In-situ Polymerization of Carboxyl-functionalized Graphene Oxide and Polyaniline Composites for Supercapacitor

Zhao Xia Hou[1, a] , Si Ming Li[1], Lin Li[1], Hai Bo Long[1], Mei Han Wang[1]

[1]*Liaoning Province Key Laboratory of New Functional Materials and Chemical Technology, School of Mechanical Engineering, Shenyang University, Shenyang 110044, China*

[a]luckyxia2007@126.com

Keywords: Graphene oxide, Polyaniline, Composites, Carboxyl-functionallization, Electrochemical performance.

Abstract. Carboxyl-functionallized graphene oxide and polyaniline composites (FGO/PANI) were fabricated by in-situ polymerization method. The microstructure, morphology and electrochemical performance were characterized. Graphene oxide/polyaniline composites (GO/PANI) are short rod-like and agglomerate severely. PANI in FGO/PANI appeares long and thin rod and dispersed uniformly. Some of the –C-O-C– are converted to –OH by HBr and –OH connverts to COOH– by oxalic acid. The specific capacitance of FGO/PANI（297 F/g）is higher than GO/PANI (226 F/g). The charge transfer resistance of GO/PANI was reduced after carboxyl-functionallization.

Introduction

A large amount of research have been made on graphene-based or graphene-derived materials as electrodes in supercapacitors due to the reasonably high electrical conductivity[1-3]. Graphene oxide (GO) is of the similar structure with graphene, in addition, a lot of active functional groups are distributed in its surface, it is considered a functional graphene as an important derivative of traditional graphene. At present, many functional groups such as polylysine, amine, polyamide, porphyrin and fullerene have been grafted on graphene oxide or graphene. The grafting of these functional groups has made the application of graphene more widely, and carves out a new way for the development of future energy.

Carboxyl group, as an important functional one in organic synthesis, is a precursor of the preparation of many organics by the acylation, esterification and ammoniation. In the functionalization of GO, carboxyl groups can be used to further introduce the active groups of biomolecules, macromolecules and small molecules into graphene. It is found that, carboxyl is mainly in GO layer flat edge position[4], and the epoxy groups and hydroxyl mainly exist in the graphene oxide layer plane, most of the preparation of graphene/ polyaniline (PANI) composites[5-7] ignore the –OH and –O– in the plane, and just use the carboxyl in the edge of the lamella, this may cause PANI to move around the graphene sheet and result in incomplete and unstable composition. Adoption of a certain functional approach to the epoxy and hydroxyl groups in the plane of GO into carboxyl, then compositing with PANI, can make the PANI conductive polymers order and stable in the graphene surface.

Experimental

Chemicals. All reagents used in this work are analytical grade. Graphite powder were purchased from Tianjin Ruijinte Chemical Reagent Company. Aniline(An), oxalic acid, ammonium persulfate (APS), hydrobromic acid were purchased from Tianjin Bodi Chemical Engineering Corporation.

Synthesis of FGO. GO was prepared by a modyfied Hummers method. Tipically, HBr was added to 1 mg/mL GO suspension with constant stirring at 90 ℃ for 12 h. 1.0 g, 1.5 g or 2.0 g oxalic acid were added to the mixture and continuously stirred at 90 ℃ for 4 h, respectively. Suspension were centrifuged and washed to neutral, and then dried at 60 ℃ for 12 h. Samples were marked as FGO_1, FGO_2 and FGO_3, respectively .

Synthesis of FGO/PANI composites. Tipically, APS and FGO_3 were added to 100 mL of 1 mol/L HCl and stirred for 2 h, respectively. An was added to FGO_3 suspension. And then, APS solution was droped to the FGO_3 suspension with stirring and keep reacting for 0.5 h. The resultant mixture solution was ultrasonicly treatment for 10 min and washed consecutively to neutral with deionized water. Finally, the FGO_3/PANI composites were dried at 60 °C for 12 h. Sample marked as FGO_3/PANI.

Preparation of the electrode. PANI, GO/PANI and FGO_3/ PANI acted as active materials to prepare the electrode, respectively. The mass ratio of active materials: binder (PTFE) is 90:10. The electrode dried at 120 °C for 12 h. The two-electrod system was assemblied with a cellulose paper as separator, carbon fibre paper as current collector and 1M H_2SO_4 aqueous as electrolyte.

