme of electrospinning setup

Experimental

Materials

Poly(butylenes succinate) (PBS) with a molecular weight of 20,000-30,000g/mol was supplied by Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Science. ‘*Yunnan Baiyao*’, a traditional Chinese drug, was produced by *Yunnan Baiyao* Group Co. Ltd., and used as an additive. $\text{CHCl}_3(\text{CF})$ and iso-propylalcohol were obtained from Shanghai Chemical Reagent Co. Ltd. China. The mixture of iso-propylalcohol and chloroform with the weight ratio 1:9 was used as solvent. All materials were used without any further purification.

Instrumentation

The electrospinning setup consisted of a syringe, a needle, a grounded collecting plate, a flowmeter and a variable DC high-voltage power generator (0–100 kV, F180-L, Shanghai Fudan high school). The scheme of the electrospinning process was showed in Fig .1. The needle tip was connected to a DC high-voltage generator via an alligator clip.

Analysis of chemic components was studied through IR investigation. And fiber diameters, porous sizes and morphology images of films were analyzed using a scanning electron microscope. Fibers for SEM analyzed were collected on a steel mesh, mounted on a SEM disc and sputter-coated with Platina. Typical images were analyzed under various conditions.

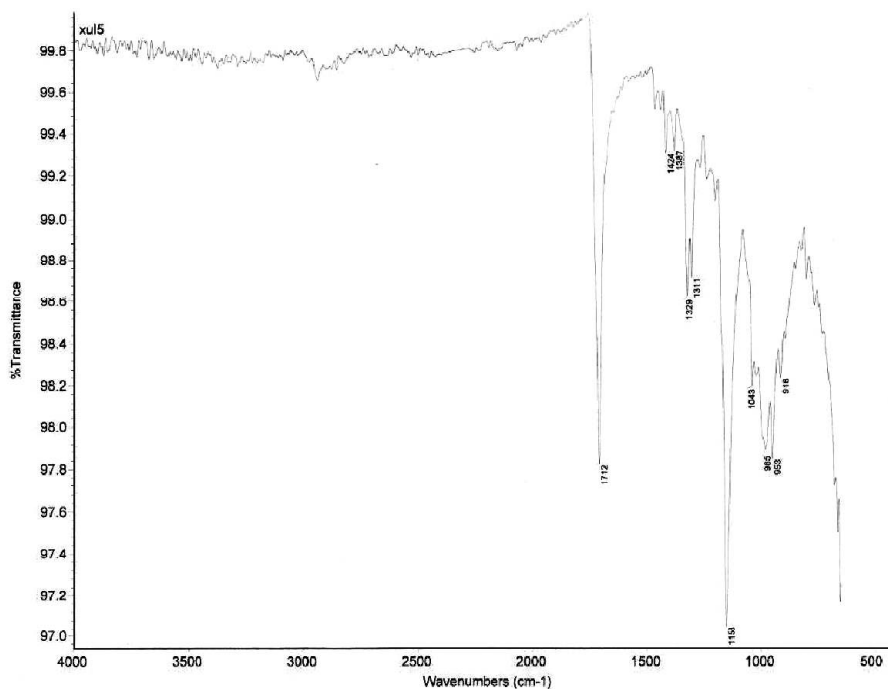
Electrospinning Process

All concentration measurements were done in weight by weight (w/w). A control amount of PBS particles and 'Yunnan Baiyo' powder were dissolved in the mixed solvent with the weight ratio 1:6:43 ('Yunnan Baiyo': PBS: mixed solvent). The obtained solution was magnetically stirred at 25°C for 4 hours in an electromagnetism stirrer (Angel Electronic Equipment (Shanghai) Co.,LTD) with a stirring speed of about 1000 rounds/min. The solution was dropped into a 20-ml syringe which was mounted in a syringe pump. A grounded metal mesh screen was placed vertically under the needle tip. The inner diameter of the needle orifice was 0.57mm. The tip-to-collection distance was 10cm. The applied voltages connected to the needle varied from 8 to 15KV. The flow rate varied from 1.5 to 8ml/h. All electrospinning processes were carried out under room temperature in a vertical spinning configuration.

4. RESULTS AND DISCUSSION

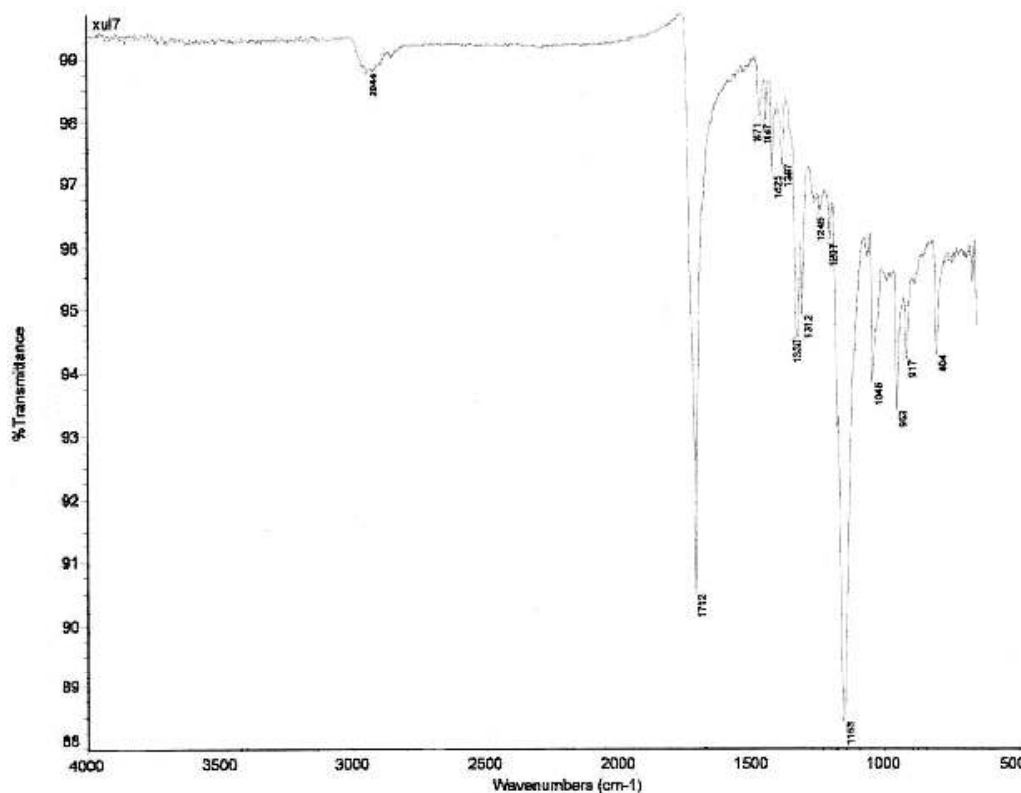
IR spectra

Fig. 2 displays the IR spectra for pure PBS fibers and the electrospun fibers. It is obvious that the absorption peaks at about 2944cm⁻¹, 1712cm⁻¹, 1424cm⁻¹(1387cm⁻¹), 1329cm⁻¹(1311cm⁻¹), 1153cm⁻¹, 1043cm⁻¹, 985cm⁻¹(953cm⁻¹) and 917cm⁻¹ assigned to hydratyl group (ν -oh), carboxy group(-co), benzene ring, respectively, correspond to pure PBS, see Fig.2(a). In Fig.2(b), besides these peaks assigned to pure PBS, there are



