Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5602-5604

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18166

Preparation and Characterization of the Flexible Polypyrrole Film with High Density†

FENG CHEN and XIANGHONG PENG*

Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University, Wuhan 430056, P.R. China

*Corresponding author: Tel: +86 27 84226806; E-mail: pengxianghong103@163.com

AJC-15754

High density polypyrrole (Ppy) films show higher thermal deposition temperature and better electrochemical stability under long oxidative polarization. The high density polypyrrole films is usually synthesized at low temperature (-40 °C). In this paper, the high density polypyrrole film has been prepared by the two electrode method at room temperature by simple method. The structures and the morphologies of polypyrrole film are characterized by FTIR, Raman, TGA and SEM. The density and the cyclic voltammetry of polypyrrole film are measurement. The density of polypyrrole film is 1.17 g/cm^3 and 1.03 g/cm^3 with the current density of 1 and 5 mA/cm^2, respectively. The polypyrrole film can be folded 180° for 20 times without mark. The film exhibit a more homogeneous surface with semimicrosphere and cauliflower microspheres on the side. The cyclovoltametric curves show no peaks, indicating that the polypyrrole film is a kind of excellent electrode material in double-layer capacitance. The high density polypyrrole film with flexible may be potential applications in the field of the flexible supercapacitor electrodes.

Keywords: Polypyrrole, Electrode, Electrochemical method, Current density, Flexible.

INTRODUCTION

Polypyrrole (Ppy) is one of the most important conducting polymers which have been studied extensively in the last decades[1]. The unique structure and properties of polypyrrole provide the wide applications in the field of batteries, supercapacitors, microwave shielding and corrosion protection and so forth. However, polypyrrole is mechanically weak and insulating in its neutral state, polypyrrole usually composite with other materials to improve its flexible or electrochemical properties, including the carbon nanotube[2], oxidizable metals and carbon fiber[3,4]. The high density polypyrrole film expected a macroscopically compact and ordered structure, using as a functional conducting polymer with various physical properties. As reported, the high density polypyrrole film (1.4 g/cm^3) usually synthesis at low temperature (-40 °C) and low current density in the presence of PF_6^- by electrochemical method[5]. Most of the density of polypyrrole film are from 0.6-0.8 g/cm^3 through electrochemical method at room temperature under high current density. The high density polypyrrole films show higher thermal deposition temperature and better electrochemical stability under long oxidative polarization. In this work, the high density polypyrrole film with flexible was synthesized at room temperature, such thermal stability of polypyrrole films would be an excellent flexible supercapacitor electrodes.

EXPERIMENTAL

Pyrrole monomer was purchased from Aladdin Company. Other chemical reagents were commercially obtained from China.

Preparation of the polypyrrole film: The polypyrrole film was prepared by a two-electrode cell, using FTO electrode as a working electrode and the counter electrode. The FTO sheet with a surface area of 1 cm × 1 cm was placed 2 cm apart. FTO electrode was washed with double-distilled water and ethanol. The two electrodes were fixed in 50 mL beaker in an acetonitrile/water (99/1) solution of 0.3 mol/L pyrrole and 0.1 mol/L *p*-toluenesulfonic acid. Polypyrrole film was formed on the FTO under 1 and 5 mA/cm^2 at room temperature for 1 h by DC power supply (MPS-6003L-1, China).

Fourier transform infrared spectroscopy (FTIR) of polypyrrole film was recorded on a TENSOR 27 spectrometer (BRUKER OPTICS, Germany) in a range from 4000-400 cm^{-1}. Thermal gravimetric analysis (TGA) was conducted on TG209 F3 (NETZSCH, Germany) under nitrogen protection at a heating rate of 20 °C min^{-1} from 50-700 °C. The morphologies of polypyrrole film were characterized by scanning electron microscope

