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Force Spectroscopy Studies of Polymer Nanofibers Spun by Electrospinning Method.

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ABSTRACT

Nanofibers synthesis from polymers is gaining importance in many applications. In this work we synthesized have fibers with polymers like Polyacrylonitrile, SU-8 2050, Polyvinylpyrrolidone. The spinning parameters were optimized. Here the grown fibers were characterized by AFM for its sized, shape uniformity, and roughness. Here we describe our recent measurements using force spectroscopy to interrogate the chemical identity of various polymer solutions surface and under the potential control. Differences in adhesion forces between polymer surface and AFM tip used to clarify changes in polymer solution identity as function of potential control. To determine the force resolution were done by SPIP software tool and can be measured diameter with IMAGE J software tool.
Keywords: PVP, PAN, SU-8, Electro spinning, Nano fibers, AFM, Force spectroscopy, Adhesion.

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INTRODUCTION

Nano fibers are an exciting new class of material used for several value added application such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, energy storage, battery separators and fuel cells [1]. Nano fibers are defined as fibers with diameter less than 100nm, in the textile industries definition to extended as fibers as large as 1000nnm diameter [2]. These fibers are produced by the interfacial polymerization, electro spinning and force spinning.

Electro Spinning Process

The electro spinning has been known since 1934 when the first patent electro spinning was filed [12]. Now consider the following figure as shown as following below.

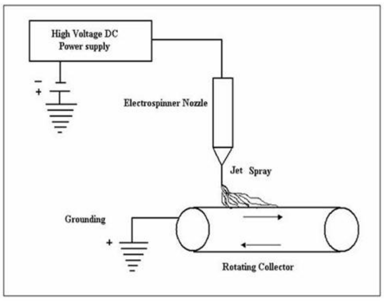

Figure 1: Representation process of electro spinning.

When sufficiently high voltage applied to a liquid droplet, the body of the liquid becomes charged and electrostatic repulsion counteracts the surface tension and droplet is stretched at a critical point a stream of liquid erupts from the surface. Electro spinning, spinning using electrostatic forces fine fibers from polymer solution or melts and fibers thus produced have a thinner diameter and a large surface area [13]. Fiber properties depend on field uniformity, polymer viscosity, electric field strength and DCD (distance between nozzle and collector). Advancements in microscopy such as scanning electron microscopy have enabled us to better understand the structure and morphology of nano fibers [12]. In this work we made polymer thin films and also fibers with the same polymers. The roughness of the film also to formation of fibers is compared. Apart from this the adhesion of the fiber formed is characterized by conducting force spectroscopy experiment on the fiber at different locations.

EXPERIMENTAL PROCEDURE

Materials Used

Polyacrylonitrile MW 1,50,000 $(C_3H_3N)_n$, N,N-Dimethylformamide anhydrous, 99.8% $HCON(CH_3)_2$ MW 73.09, SU-8 2050 Solution and Polyvinylpyrrolidone MW 90,000 $(C_6H_9NO)_n$, Ethanol 99.9% (CH_3CH_2OH).

We tried three different polymers for the analysis they are

- Polyacrylonitrile (PAN) solution
- SU-8 2050 solution
- Polyvinylpyrrolidone (PVP)

The PAN properties of high surface area and in increase electrical conductivity. This solution can be used in producing fiber, films and paints [14,15]. The SU-8 2050 solution could be especially suitable for integration with photo resist based carbon MEMS to produce multi scale hierarchical assemblies and it is more significantly used in Bio MEMS and bio sensor etc.., and PVP used into TV and picture tube applications etc...

