Flexible Carbon Cloth Based PPy-Ag Nanoparticles Composite Film for Supercapacitors

Bo Gao, Dapeng Wang, Nan Qu and Chengai Zhao*
Department of Resources and Environment, Jilin Agriculture University, Changchun, China
*Corresponding author e-mail: wendy@jlau.edu.cn

Abstract. Polypyrrole-Ag nanoparticles composite film was prepared based on flexible carbon cloth as substrate using silver nitrate as oxidizing agent through simple one-pot chemical synthesis method. The composite sample was characterized by scanning electron microscopy, X-ray diffraction, cyclic voltammetry and galvanostatic charge-discharge techniques. The electrochemical measurements showed such an electrode had a specific capacitance of 257 F g⁻¹ and good cycle stability at a discharge current density of 1 A g⁻¹. The composite electrode also had a wide working potential window, which can be applied in the field of power energy storage devices.

1. Introduction
Recently, lots of attentions have been paid to conductive polymers because of their unique potential applications in many fields such as power sources, electronic devices and sensors [1-3]. They are good candidates for constructing supercapacitor electrodes because of their high pseudo capacitors based on the redox reaction between the electrode surface and electrolytes. Now, the most frequently used conductive polymers such as polyaniline (PANI), polythiophene and polypyrrole (PPy) have been used as electrode materials for supercapacitors [4, 5]. Furthermore, deposition of metal particles, such as highly conductive noble metals [6, 7], on the conductive polymers will enhance the conductivity of polymers, which can meet the requirements for electrode materials.

Carbon materials, as electrochemically active materials, are good candidates as supporting skeletons for supercapacitors [8, 9]. In this sense, flexible carbon cloth (CC) sheets not only have a high specific surface area but also have an excellent 3D conductive skeleton, which support a high electrolytic accessible surface area of electrochemical active materials and a direct path for electrons. Here, we used silver nitrate as oxidizing agent to deposit PPy onto the surface of CC through one-pot in situ chemical synthesis. Meanwhile, during the reaction process, silver cations were reduced to silver nanoparticles and formed PPy-Ag composites on the surface of CC (PPy-Ag/CC).

2. Experimental
2.1. Materials and reagents
Prior to the sample preparation, a pyrrole monomer was distilled and stored at 4°C. Silver nitrate and hydrochloric acid (analytical purity) were used as received. A commercially available carbon cloth (CC) (Jilin Shuang Peng carbon cloth factory) was used as the supporting material for PPy. For control
experiment, a CC sheet with dimensions of 10mm×10mm×1.0mm was treated in 25% hydrochloric acid at 40°C for 30min, cleaned successively in acetone and deionized water until neutral and dried at 50°C for 5h.

2.2. Sample preparation
To prepare the electrode sheet of PPy-Ag/CC material, 350μL of pyrrole and 0.85g of silver nitrate were, respectively, dissolved into 50mL of deionized water by magnetic stirring for 10min. Then 1mL of pyrrole and 1mL silver nitrate solution were carefully transferred into a centrifugal tube containing a piece of pre-treated CC. The reaction was kept for different periods of time at room temperature and then the PPy-Ag/CC sample was washed with deionized water and dried at 50°C for 3h.

2.3. Instruments and measurements
The morphology of the PPy-Ag/CC composite was characterized by a field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, and Japan) at 5kV. The crystallinity of the nanocomposites was analyzed X-ray powder diffraction (XRD, SHIMADZU XRD-6000) on a Ni-filtered Cu-Kα radiation at 40kV and 200mA with the 2θ ranging from 10° to 80° and a step scan rate of 15°min⁻¹. Electrochemical experiments were carried out in a three-electrode system with a CHI 660D electrochemical workstation with PPy-Ag/CC (10mm×10mm) as working electrode, platinum sheet as auxiliary electrode and Hg/Hg₂Cl₂ electrode (SCE) as reference electrode. 0.5M K₂SO₄ was used as electrolyte. Cyclic voltammetry (CV) was carried out in a potential range of -0.2~1.2V at varying scan rates. Galvanostatic charge/discharge (GCD) curves were demonstrated at step increasing current densities with the cutoff voltage of 0.9V. The battery testing system (Neware) was used to measure the cycle life of the sample with the cycle times of 1000. In order to eliminate O₂ in the electrolyte, the K₂SO₄ solution was charged pure N₂ for 5min before the electrochemical measurements.