(a)

Electrospun Nanoporous Microspheres for Nanotechnology



(b)

Figure 2: IR spectra for (a) pure PBS (b) the electrospun nanoporous microspheres and fibers

new peaks appeared at about 1471cm⁻¹(1447cm⁻¹), 1245cm⁻¹(1207cm⁻¹), and 804cm⁻¹ corresponding to 'Yunnan Baiyo'.

SEM Analysis

Figures 3,4 and 5 showed SEM pictures of the electrospun microspheres with different voltages applied in the electrospinning process. The flow rate was 1.5ml/h. It could be seen that the diameters of the microspheres ranged from 5μm to 40μm, and there had appeared ever-increasing numbers and ever-decreasing sizes of the electrospun nanoporous microspheres with the increase of voltage.

Figures 6-9 illustrated SEM images of the electrospun microspheres with different flow rates applied in the electrospinning process. The applied voltage was 10KV. It could be seen that the diameters of the microspheres ranged from 5μm to 50μm, and there had appeared ever-decreasing numbers and ever-increasing sizes of the electrospun nanoporous microspheres with the increase of flow rate.

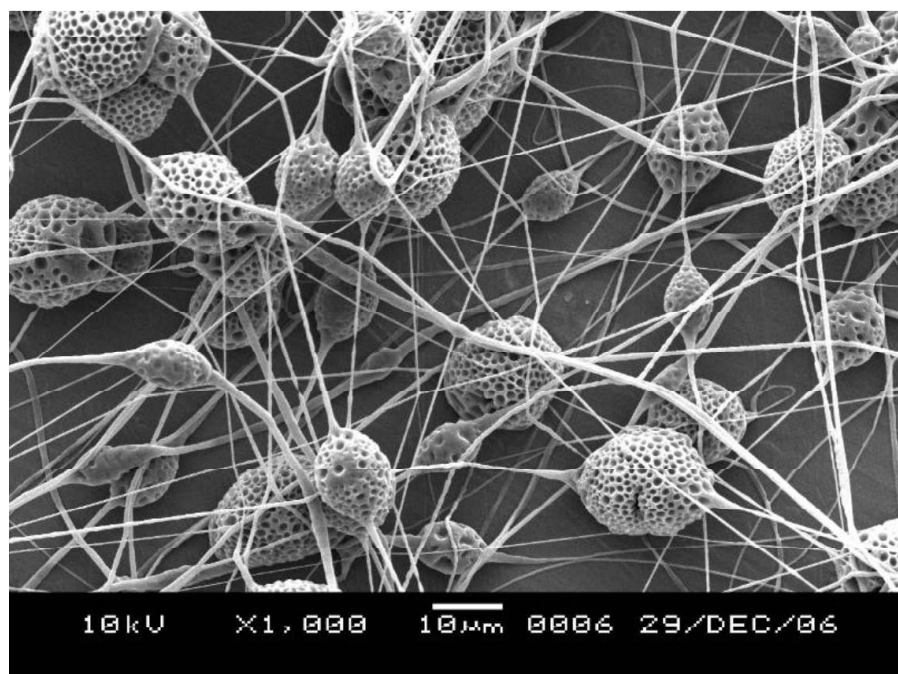
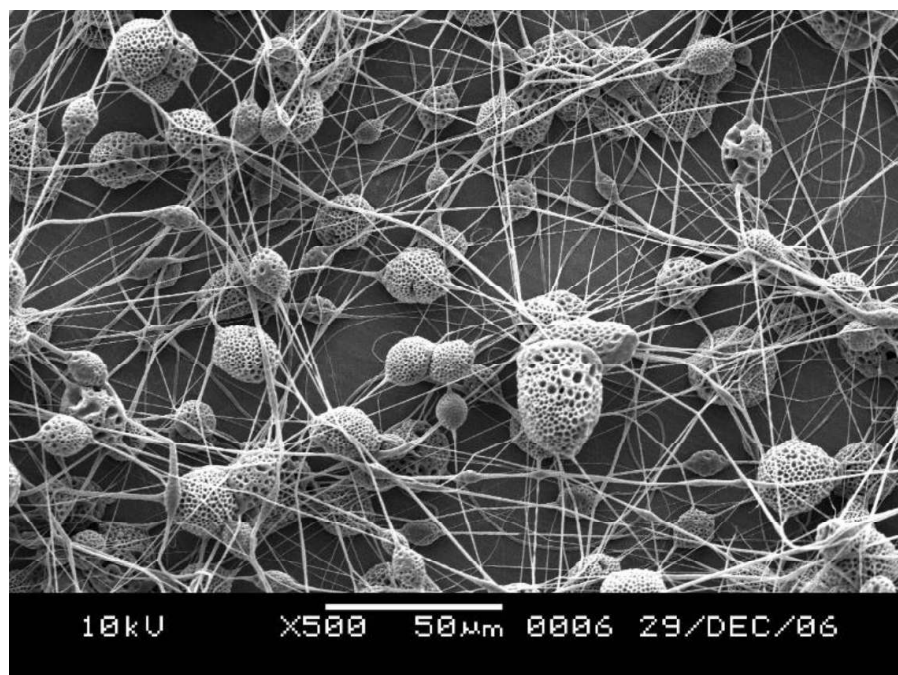


Figure 3: SEM pictures of the electrospun nanoporous microspheres. The voltage is 8KV.