Characterization. X-ray diffraction (XRD) was analyzed by a PW3040/60 X'Pert Pro MPD XRD (PANalytical) with Cu Kα radiation ($λ = 0.15444$ nm) at 40 kV and 40 mA with 5°/min from 5° to 80°. Foutier transform infrared spectrometer (FT-IR) was recorded with Bruker IFS 55 FT-IR spectrometer at room temperature from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}, KBr powder pellet. The microstructure was observed by an S4800 Scanning Electron Microscope (SEM, Hitachi, Tokyo, Japan). All the electrochemical performance was studied on a PARSTART 2237 electrochemical workstation(China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out in a two-electrod system with 1M H_2SO_4 aqueous electrolyte. CV were conducted within the potential range of 0~0.8 V at a scan rate of 5, 10, 25, 50, 100 and 200 mV/s. The frequency limits were typically set from 0.01 Hz~100 kHz with a voltage amplitude of 5 mV.

Results and Discussion

Microstructure and morphology analysis. XRD patterns of graphite and GO are shown in Fig. 1 (a) and XRD patterns of PANI, GO/PANI and FGO_3/PANI are shown in Fig. 1 (b). Graphite shows its characteristic peaks around 26.6 ° and 54.5 °, contributed to (002) and (004), respectively. A broad peak around 11 ° and a weak peak around 43 ° are observed in GO, contributed to (001) and (100). These peaks indicate that oxidative groups and H_2O molecules have been inserted into the interlayer of the graphite.

Diffraction peaks around 25.4 °, 20.5° and 14.9 ° are corresponding to the characteristic peaks of PANI at (200), (020) and (011), respectively. The peaks of PANI are stronger than GO/PANI and FGO_3/PANI, which indicates the degree of structural order decreases after composition. While the degree of structural order of FGO_3/PANI is better than GO/PANI. The diffration peaks of GO can not be observed in Fig. 1 (b), which is owing to that the weight of PANI acounts for 90 % in the composites, the diffraction peaks of PANI are overwhelming.

Fig. 1. XRD patterns of graphite, GO, PANI, GO/PANI and FGO_3/PANI

Fig. 2. FT-IR spectra of GO, FGO_1, FGO_2 and FGO_3 (a) PANI, GO/PANI and FGO_3/PANI (b)

Fig. 2 (a) shows the FTIR spectra of GO, FGO_1, FGO_2 and FGO_3. The absorption peak at 1089 cm^{-1} is related to the stretching of –C-O-C–. The absorption peak at 1383 cm^{-1} is related to the stretching of C-OH. The absorption peak at 1622 cm^{-1} is related to the bending of C=C. The absorption peak at 1732 cm^{-1} is related to the stretching of C=O in –COOH. The absorption peak at 3400 cm^{-1} is related to the stretching of –OH. Compared with the ratio of peaks at 1732 cm^{-1} and 1622 cm^{-1}, the absorption peaks at 1732 cm^{-1} intense obviously after carboxyl functionalization and increase with the content of oxalic acid. In addition, the absorption peaks at 1383 cm^{-1} and 1089 cm^{-1} are evidently decreased after functionalization. It is indicated that some of the –C-O-C– are converted to –OH by HBr and esterification reaction take place between oxalic acid and –OH.

Fig. 2 (b) shows the FTIR spectra of PANI, GO/PANI and FGO_3/PANI. The three spectra are quite similar owing to the overwhelming majority of PANI in composites. The main characteristic peaks of PANI located at 1460 cm^{-1}, 1298 cm^{-1}, 1130 cm^{-1} and 788 cm^{-1} are assigned to C=C strenching of the benzenoid rings, C-N strenching of second amine, C=N stretching of quinoid rings and C-H bending of benzenoid rings, respectively. The broad intensive band from 1770 to 1530 cm^{-1} should be attributed to the absorption of C=C stretching of the quinoid rings and C=C bending of benzenoid rings. The broad intense band from 3600 cm^{-1} to 3200 cm^{-1} is assigned to the stretching of –OH and –N-H. In addition, under close observation, the ratio of the peak area at 1460 cm^{-1}, 1298 cm^{-1} and 1130 cm^{-1} are different, the maximum is PANI and the minimum is FGO/PANI.
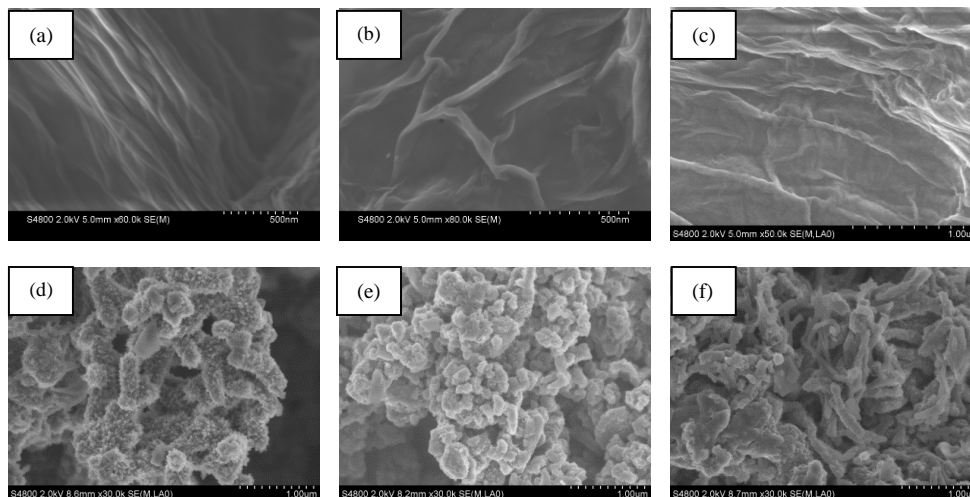