Thin Film Coating for Various Polymers

Thin Film of PAN Solution

The 10%wt of Polyacrylonitrile is dispersed in 10ml DMF (Dimethyl formamide) solution and stirred for 24 hrs at 60^0C. As prepared solution we made thin film by using spin coating at 8000 rpm for the set time of 60 seconds. After that unloading the sample from that spin coater the surface roughness of the PAN substrate is measured by Atomic force microscopy

Thin film of PVP Solution

10%wt of Polyvinylpyrrolidone (PVP) is dispersed in 10ml Ethanol solution and stirred for 24 hrs at 60^0C. As prepared solution we made thin film by using spin coating at 8000 rpm for the set time of 60 seconds. After that unloading the sample from that spin coater is measured the surface roughness of this PVP substrate by Atomic force microscopy.

Thin film Of SU-8 2050 Solution

We made thin film by using spin coating at 8000 rpm for the set time of 60 seconds on the glass slide with SU-8 2050 solution. After that unloading the sample from that spin coater is measured the surface roughness of this SU-8 2050 substrate by Atomic force microscopy.

Electro Spinning of Nanofibers

Preparation of PAN Nanofibers

10% wt of Polyacrylonitrile is dispersed in 10ml DMF solution and stirred for 24 hrs at 60^0C. The as prepared viscous sample is loaded in 5 ml syringe for electro spinning. A flow rate of 0.5ml/hr by a syringe pump at a distance of 12 cm is kept between the needle tip and the static collector .A voltage of +15 kV is applied to the tip of needle by external power supply, PAN fiber were collected from the collector.

Preparation of PVP Nanofibers

10% wt of Polyvinylpyrrolidone is dispersed in 10ml Ethanol solution and stirred for 5 hrs at 60^0C. The as prepared viscous sample is loaded in 5 ml syringe for electro spinning. A flow rate of 0.5ml/hr by a syringe pump at a distance of 12 cm is kept between the needle tip and the static collector .A voltage of +15 kV is applied to the tip of needle by external power supply, PVP fiber were collected from the collector.

Preparation of SU-8 2050 Nanofibers

The Su-8 2050 viscous sample is loaded in 5 ml syringe for electro spinning. A flow rate of 0.5ml/hr by a syringe pump at a distance of 12 cm is kept between the needle tip and the static collector .A voltage of +15 kV is applied to the tip of needle by external power supply, SU-8 2050 fiber were collected from the collector.

RESULTS AND DISCUSSION

Measurement of surface roughness between Nanofiber and thin film

Table 1: Surface Roughness values between Nanofibers and Thin Films

	PAN Solution thin film	PAN solution of nano fiber	SU-8 2050 Solution of thin film	SU-8 2050 solution of nano fiber	PVP Solution of Thin film	PVP Solution of nano fiber
S_a	118.293nm	235.192nm	21.386nm	92.5069nm	14.787nm	499.911nm
S_q	219.978nm	279.629nm	26.576nm	115.679nm	17.840nm	856.61nm
S_{sk}	4.05649	-0.76702	-0.5011	0.21820	0.4061	-4.6739
S_{ku}	24.0688	2.73471	2.8695	2.8065	2.7035	35.522

AFM images of Polyacrylonitrile (PAN) solution

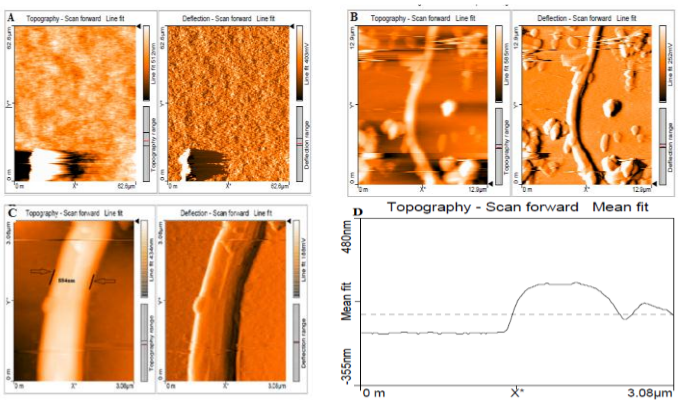

Figure 2: AFM images of SU-8 2050 solution at different magnification A) Thin film at 62.6µm B) nano fiber at 14.4µm C) nanofiber at 2.93 µm D) Topography height map.