Electrospun Nanoporous Microspheres for Nanotechnology

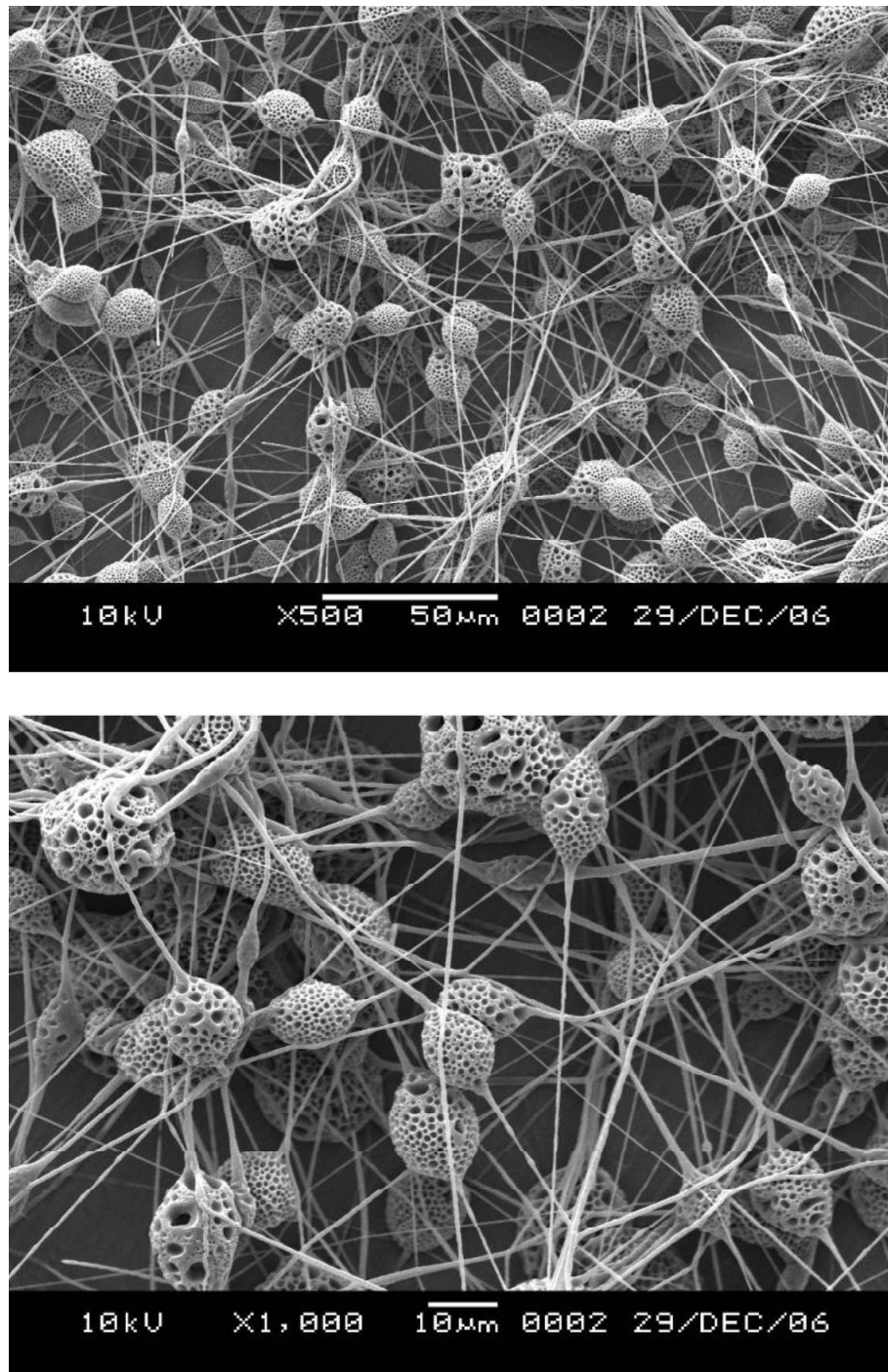


Figure 4: SEM pictures of the electrospun nanoporous microspheres. The voltage is 10KV.

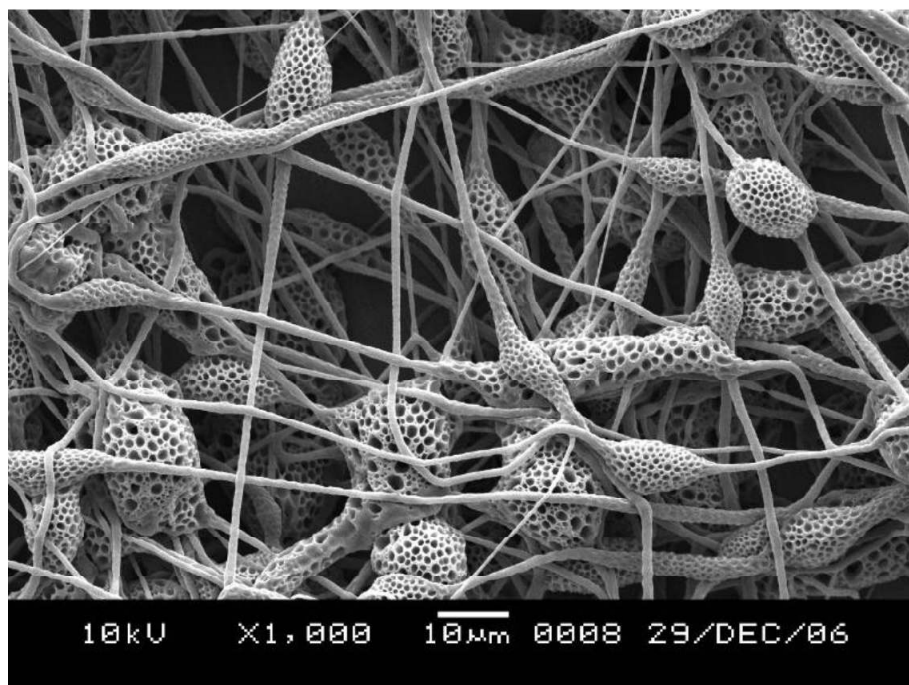
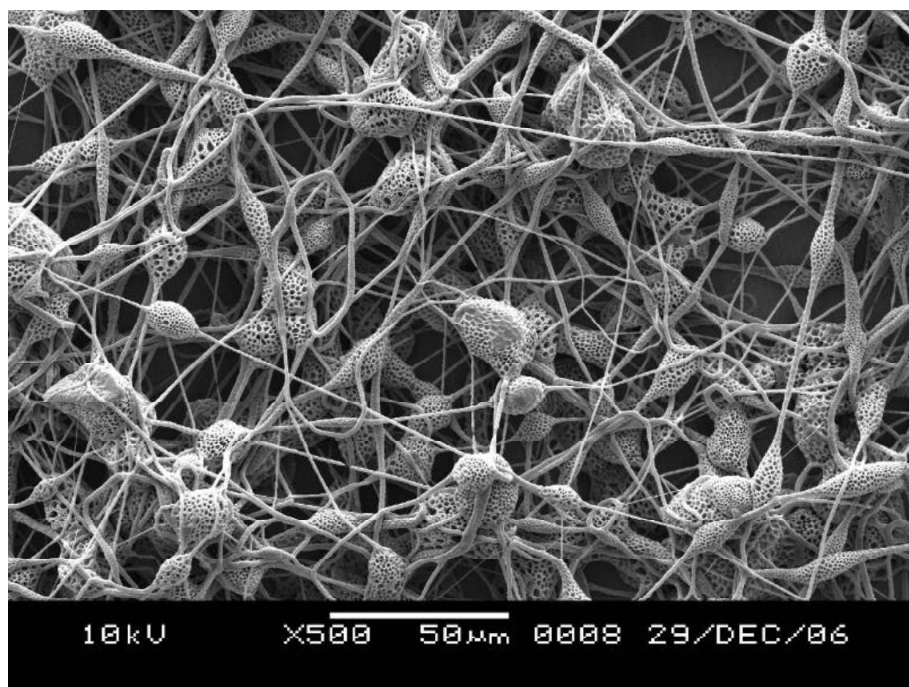