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

(VEGA 3, TESCAN). The polypyrrole film was tailor into a rectangle, using calipers to measure the length, width and thickness to calculate the volume, then the density value was calculated by the weight and the volume of polypyrrole film. Each sample was measured three times, taking the average value. Raman spectra were recorded on a RM 2000 microscopic confocal Raman spectrometer (Renishaw, England) employing a 785 nm laser beam and a charge coupled device detector with 1 cm^{-1} resolution. The modified carbon paste electrode was fabricated as following: 10 mg crushed polypyrrole film, 90 mg graphite powder and 19 μL paraffin oil was mixed to form a uniform mixture, then the carbon paste was packed into the cavity of empty carbon paste electrode (d = 3 mm). The resulted electrode was polished manually on a piece of weighting paper to get a smooth surface which was denoted as CPE. Cyclic voltammetry (CV) measurements were performed at a PARSTAT 4000 (AMETEK Inc.) electrochemical workstation connected to a conventional three-electrode cell, including a CPE working electrode, a saturated calomel reference electrode (SCE) and a Pt wire counter electrode. 0.2 mol/L phosphate buffer (PBS) was selected as the supporting electrolyte. The results obtained by the following formula[2]

$$C = \frac{Q}{m\Delta U} = \frac{I\Delta t}{m\Delta U} = \frac{I}{mv}$$

All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

The FTIR spectra of polypyrrole film are shown in Fig. 1. The peak at 1508 cm^{-1}(-C=C-) and 1408 cm^{-1} (-C-N-) are assigned to the asymmetric and symmetric stretching vibration of the polypyrrole, respectively. The peak at 698 cm^{-1} belongs to C-H ring-wagging vibration of the polypyrrole ring[6]. Raman spectra are shown in the Fig. 2, the Raman spectra of polypyrrole include the peaks at 977, 1050, 1350 and 1578 cm^{-1}[7,8]. The small peaks near 977 and 1050 cm^{-1} have been associated with the polaron structure. the broad peak snear 1350 and 1578 cm^{-1} should correspond to ring stretching mode of the polymer backbone and conjugated structure, respectively[7,8].

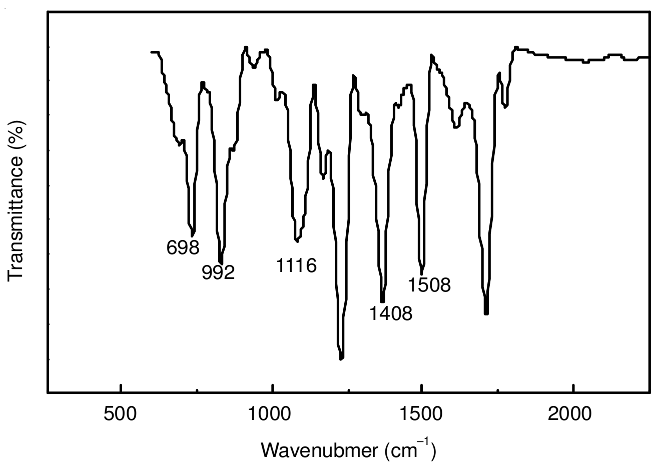

Fig. 1. FTIR spectrum of polypyrrole film

Thermal properties of polypyrrole film: The TGA curves of the polypyrrole film with the current density of 1 and 5

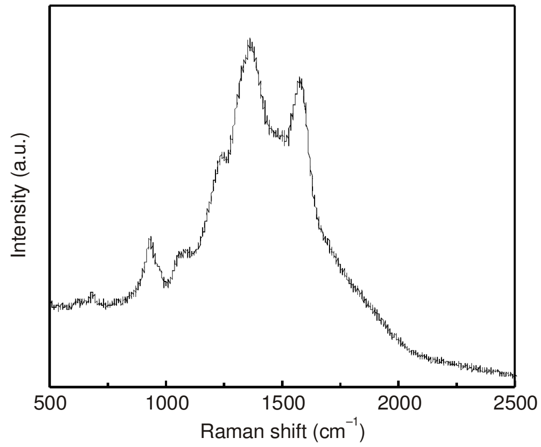

Fig. 2. Raman spectrum of polypyrrole film

mA/cm^2 are shown in Fig. 3. The first weight lose of polypyrrole film is caused by removing dopant and the second weight lose correspond the polymer degradation. The weight loss of polypyrrole film are about 23.19 and 29.23 % under 1 and 5 mA/cm^2current density, respectively, indicating that the film synthesis at 1 mA/cm^2 own good thermal stability. The density of the polypyrrole film is 1.17 and 1.03 g/cm^3 with the current density of 1 and 5 mA/cm^2, respectively. As reported, the density of polypyrrole film is usually from 0.6 to 0.8 g/cm^3 by electrochemical method, the high density polypyrrole film is 1.4 g/cm^3 with current density of 0.02-0.05 mA/cm^2 at -40 ºC temperature[5]. In this work, the high density polypyrrole films have been synthesized at room temperature.