3. Results and discussion
The CC sheet is important to accelerate the reaction between silver nitrate and pyrrole, which is proved by a parallel experiment without adding CC to the system. As a result, there was no remarkable reaction taking place even after 24h, which demonstrates that CC may act as catalyst in the experiment.

![Figure 1](image-url)

*Figure 1.* (a) SEM image of blank CC; (b) SEM image of PPy-Ag/CC composites; (c) TEM image of PPy-Ag/CC composites; (d) SEM image of intertwined CC fibers.
The SEM images of the CC modified before and after reaction are shown in Fig. 1a and Fig. 1b, insets of which are the magnification of the surface of CC fibers. We can see that the fibers of blank CC sheet have a smooth surface with some fine grooves before modification. After modification, the fibers of CC sheet are coated with a rough layer, as shown in Fig. 1b. From inset of Fig. 1b, a large number of nanoparticles deposited uniformly on the CC sheet skeleton are observed. Fig. 1c shows the TEM image of PPy-Ag composites, from which the Ag and PPy components can be easily identified. The Ag nanoparticles are entrapped or anchored in the PPy particles except for some bigger Ag particles. These CC fibers intertwine with each other to form a 3D highly porous structure (Fig. 1d), which is in favor of the transport of electrons and ions in the supercapacitor devices.

![XRD patterns of blank CC and PPy-Ag/CC composites.](image)

**Figure 2.** XRD patterns of blank CC and PPy-Ag/CC composites.

Fig. 2 displays XRD patterns of blank CC and PPy-Ag/CC composites. The crystalline peaks of CC sheet are a broad peak at 16.2° and 31.7°, which is coincident with the characteristic peak of amorphous PPy according to the literature [10, 11]. Therefore, we cannot see the characteristic peak of PPy. Through the XRD pattern of PPy-Ag/CC composites, four diffraction peaks at 2θ = 38.1°, 44.2°, 64.3°, 77.4° are obvious, which are corresponding to Bragg’s reflections from (111), (200), (220) and (311) planes of Ag (JCPDS-0783). The above results confirm that Ag⁺ cations act as oxidant to pyrrole and reduced to be Ag during the reaction process.
Figure 3. (a) Cyclic voltammograms of blank CC (curve 1) and PPy-Ag/CC composites (curve 2) with the reaction time 9h at a scan rate of 25 mVs\(^{-1}\) in 0.5M K\(_2\)SO\(_4\). (b) Cyclic voltammograms of PPy-Ag/CC composites with the reaction time 9h at a scan rates of 25, 50, 75 and 100 mV s\(^{-1}\) (curves 1 to 4).

In order to check the oxidation and reduction potentials and the effect of Ag nanoparticles on the electrochemical performance, CV analysis was carried out. Fig. 3a shows the CV curves of the blank CC and the PPy-Ag/CC composites in 0.5M K\(_2\)SO\(_4\) electrolyte at a scan rate of 25mVs\(^{-1}\). Two pairs of strong redox peaks are visible for PPy-Ag/CC, but no well-defined peaks are observed in the case of blank CC. The pairs of redox peaks located at 0.28V, 0.78 V and 0.57V, 0.91V are probably owing to the reduction and oxidation of Ag [12], which proves the presence of Ag in the composite. Fig. 3b exhibits the CV curves of the composite electrode at different scan rates. With the scan rate increasing, the current density increases and the redox peaks shift slightly. At higher scan rate, the electrolyte ions only approach the external surface of the composite electrode, which leads to the shifts of the redox peaks.

Figure 4. (a) The GCD curves of PPy-Ag/CC composites electrode obtained at the reaction time (1) 6h, (2) 9h, (3) 12h and (4) 15h at the current density of 1 A g\(^{-1}\) in 0.5M K\(_2\)SO\(_4\). (b) The GCD curves of PPy-Ag/CC composites electrodes with the reaction time 9h at increasing current densities of 1, 2, 5, 10 A g\(^{-1}\).