Figure 5: SEM pictures of the electrospun nanoporous microspheres. The voltage is 15KV.

Electrospun Nanoporous Microspheres for Nanotechnology

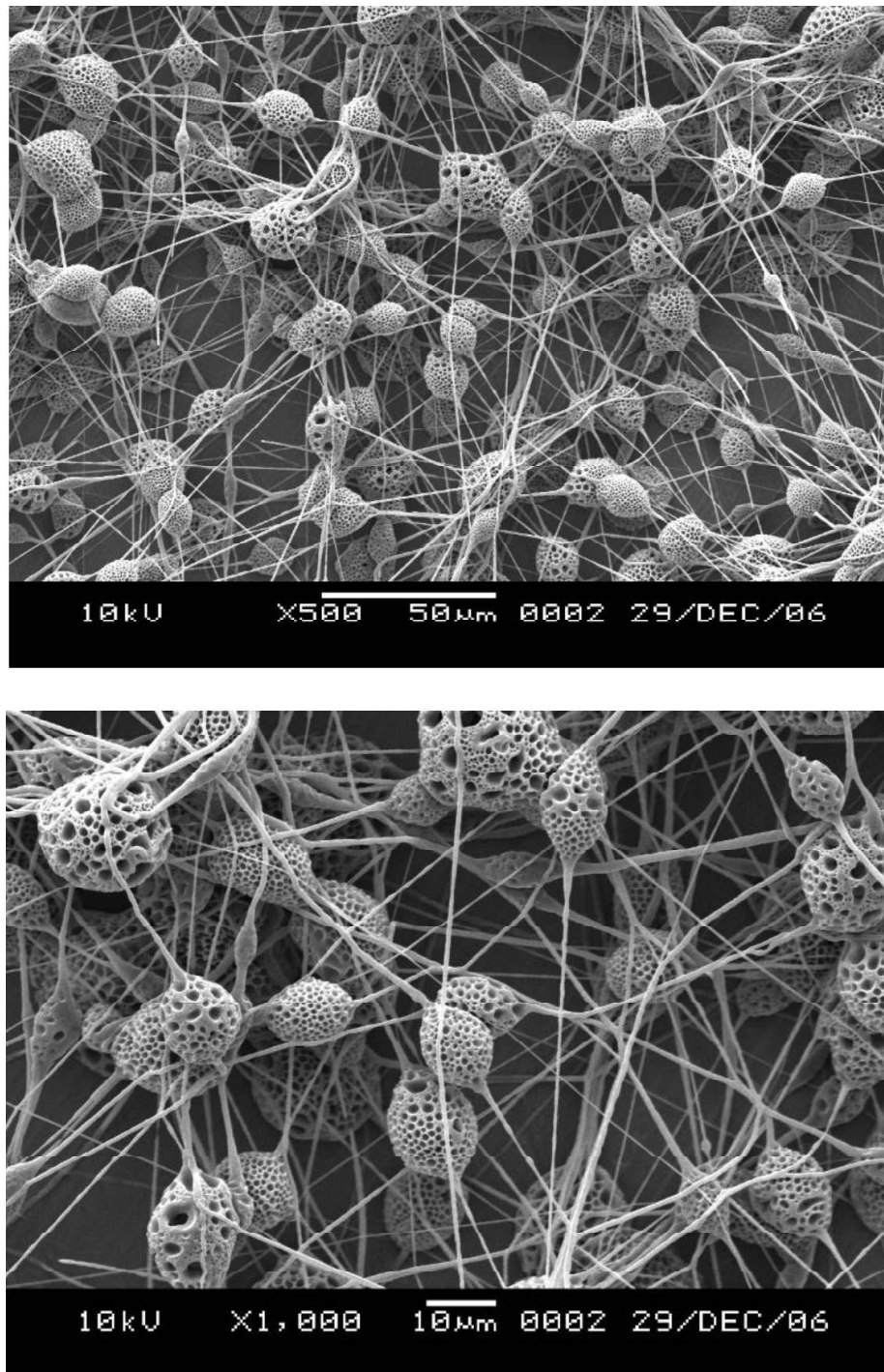


Figure 6: SEM pictures of the electrospun nanoporous microspheres. The flow is 1.5ml/h.