AFM images of Polyvinylpyrrolidone (PVP) solution

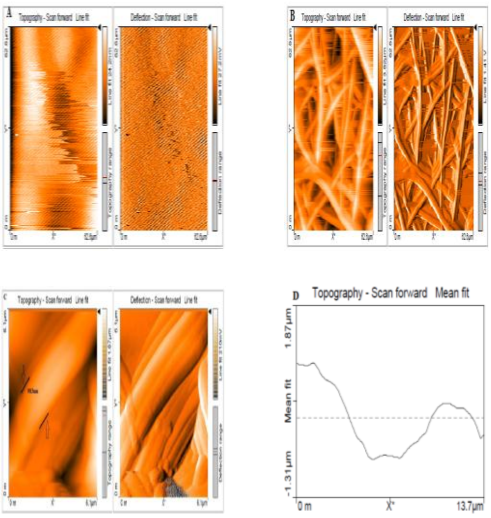

Figure 3: AFM Images of PVP solution at different magnification A)Thin film at 62.6µm B) nanofibers at 62.6µm C) nanofiber at 6.1µm D) Topography height map.

Measurement of Force versus Distance curve for various Polymer solutions by using Force Spectroscopy

Measurement of Force versus Distance curve comparison for the PAN nanofiber and thin film

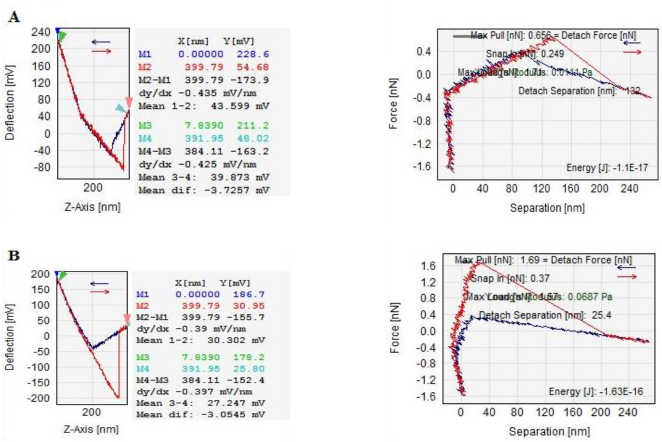

Figure 4: Force versus distance curve for PAN based solutions in reverse direction A) PAN nanofiber B) PAN thin film.

In fig 4(A) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber in this case could be measured the stiffness at 0.0111P_a value. The maximum load will contain the maximum force value at 1.70nN for this curve, to align all curves in the force volume image to have the 0.249nN value for Snap in force and in this plot detach separation will contain separation values at the detected detach 132nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 0.656nN and molecules attached between tip and sample can be stretched and dissipated energy is -1.1E^{-17}. In fig 4 (B) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber in this case could be measured the stiffness at 0.0687P_a value. The maximum load will contain the maximum force value at 1.58nN for this curve, to align all curves in the force volume image to have the 0.249nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach 25.4nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 1.69nN and molecules attached between tip and sample can be stretched and dissipated energy is -1.63E^{-16}.

In fig 5 (C) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber. The maximum load will contain maximum force value at 0.579nN for this, to align all curves in the force volume image to have the 1.19nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach 0.0423nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 0.281nN and molecules attached between tip and sample can be stretched and dissipated energy is -9.55E^{-17}.

In fig 5 (D) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber. The maximum load will contain maximum force value at 7.14nN, to align all curves in the force volume image to have the -5.97nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach 8.92nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 8.23nN and molecules attached between tip and sample can be stretched and dissipated energy is 5.19E^{-15}.

