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Fabrication and Electrochemical Study of Fractal Polypyrrole

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Abstract: Fractal Polypyrrole actuators were fabricated by electrochemical deposition method. The fractal shapes of the actuators were controlled by the position and the shape of the counter electrode. Such fractal polypyrrole bend and revert in a regular direction upon electrochemical doping and undoping. Good reversibility was derived.
Key words: ploypyrrole, fractal, actuator

1. Introduction

Polypyrrole is an important member of intrinsically conducting polymers which can be prepared by electrochemical or chemical method. It was a stable polymer with excellent electrical, chemical, thermal, and mechanical retention [1~6]. Deposition of polypyrrole on mechanically inactive layers such as metals produces mechanical bending actuators which can be used as electrochemomechanical devices.[7~15] In addition, recent studies also exhibited that fractal polypyrrole can be used to mimic the actions of neutron connection such as nonlinear transmission and learning effect[16]. For such a study, the polypyrrole should be fabricated as a tree with two-dimensional (2D) or three-dimensional (3D) fractal dendrite morphology, whose connection and/or disconnection can be controlled with electric. In this report, we will show an electrochemical method for the fabrication of the fractal polypyrrole. The shape of the polypyrrole was controlled by the position and the shape of the counter electrode. Electrochemically induced actuation in the fractal poly-pyrrole/Au was also studied.

2. Experiments

Electropolymerization was performed in a two-electrode system on the basis of needle-circle electrolytic cell, consisting of a stainless steel needle(0.2mm in diameter) as anode or working electrode, copper plate as cathode or counter electrode with circle type, semicircle type and needle type (Figure 1). A working electrode of stainless steel needle (diameter of 0.2 mm) was set in the center of the cell and the tip of the needle electrode was kept close to the bottom of the cell.

The solution consists of 0.1 M monomer pyrrole, 0.1 M sodium dodecylbenzene sulfonate (DBS) as supporting electrolyte, and acetonitrile as solvent. The pyrrole monomer was distilled before using. The height of solution in the cell was controlled between 2 and 4 mm.

A glass lid was used to cover the cell to prevent the volatilization of solvent. At room temperature, the experiments were carried out under constant applied voltage (10V) supplied by a Electrochemical Station.

One piece of above fractal polypyrrole film was flaked away from the substrate and was deposited a 100nm-thicker gold film. Then the bilayer was connected to the potentiostat-galvanostat with conducting gel and sealed with epoxy resin. The movement of the polypyrrole/Au bilayer aroused by the doping/undoping process was recorded with a potentiostat-galvanostat (CHI Ins. Corp., USA) connected to a computer and a digital camera. Potentiostatic and potentiodynamic studies were carried out with a conventional three-electrode system in a 0.1M DBS^-Na^+ aqueous solutions. The voltage is between –1.0 V and 0.35V (vs Ag/AgCl) and the scan rate is 10mV/s. The free-end of the bilayer describes an angular movement around the fixed-end.

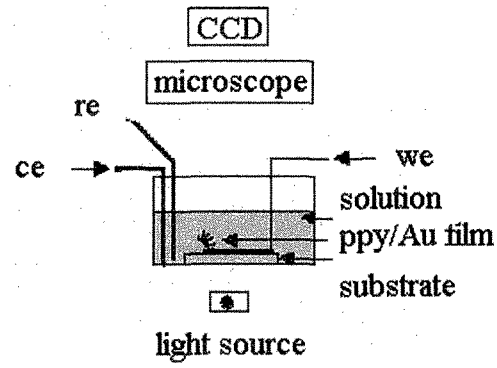

Fig 1: Experimental setup for the fabrication of fractal polypyrrole.

3. Results and discussions

3.1 Fabrication of fractal polypyrrole

The fractal patterned polypyrrole was electrodeposited with three kinds of counter electrodes, that is, circle, semicircle and needle counter electrodes. The pictures of the films were shown in Figure 2. Obviously, the morphology of the polypyrrole films depends on the shape of the counter electrodes.