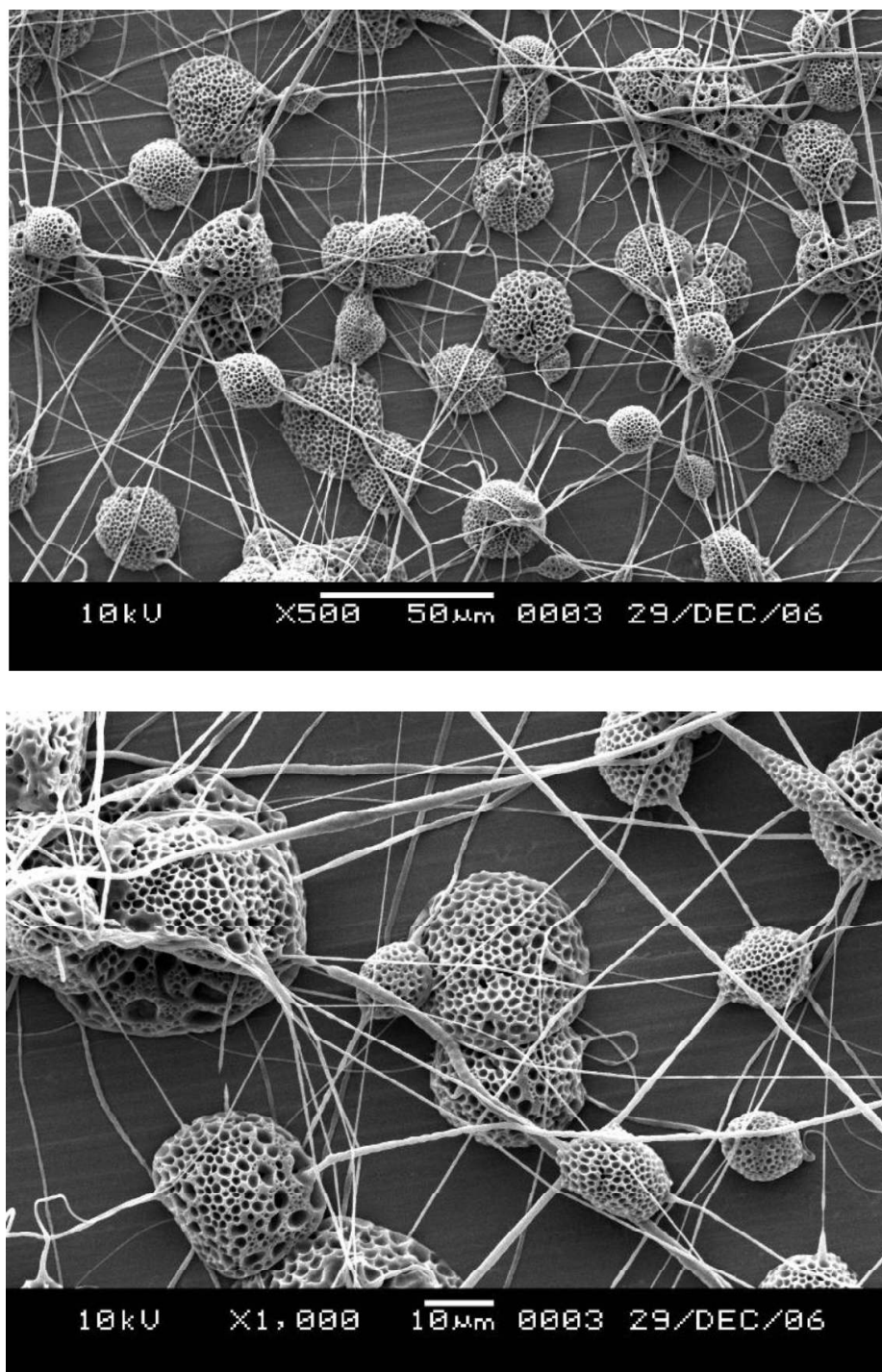


Figure 7: SEM pictures of the electrospun nanoporous microspheres. The flow is 3ml/h.

Electrospun Nanoporous Microspheres for Nanotechnology

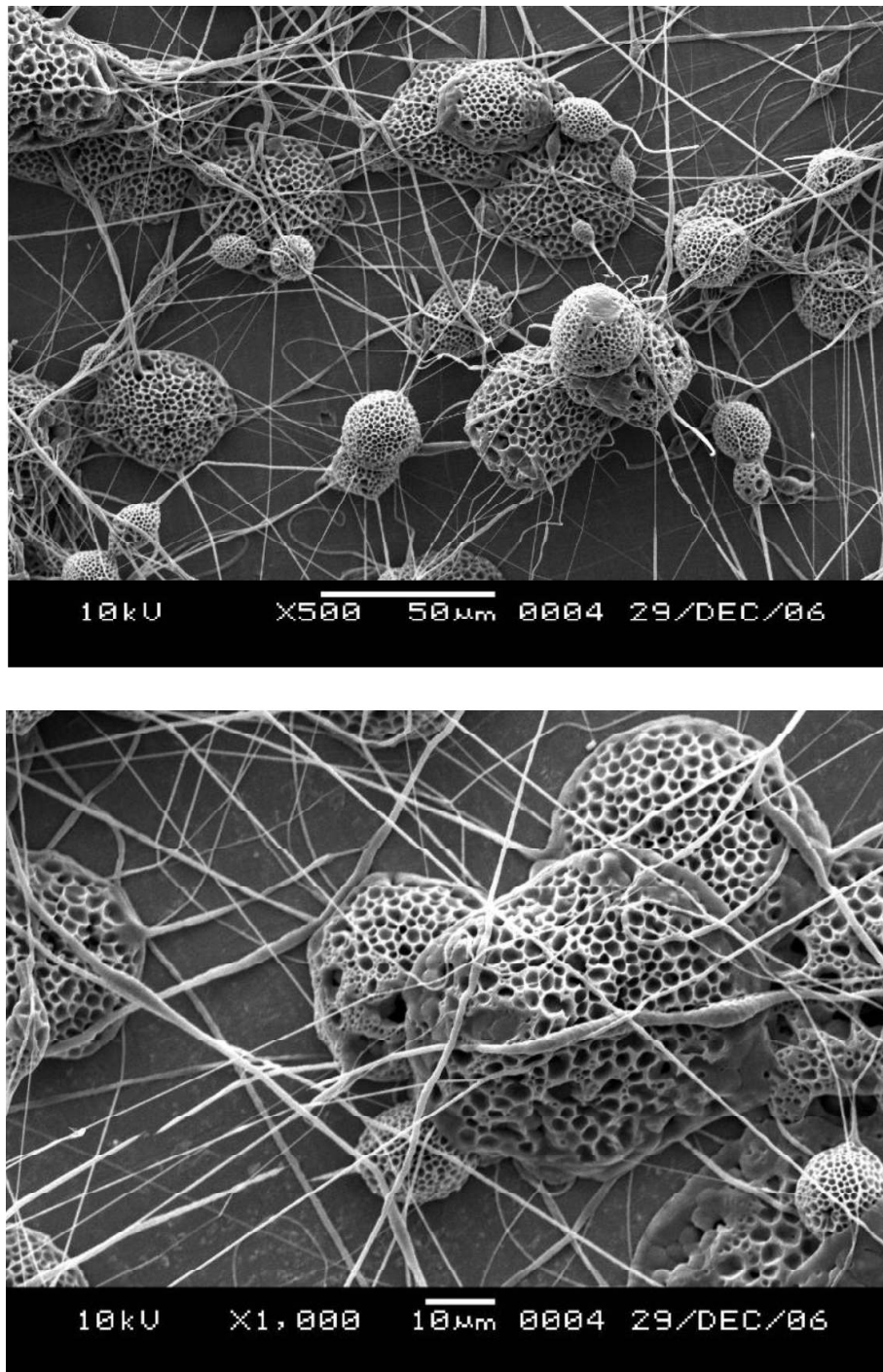


Figure 8: SEM pictures of the electrospun nanoporous microspheres. The flow is 5ml/h.