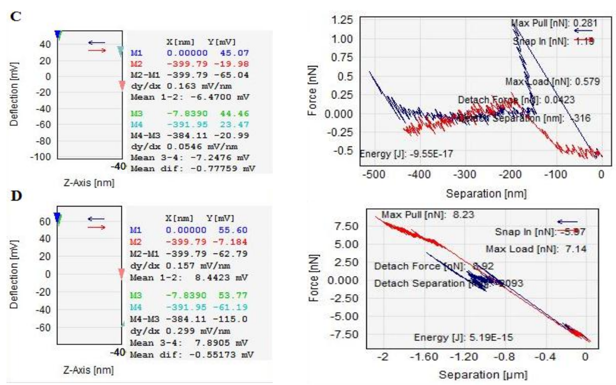

Figure 5: Force versus distance curve for PAN based solutions in forward direction C) PAN nanofiber D) PAN thin film.

Measurement of Force versus Distance curve comparison for the su-8 2050 nano fiber and thin film

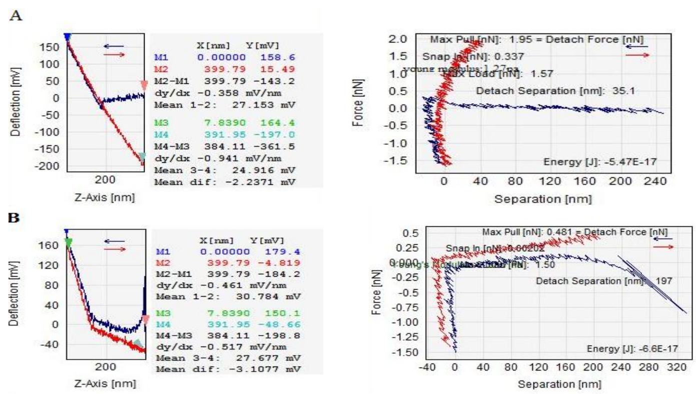

Figure 6: Force versus distance curve for SU-8 based solutions in reverse direction A) SU-8 nanofiber B) SU-8 thin film.

In fig 6 (A) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber in this case could be measured the stiffness at 1.27P_a value. The maximum load will contain the maximum force value at 1.57nN for this curve, to align all curves in the force volume image to have the 0.0337nN value for Snap in force and in this plot detach separation will contain separation values at the detected detach 35.1nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 1.95nN and molecules attached between tip and sample can be stretched and dissipated energy is -5.47E^{-17}.

In fig 6 (B) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber in this case could be measured the stiffness at 0.0037P_a value. The maximum load will contain the maximum force value at 0.481nN for this curve, to align all curves in the force volume image to have the 1.50nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach 197nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 1.59nN and molecules attached between tip and sample can be stretched and dissipated energy is -6.6E^{-17}

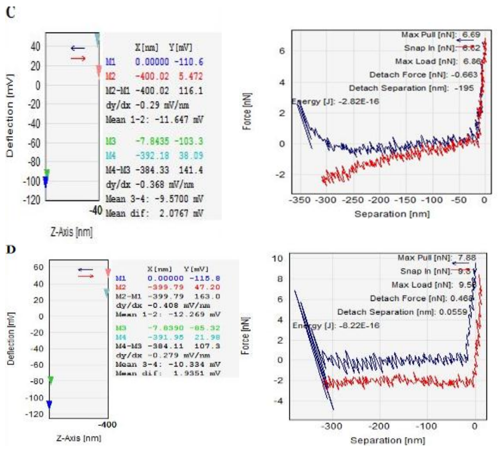

Figure 7: Force versus distance curve for SU-8 based solutions in forward direction C) SU-8 nanofiber D) SU-8 thin film

In fig 7 (C) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber. The maximum load will contain maximum force value at 6.86nN for this, to align all curves in the force volume image to have the 9.5nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach -195nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 6.69nN and molecules attached between tip and sample can be stretched and dissipated energy is -2.82E^{-16}.