When the circular counter electrode was used, the fractal polypyrrole film exhibits central radiation (Figure 2a). For the semicircular-type counter electrode, the polypyrrole film extended as semicircular radiation (Figure 2b). Apparently, the dependent of the shape of the fractal polypyrrole film on the electrodes comes from the distribution of the electric field. Normally the growth of fractal polypyrrole adopts the diffusion-limited-aggregation mechanism. Polypyrrole grows along the direction of the electric field. As a

Fig 2: The fractal morphology of polypyrrole films fabricated by using different type of counter electrode (a) circular; (b) semicircular (c) needle.

result, dendrite polypyrrole grows towards the counter electrodes. For the needle-type counter electrode, the situation is somewhat different. We found that polypyrrole also grew in the counter direction, whose morphology is exhibited in Figure 2c. Such an abnormal comes from the electric current induced magnetic influence on the fractal growth of polypyrrole. Due to the convection induced by the magnetic field, the fractal growth of polypyrrole holds several parallel branches apart from the electric field.

3.2 Electric actuation of fractal polypyrrole

There is no obvious response for the polypyrrole/Au bilayer during the first several cycles. However, after 20 times cyclic voltammetry (CV) cycles, the polypyrrole/Au bilayer began shrink/relax slowly but steadily. This action is in agreement with the finding in the polypyrrole fabricated by the onchip method [3] Such a phenomena was elucidated by the structure change during the first several cycles.[3]

Figure 3 shows the contract-extend movement of fractal polypyrrole/Au bilayer in response to a change in the applied voltage from –1.0 V to +0.35 V (top to bottom) after the first several CV cycles. During the oxidation process, the polypyrrole/Au bilayer contracted while during the reduction process the polypyrrole/Au bilayer extended to its original state. The angular movement rate was 0.5 rad/s when the scanning rate was 10 mV/s while it was 3 rad/s when the scanning rate reached 1 V/s, which is relatively slow comparing with the polypyrrole fabricated by the on chip method. [8] The decrease of the response speed of the fractal polypyrrole may be aroused by the diffusion-limited-aggregation which yield a higher degree of crosslinking (a tighter network), and thus the ability of the polymer to strain is reduced.

Figure 4 shows the voltammertric behavior of the polypyrrole/Au bilayer. Even after hundreds times dopping/undopping process the change of the voltammetric behavior of the polypyrrole/gold bilayer was still neglectable. So the dopping/undopping process and the contract/extend movement are reversible.

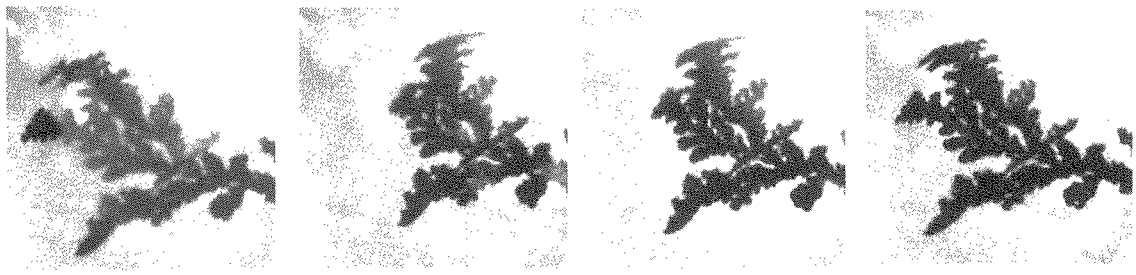

Fig 3: The contract-extend movement of the fractal polypyrrole/Au bilayer under the applied voltage from –1.0 to +0.35 V (top to bottom). The phenomenon is fully reversed upon return to –1.0V.

4. Conclusion

Fractal polypyrrole with different shapes was prepared by electrochemical method via a control of the counter electrodes. The bilayer of the fractal polypyrrole/Au shrinks and swells reversibly. As the fractal polypyrrole is neutron-like, it provided a good system for the mimic of the neutron connection. In addition, the contract-extend movement of the bilayer can be controlled at any stage through adjusting the applied voltage, it is anticipated that such kind of material may be applied for the study of the dynamic neutron interaction.