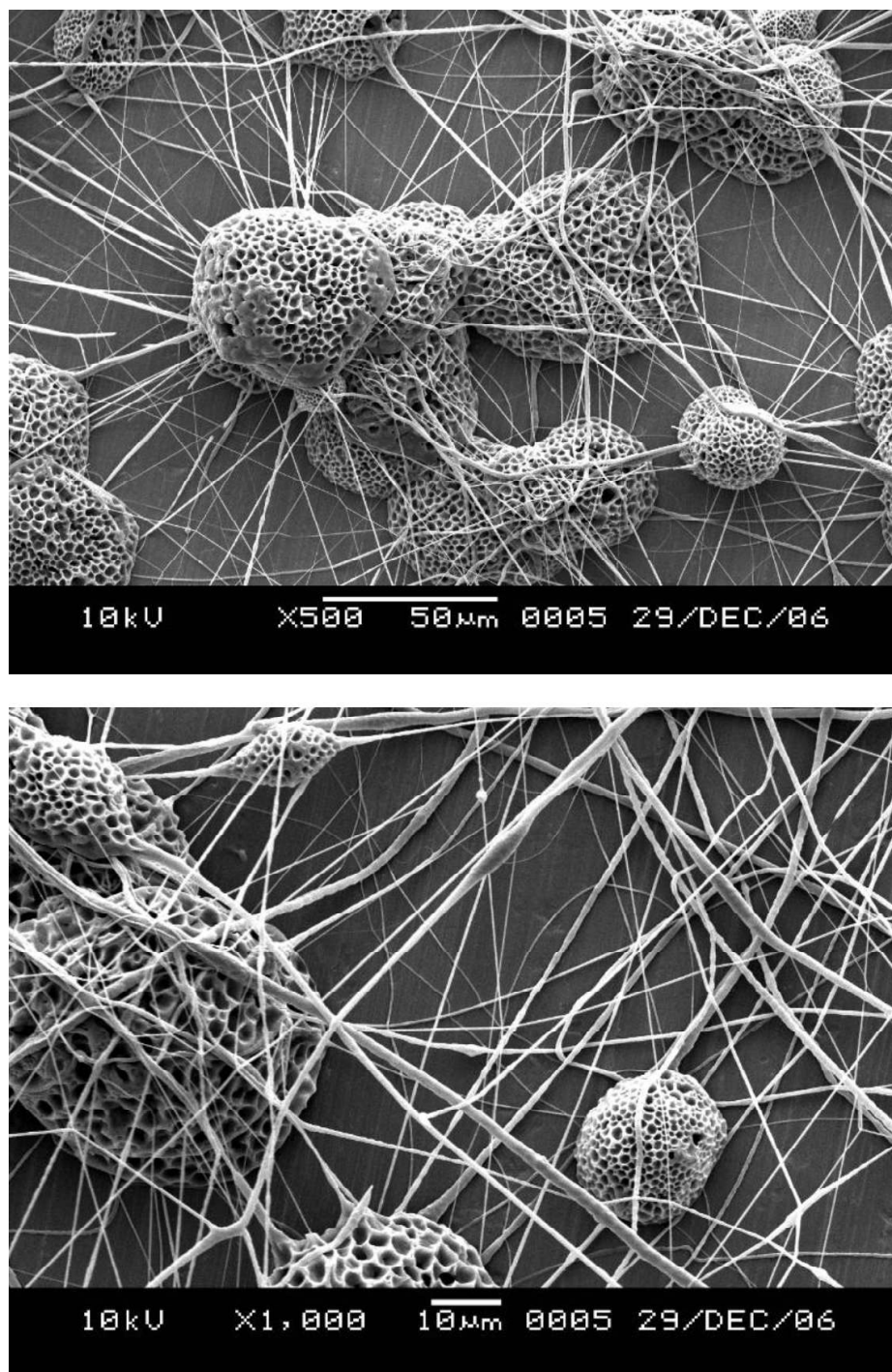


Figure 9: SEM pictures of the electrospun nanoporous microspheres. The flow is 8ml/h.

Electrospun Nanoporous Microspheres for Nanotechnology

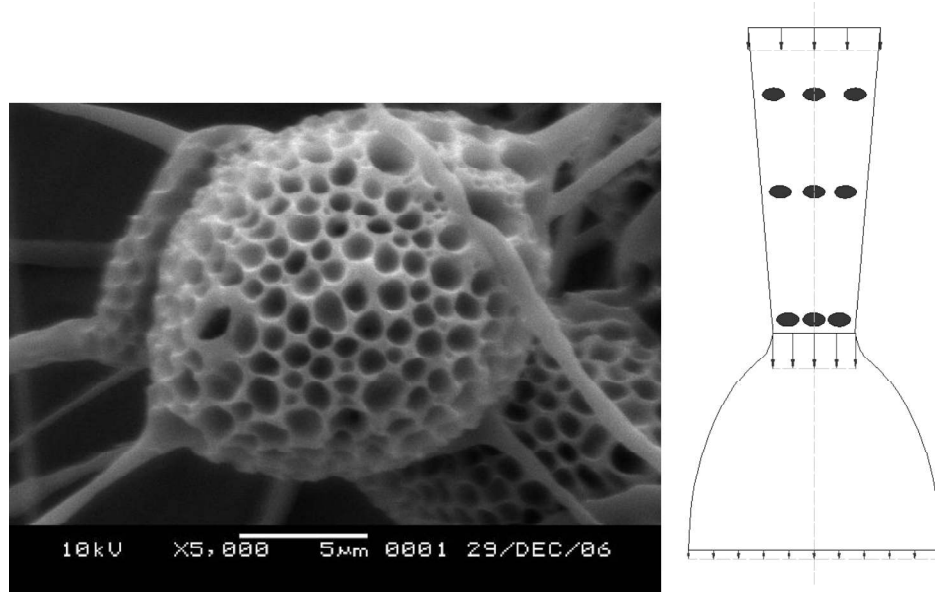


Figure 10: Macromolecular chains are compacted during the electrospinning

During the electrospinning process, the charged jet is accelerated by a constant external electric field, and the spinning velocity probably reached maximum and perhaps exceeded the velocity of sound in air in a very short time before the spinning became instability[26]. According to the mass conservation equation

$$\pi r^2 \rho u = Q \quad (1)$$

where r is the radius of the jet, u the velocity, Q the flow rate, ρ the density, the radius of the jet decreases with the increase of the velocity of the incompressible charged jet. Macromolecules of the polymers are compacted together tighter and tighter during the electrospinning process as illustrated in Figure 10. There must exist a critical minimal radius r_{cr} for all electrospun jet $r \leq r_{cr}$ for continuous ultrafine fibers, and the critical maximal velocity is

$$u_{cr} = Q / \pi \rho r_{cr}^2 \quad (2)$$

However, the velocity can exceed this critical value u_{cr} if a higher voltage is applied and the distance between the needle and the collecting plate is infinite long.