In fig 7 (D) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber. The maximum load will contain maximum force value at 9.56nN for this, to align all curves in the force volume image to have the 9.51nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach 0.0559nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 7.88nN and molecules attached between tip and sample can be stretched and dissipated energy is -8.22E^{-16}.

Measurement of Force versus Distance curve comparison for the Polyvinylpyrrolidone (PVP) nano fiber and thin film

In fig 8 (A) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber in this case could be measured the stiffness at 0.0153P_a value. The maximum load will contain the maximum force value at 1.77nN for this curve, to align all curves in the force volume image to have the 0.411nN value for Snap in force and in this plot detach separation will contain separation values at the detected detach 106nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 1.02nN and molecules attached between tip and sample can be stretched and dissipated energy is -1.92E^{-17}.

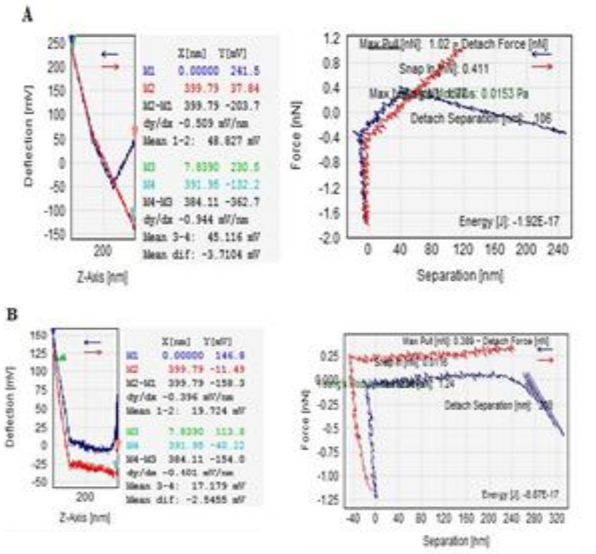

Figure 8: Force versus distance curve for PVP based solutions in reverse direction B) PVP nanofiber B) PVP thin film

In fig 8 (B) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber in this case could be measured the stiffness at 0.00233P_a value. The maximum load will contain the maximum force value at 1.244nN for this curve, to align all curves in the force volume image to have the 0.0116nN value for Snap in force and in this plot detach separation will contain separation values at the detected detach 208nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 0.389nN and molecules attached between tip and sample can be stretched and dissipated energy is -8.87E^{-17}.

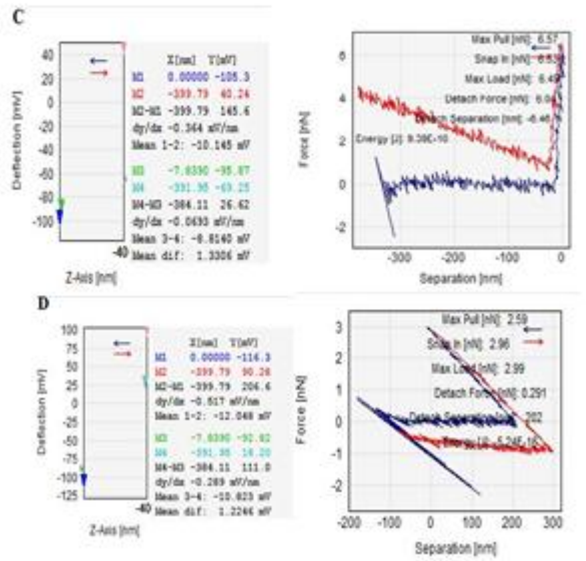

Figure 9: Force versus distance curve for PVP based solutions in forward direction C) PVP nanofiber D) PVP thin film

In fig 9 (C) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber. The maximum load will contain maximum force value at 6.49nN for this, to align all curves in the force volume image to have the 6.53nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach -6.46nm on the retract curve. When the cantilever is pulled away from the surface, adhesion force can be measured at 6.57nN and molecules attached between tip and sample can be stretched and dissipated energy is 9.39E^{-16}.