Fig.4a shows the GCD curves of the PPy-Ag/CC composites electrodes prepared with different periods of time. The specific capacitance (\(C_m\)) can be calculated with (1) [13] below:
\[
C_s = \frac{C}{m} - \frac{I \Delta t}{\Delta V m}
\]  

Where \( C_m \) is the specific capacitance in F g\(^{-1}\), \( I \) is the charge-discharge current in A, \( t \) is the discharge time in s, \( \Delta V \) is potential drop during discharge in V and \( m \) is the mass of active material in g. The calculated \( C_m \) of the electrodes prepared under 6, 9, 12 and 15h was 167, 257, 67 and 33 F g\(^{-1}\), respectively. We can see that the electrode prepared with the reaction time 9h had the largest \( C_m \) value. However the \( C_m \) value instead decreased with longer reaction time as well as more active materials grown on the surface of CC, which may be due to the fact that excessive deposition of active materials will impede the transport of electrolyte ions into the electrodes greatly. Furthermore, we explore the charge-discharge capability of the PPy-Ag/CC composites electrode with the reaction 9h. Fig. 4b shows the discharge curves at different discharge current of 1, 2, 5, 10 A g\(^{-1}\) and the corresponding \( C_m \) value are 257, 110, 35, 13 F g\(^{-1}\), respectively. A conclusion can be reached that the specific capacitance decreased as the discharge current density increasing for the PPy-Ag/CC composites electrode.

An important factor for the PPy-Ag/CC composites electrode is the cycle stability subjected to long-term charge-discharge cycles. Fig. 5 shows the specific capacitance of PPy-Ag/CC composites with the reaction time 9h at a discharge current density of 1 A g\(^{-1}\) in 0.5M K\(_2\)SO\(_4\) electrolyte for 1000 cycles. PPy-Ag/CC composites electrode exhibits good cycling behavior. Compared with the initial \( C_m \) value 257 F g\(^{-1}\), it decreased to 206 F g\(^{-1}\) in the first 350 cycles and kept nearly the same in the subsequent 650 cycles. The initial 19.8% decline of \( C_m \) value may be due to the loss of unstable PPy-Ag composites during the intercalating/deintercalating process of electron and electrolyte ions.

**Figure 5.** Variation of specific capacitance as a function of cycle number for the PPy-Ag/CC composites electrode in the 0.5M K\(_2\)SO\(_4\) electrolyte at a discharge current density of 1 A g\(^{-1}\).  

4. Conclusion
In summary, the direct-grown of PPy-Ag composites on the CC substrate was successfully obtained through one-pot *in situ* chemical polymerization. Nanoparticles on the surface of CC were observed by SEM. XRD patterns and CV curves proved the existence Ag in the composite. The PPy-Ag/CC composites electrode exhibits wide operated potential window of 1.2V in the electrolyte of K\(_2\)SO\(_4\) and achieves specific capacitance of 257 F g\(^{-1}\) at a discharge current density of 1 A g\(^{-1}\). Such an electrode also exhibits good electrochemical cycle stability with about 80% initial specific capacitance remained after 1000 continuous cycles.
Acknowledgments
This work was financially supported by Jilin Provincial Education Department Foundation (Grant No. JJKH20170293KJ); Doctor Foundation of Jilin Agriculture University (Grant No. 2015032).

References
[1] T. F. Otero, I. J. Cantero. Power Sources. 81 - 82 (1999) 838 - 841.
[2] M. Bazzaoui, E. A.Bazzaoui, L.Martins, J. I.Martins. Synth. Met. 130 (2000) 73 - 83.
[3] J. O.Iroh, W. J.Su. Appl. Polym. Sci. 71 (1999) 2075 - 2086.
[4] Z. L.Wang, R.Guo, L. X.Ding, Y. X.Tong, G. R.Li. Sci. Rep. 3 (2013) 1204 - 1211.
[5] G.Wang, L. Zhang, J.Zhang. Chem. Soc. Rev. 41 (2012) 797 - 828.
[6] W.Chen, C. M.Li, P.Chen,C. Q.Sun.Electrochim.Acta. 52 (2007) 2845-2849.
[7] W.Zhao, H.Wang, X.Qin,X.Wang, Z.Zhao, Z.Miao, L.Chen, M.Shan, Y.Fang, Q.Chen. Talanta. 80 (2009) 1029 - 1033.
[8] Y. G.Wang,H. Q.Li,Y. Y.Xia. Adv. Mater. 18 (2006) 2619 - 2623.
[9] D.Zhang, X.Zhang, Y.Chen, P.Yu, C.Wang,Y.Ma.J. Power Sources. 196 (2011) 5990-5996.
[10] L.Seo, M.Pyo, G.Cho. Langmuir. 18 (2002) 7253 - 7257.
[11] H.Mi, X.Zhang, X.Ye, S.Yang.J. Power Sources. 176 (2008) 403 - 409.
[12] J. K.Gan,Y. S.Lim,N. M.Huang,H. N.Lim. RSC Adv. 5 (2015) 75442 - 75450.
[13] A. K.Mishra,S.Ramaprabhu. J. Phys. Chem. C 115 (2011) 14006 - 14013.