In case when the radius of the jet reaches the value of the critical value $r = r_{cr}$, and the jet speed exceeds its critical value $u > u_{cr}$, in order to keep conservation of mass equation, the jet dilates by decreasing its density, leading to porosity of the electrospun fibers, we call this phenomenon as electrospinning-dilation.

In case of higher voltage, the charged jet can be more easily accelerated to the critical speed before the charged jet is collected. Higher voltage means higher value of the jet speed (u_0) at $r = r_{cr}$, and a more drastic electrospinning-dilation process happens, resulting

in lower density ($\tilde{\rho}$) of dilated microsphere and smaller size (R) of the microsphere and smaller pores as well, see Figure 11. This phenomenon can be also explained by the following equation:

$$\pi r_{cr}^2 \tilde{\rho} u_0 = \pi R^2 \tilde{\rho} u_{min} = Q \quad (3)$$

where $\tilde{\rho}$ is the density of dilated microsphere, u_0 is the velocity of the charged jet at $r = r_{cr}$, R is the maximal radius of the microsphere, u_{min} is the minimal velocity.

According to Eq.(2), the higher the flow rate, the higher the critical speed. That means electrospinning-dilation is easy to happen when the flow rate is relatively low, see Figure 12.

In conclusion we suggested a general strategy for the synthesis of microspheres with nanoporosity by electrospinning, the porous sizes having uniform but tunable diameters can be controlled by voltage applied or flow rate in the electrospinning process. The flexibility and adaptation provided by the method have made the method a strong candidate for producing nanoporous materials.

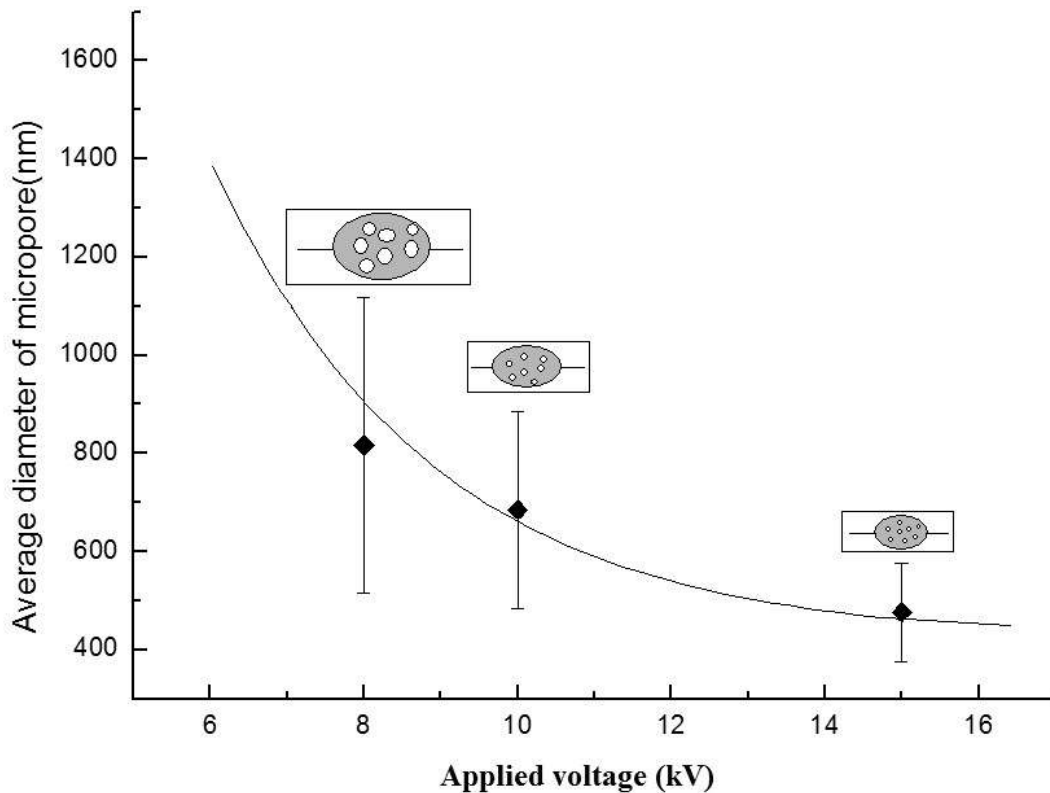


Figure11: Effect of applied voltage on the diameter of the electrospun nanoporous microspheres

Electrospun Nanoporous Microspheres for Nanotechnology

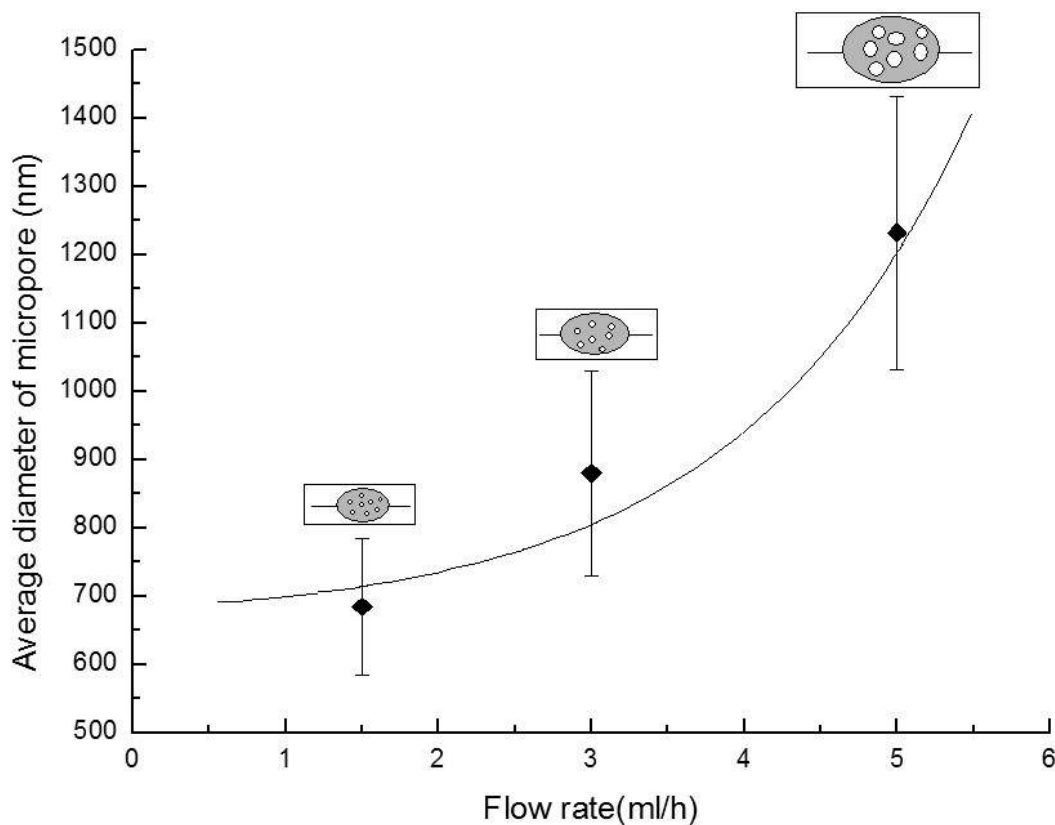


Figure12: Effect of flow rate on the diameter of the electrospun nanoporous microspheres