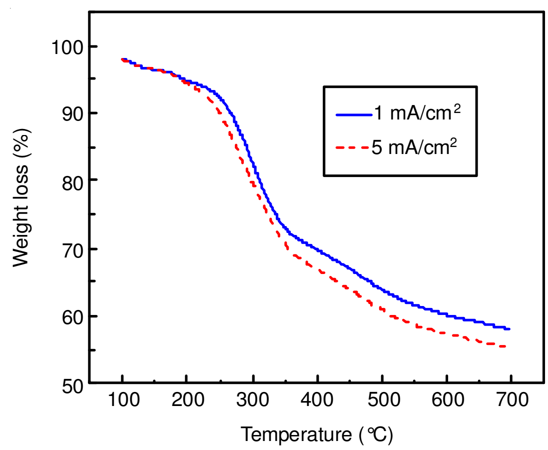

Fig. 3. TGA curves of polypyrrole film

Morphologies and flexible of polypyrrole film: The SEM images of polypyrrole film are shown in Fig. 4. The surface of polypyrrole film exhibited a more homogeneous and semimicrosphere with compact layer (Fig. 4a). The magnified image of a semmicrosphere indicate there exhibit the complex density polypyrrole layer which benefit for the flexible properties of film, as shown in Fig. 4b. In the initial polymerization, a small amount of water can influence the formation of the intermediate cation and reduce the amount of the dissolved intermediate polypyrrole. The water also reduces rejection between the intermediate cation and makes pyrrole form orderly pile molecular chain. So the pyrrole is assembled to form the semimicrosphere in an acetonitrile/water (99/1) solution. At the edge of the film, the pyrrole monomers can be grown in three-dimensional space to form cauliflower dendritic protrusions (Fig. 4c).

It is observed that polypyrrole film show no folding traces when the film is folded 180º for 20 times, as shown in Fig. 4d. After bending 100 times, the film shows little breaking trace. The result indicates that the film has excellent flexibile properties which can be folded by large angle or strength. The flexible material has the potential application for the flexible supercapacitor electrode. The flexible properties of polypyrrole film due to its homogeneous surface and high density.

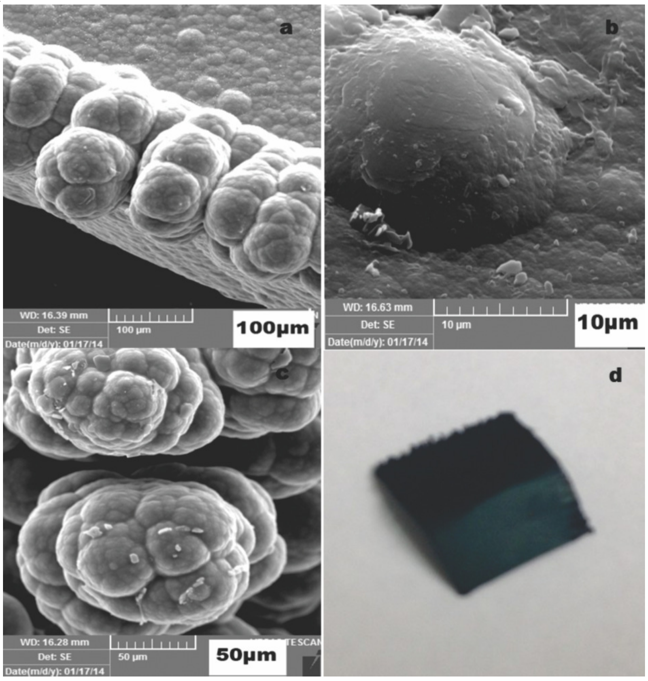

Fig. 4. SEM images of polypyrrole film (a-c), (a) the surface of film, (b) magnified image of a semimicrosphere, (c) the edge of the film, (d) the photo of polypyrrole film bending for 100 times