In fig 9 (D) Force versus Distance curve is plotted to refer as force curve. Here by applying force with 20nN on the nanofiber. The maximum load will contain maximum force value at 2.99nN for this, to align all curves in the force volume image to have the 2.96nN value for Snap in force and in that plot detach separation will contain separation values at the detected detach 202nm on the retract curve. When the cantilever is

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pulled away from the surface, adhesion force can be measured at 2.59nN and molecules attached between tip and sample can be stretched and dissipated energy is -5.24E^{-16}.

Comparison of strength of nanofibers and diameter for various polymer solutions

Table 2: Comparing nanofibers strength and diameter for various polymer solutions

Solutions	Diameter	Nanofiber strength	Stiffness of the thin film
PAN	884nm	0.011119Pa	0.67Pa
SU-8 2050	683nm	1.52Pa	0.0037Pa
PVP	983nm	0.0152pa	0.0024Pa

CONCLUSION

The mechanical characterization method presented here can be applied to a PAN, SU-8 2050 and PVP solutions of nanofibers. Depending on the type of material, rpm, applied voltage in electro spun, length and size of the fibers will vary here force spectroscopy is experimental method used to find the mechanical properties of the sample such as elastic modulus, stiffness of the thin film and strength of the nanofiber. So according to this experimental results SU-8 solution has a less diameter (i.e. 683nm) as compared to PAN (884nm) and PVP (983nm) solutions. However from the experimental data SU-8 2050 solution of nanofiber having a more strength at 1.52Pa, by applying force could be measured stiffness of the thin film of PAN solution of thin film have more stiffness at 0.67Pa as compared to other two solutions of PVP and SU-8 2050.

REFERENCES

[1] S.Chandra Sharma, Rajesh Vasita, K. Upadhyay Devendra, Ashutosh Sharma,S. Dhirendra Katti and R Venkataraghavan. Ind Eng Chem 2010;49:2731–2739.
[2] Nano glossary. Nanotechnology Task Force. Berlin: Federal Institute for Materials Research and Testing. 57(6), (2011), 837–845.
[3] RJ Young. Introduction to Polymers, Chapman, 1987;58:15.
[4] International Union of Pure and Applied chemistry IUPAC Gold Book, Ploymerization (2000).
[5] J Clayden, N Greevesand, S Warren. Organic Chemistry, Oxford University, 2012;5:412-22170.
[6] Alexander V Bazilevsky, Alexander L Yarin and Constantine M Megaridis. Langmuir 2007;23(5):2311–2314.
[7] Zeng, Xiaoyi, Xu, Xuesi, Chen, Qizhi, Liang, Xinchao, Bian, Lixin, Yang, Xiabin, Jing. J Control Rel 2003;92:227– 231.
[8] S Sinha-Ray, D Pelot, ZP Zhou, A Rahman, XF Wub and AL Yarin. J Mater Chem 2012;22:9138.
[9] Kamal Sarkar, Carlos Gomez, Steve Zambrano, Michael Ramirez, Eugenio de Hoyos, Horacio Vasquez, Karen Lozano. 2011;13:1-60.
[10] K Lozano, and K Sarkar. 2009;14(1):280-325.
[11] K Lozano, and K Sarkar. 2009;15(10):280-207.
[12] Z Jing, et al. J Control Rel 2003;92:227– 231.
[13] Dietmar W. Hutmacher and Paul D Dalton. Chemistry 2001;27:1- 201.
[14] A Ashraf Ali, GC Rutledge. J Mater Proc Technol 2009;209:4617–4620.
[15] JU Young-Wan, Gyoung-Rin Cho, Hong-Ryun Jung,Wan-Jin Lee. Electrochimica Acta 2008;53:5796–5803.