ACKNOWLEDGEMENT

This material is based on work supported by National Natural Science Foundation of China under the grand No. 10372021 and by the Program for New Century Excellent Talents in University.

References

- [1] Zhao X B, Xiao B, Fletcher A J, *et al.* Hysteretic Adsorption and Desorption of Hydrogen by Nanoporous Metal-organic Frameworks, *SCIENCE* 306 (2004) 1012-1015.
- [2] Matsuishi S, Toda Y, Miyakawa M, *et al.* High-density Electron Anions in a Nanoporous Single Crystal, *SCIENCE*, 301 (2003) 626-629.
- [3] Halder G J, Kepert C J, Moubaraki B, *et al.* Guest-dependent Spin Crossover in a Nanoporous Molecular Framework Material, *SCIENCE*, 298 (2002) 1762-1765.
- [4] Chan V Z H, Hoffman J, Lee V Y, *et al.* Ordered Bicontinuous Nanoporous and Nanorelief Ceramic Films from Self Assembling Polymer Precursors, *SCIENCE*, 286 (1999) 1716-1719.

- [5] Shiflett M B, Foley H C. Ultrasonic Deposition of High-selectivity Nanoporous Carbon Membranes, *SCIENCE*, 285 (1999) 1902-1905
- [6] Chui S SY, Lo S M F, Charmant J P H, *et al.* A Chemically Functionalizable Nanoporous Material, *SCIENCE*, 283 (1999) 1148-1150.
- [7] M. S. El Naschie, Nanotechnology for the Developing World, *Chaos Solitons & Fractals* 30 (4) (2006) 769-773.
- [8] Harel E, Granwehr J, Seeley J A, Pines A. Multiphase Imaging of Gas Flow in a Nanoporous Material using Remote-Detection NMR, *Nature Materials*, 5 (2006) 321-327.
- [9] Stevens M M, George J H. Exploring and Engineering the Cell Surface Interface, *Science*, 310 (2005) 1135-1138.
- [10] Discher D E, Janmey P, Wang Y L. Tissue Cells Feel and Respond to the Stiffness of Their Substrate, *Science*, 310 (2005) 1139-1143.
- [11] Norman J, Desai T. Methods for Fabrication of Nanoscale Topography for Tissue Engineering Scaffolds, *Annals of Biomedical Engineering*, 34 (2006) 89-101.
- [12] Wolfrum B, Mourzina Y, Sommerhage F, *et al.* Suspended Nanoporous Membranes as Interfaces for Neuronal Biohybrid Systems, *Nano Letters*, 6 (2006) 453-457.
- [13] Temuujin J, Senna M, Jadambaa T, *et al.* Characterization of Nanoporous Materials Prepared from Montmorillonite Clay and its Application to the Decolorization of Mare's Milk Oil, *Journal of Porous Materials* 13 (1) (2006), 49-53.
- [14] McKee M G, Layman J M, Cashion M P, *et al.* Phospholipid Nonwoven Electrospun Membranes, *Science* 311 (2006), 353-355.
- [15] Dzenis Y. Spinning Continuous Fibers for Nanotechnology, *Science* 304 (2004), 1917-1919.
- [16] Reneker D H, Yarin A L, Fong H, *et al.* Bending Instability of Electrically Charged Liquid Jets of Polymer Solutions in Electrospinning, *Journal of Applied Physics* 87 (2000), 4531-4547.
- [17] He J H, Wan Y Q, Xu L. Nano-effects, Quantum-like Properties in Electrospun Nanofibers, *Chaos, Solitons & Fractals*, In Press.
- [18] Zeng Y C, Wu Y, Pei Z G, Yu C W. Numerical Approach to Electrospinning, *International Journal of Nonlinear Sciences and Numerical Simulation*, 7 (4) (2006) 385-388.
- [19] He J H, Wan Y Q, Yu J Y. Application of Vibration Technology to Polymer Electrospinning, *International Journal of Nonlinear Sciences and Numerical Simulation* 5 (2004), 253-262.
- [20] Wan Y Q, He J H, Wu Y, Yu J Y. Vibrorheological Effect on Electrospun Polyacrylonitrile (PAN) Nanofibers, *Materials Letters* 60 (27) (2006), 3296-3300.
- [21] Wu Y, Yu J Y, He J H, Wan Y Q. Controlling Stability of the Electrospun Fiber by Magnetic field, *Chaos, Solitons & Fractals* 32 (1) (2007), 5-7.
- [22] Liu J H, Wang X, Cai S Q, Komatsu K, Namba T. Analysis of the Constituents in the Chinese drug Notoginseng by Liquid Chromatography-electrospray Mass Spectrometry, *Journal of Chinese Pharmaceutical Sciences* 13 (4) (2004), 225-237.
- [23] Zhang C X, Yuan X Y, Wu L L, Sheng J. Drug-loaded Ultrafine Poly(vinyl alcohol) Fibre Mats Prepared by Electrospinning, *e-Polymer* 2005 no. 027.

Electrospun Nanoporous Microspheres for Nanotechnology

- [24] Zhang C X, Yuan XY, Wu L L, Han Y, Sheng J. Study on Morphology of Electrospun poly (vinyl alcohol) Mats, *European Polymer Journal* 41 (2005), 423-432.
- [25] Yue Wu, Ji-Huan He, Lan Xu, Jian-Yong Yu. Electrospinning Drug-loaded Poly (Butylenes Succinate-co-butylene Terephthalate) (PBST) with Acetylsalicylic Acid (Aspirin), *International Journal of Electrospun Nanofibers and Applications*, 1 (1) (2007), 1-6.
- [26] He JH, Wan YQ, Yu JY. Allometric Scaling and Instability in Electrospinning, *International Journal of Nonlinear Sciences and Numerical Simulation*, 5 (3)(2004) 243-252.