Cyclic voltammetry of polypyrrole film: The typical rectangle-like shape of all the cyclic voltammetric curves in Fig. 5 measured at the same scan rate (50 mV s^{-1}) in 0.1 M KCl solution. There exhibit the obvious faraday current in polypyrrole film. Compare with the current density of 1 mA/cm^2, there exhibits more faraday current at 5 mA/cm^2 because the pyrrole monomers adsorb on the polypyrrole film surface. The curves at different scan rates show no peaks, indicating that the electrode is double-layer capacitance over the complete voltammetry cycle. It is reported that the highest specific capacitance of the composites of polypyrrole/manganese dioxide/polypropylene fibrous films is about 110 F g^{-1} [9] and 73.7 F g^{-1} for γ-MnO_2[10]. The mass specific capacitance (Cm) of the composite can reach 103.1-98.2 F g^{-1}. It has potential for electrode.

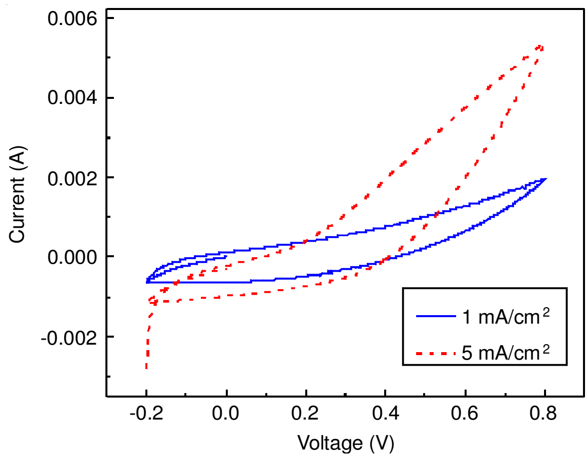

Fig. 5. Cyclic voltammetry of the polypyrrole film

Conclusion

The high density of polypyrrole with 1.17 g/cm^3 has been successfully prepared at room temperature. The polypyrrole film was folded 180º for 20 times without folding mark. The film exhibited a more homogeneous surface with semimicrosphere and cauliflower microspheres on the side. The cyclic voltammetric curves indicated the polypyrrole film was a kind of excellent electrode material in double-layer capacitance. In the next works, we will prepare composite film by the high density polypyrrole with other materials to improve the performance of the prepared electrode, including the manganese dioxide, carbon nanotubes, *etc*.

ACKNOWLEDGEMENTS

This work was supported by the Foundation of Science and Technology Bureau of Wuhan (2014010101010016 and 201250499145-3) and the Opening Project of Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University (JDGD-2013-13).

REFERENCES

1. F. Fusalba and D. Bélanger, *J. Phys. Chem.*, **103**, 9044 (1999).
2. X. Lu, H. Dou, C. Yuan, S. Yang, L. Hao, F. Zhang, L. Shen, L. Zhang and X. Zhang, *J. Power Sources*, **197**, 319 (2012).
3. L. Santos, P. Martin, J. Ghilane, P.C. Lacaze and J.C. Lacroix, *ACS Appl. Mater.*, **5**, 10159 (2013).
4. R.A. Davoglio, S.R. Biaggio, N. Bocchi and R.C. Rocha-Filho, *Electrochim. Acta*, **93**, 93 (2013).
5. C.O. Yoon, H.K. Sung, J.H. Kim, E. Barsoukov, J.H. Kim and H. Lee, *Synth. Met.*, **99**, 201 (1999).
6. L. Cai, *J. Chinese Ceramic Soc.*, **41**, 451(2013).
7. J. Mikat, I. Orgzall and H.D. Hochheimer, *Phys. Rev. B*, **65**, 174202 (2002).
8. S. Demoustier-Champagne and P.Y. Stavaux, *Chem. Mater.*, **11**, 829 (1999).
9. M. Jin, G. Han, Y. Chang, H. Zhao and H. Zhang, *Electrochim. Acta*, **56**, 9838 (2011).
10. A. Bahloul, B. Nessark, E. Briot, H. Groult, A. Mauger, K. Zaghib and C.M. Julien, *J. Power Sources*, **240**, 267 (2013).