5. Acknowledgements

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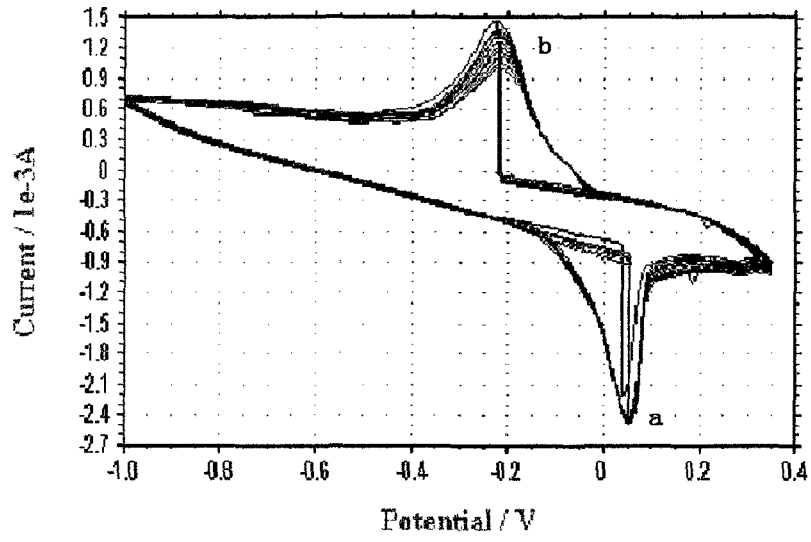

Figure 4: Voltammertric behavior of the fractal polypyrrole/Au bilayer in 0.1M DBS^-Na^+ aqueous solution. The voltage is between –1.0V and 0.35V and the scan rate is 10mV.s-1.

Reference

[1] R. H. Baughman; L. W. Shacklette; R. L. Elsenbaumer; E. J. Plichta; C. Becht, "Molecular Electronics", Ed. by P. I. Lazarev, (Kluwer, Dordrecht, Netherlands, 1991), pp267-289.
[2] Q. Pei; O. Inganas, *Synth. Met.*, 55-57, 3730(1993).
[3] E. Smela; O. Inganas; Q. Pei; I. Lundstrom, *Adv.Mat.* 5, 630, (1993); E. Smela; O. Inganas; Q. Pei; I. Lundstrom, *Science,* 261, 1119(1993).
[4] E. Smela; O. Inganas; I. Lundstrom, *J. Micromech. Microeng.*, 3,203(1993).
[5] A. P. Lee; K. C. Hong; J. Trevino; M. A. Northup, "Proceedings of the Dynamics Systems and Controls Division, Micro-Mechanical Engineering Congress and Exposition", Chicago, 1L, 6 to 11November 1994, C.J.Radcliffe, Ed.(American Society of Mechanical Engineers, New York, 1994), pp725-732.
[6] J. Rodriguez, H. J. Grande, T. F. Otero, "Conductive Polymers: Synthesis and Electrical Properties", Ed. by H. S. Nalwa, Handbook of Organic Conductive Molecules and Polymers, Vol. 2., John Wiley and Sons Ltd, Chichester, 1997, pp. 413–468
[7] I. W. Hunter and S. Lafontaine, IEEE Solid-State Sens. Actuator Workshop Tech. Dig. ,Hilton Head, SC, 22 to 25 June 1992, pp. 178-185.
[8] E. Smela; O. Inganas; I. Lundstrom, *Science*, 268, 1735(1995).
[9] G.Delapierre, *Sens. Actuators*, 17,123(1989).
[10] Kaneto, K.; Kaneko, M. ; Min, Y. ; MacDiarmid, A. G., *Synth. Met.*, 71, 2211 (1995).
[11] Jager, E. W. H.; Smela, E.; Inganas, O., *Science*, 290, 1540 (2000).
[12] Kaneko, M.; Kaneto, K., *React. Funct. Polym.*, 37, 155 (1998).
[13] Lee, A. P.; Hong, K. C.; Trevino, J.; Northrup, M. A., "Thin film conductive polymer for microactuator and micromuscle applications"; Micro-Mechanical Systems Symposium of the International Mechanical Engineering Congress and Exposition, Chicago, IL, 1994.
[14] Lewis, T. W.; Spinks, G. M.; Wallace, G. G.; De Rossi, D.; Pachetti, M., *Polym. Prepr.*, 38, 520 (1997).
[15] Madden, J. D.; Cush, R. A.; Kanigan, T. S.; Hunter, I. W., *Synth. Met.*, 113, 185 (2000).
[16] M. Fujii, T. T. Akahashi, H. Ihori, K. Arii, K. Y oshino, *Synth. Metals* 101, 397 (1999); M. Fujii, H. Ihori, K. Arii, *Thin Solid Films*, 393,393 (2001)

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