Fig. 3. SEM images of graphite oxide(a), GO(b), FGO_3(c), PANI(d), GO/PANI(e) and FGO_3/PANI(f)

The SEM images of graphite oxide, GO, FGO_3, PANI, GO/PANI and FGO_3/PANI are shown in Fig. 3. It can be seen that the stratification of graphite is obvious after chemical exfoliation and the layer is relatively thick. After ultrasonic treatment, corrugation can be observed on GO and FGO_3 sample. Rod-like PANI with flocky feature is observed in Fig. 3 (d), and exists a little agglomeration. GO/PANI appears short rod-like and severely agglomerated. PANI in FGO_3/PANI appears relatively long and thin rod and disperses uniformly, and PANI growing on graphene oxide sheets can be observed in Fig. 3 (f). It is indicated that carboxyl functionalization is favourable to the composition of PANI and GO.
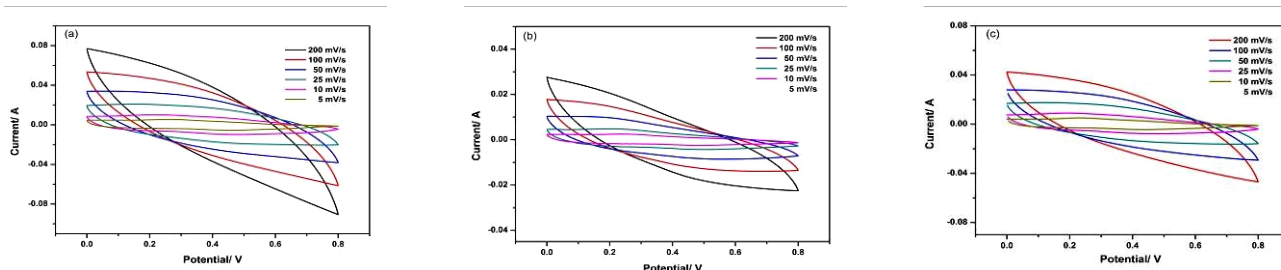

Fig. 4. CV curves of PANI (a), GO/PANI (b) and FGO_3/PANI (c) at different scanning rate

Electrochemical performance. CV curves of PANI , GO/PANI and FGO₃/PANI at different scanning rate of 5 mV/s, 10 mV/s, 25 mV/s, 50 mV/s, 100 mV/s and 200 mV/s are shown in Fig. 4 (a), (b) and (c), respectively. Two pairs of redox peaks in the CV curves of PANI, GO/PANI and FGO₃/PANI are contributed to the redox transition of leucoemeraldine/emeraldine/perniggraniline states of PANI. The gravimetric specific capacitance of the three supercapacitors at 5 mV/s were calculated from the CV curves in Fig. 4. The specific capacitance of FGO₃/PANI（297 F/g）is higher than GO/PANI (226 F/g), which indicates that carboxyl functional GO is helpful to improve the hybrids capacitance. FGO₃/PANI with the long rod structure without aggregation is better than GO/PANI with small rod aggregation in terms of specific capacitance. However, they are both lower than PANI (349 F/g), which is due to GO and FGO₃ are not conductive.

Fig. 5 shows the Nyquist plots of PANI, GO/PANI and FGO₃/PANI in the frequency range of 0.01-100 kHz at the open circuit potential with expanded plots in the inset. The Nyquist plot of FGO₃/PANI is similar to that of GO/PANI, but showing a smaller semicircle in the high-frequency region, which reveals a good capacitive behavior. The devices show relatively small equivalent series resistance (R_s) values (0.2~0.3 Ω), indicating the lower internal resistance of the devices. The second intersection point of the semicircle on the real axis, represents the total resistance (R_{ct}) at the interface between the elexctrode and electrolyte. It is easy to see that the R_{ct} of FGO₃/PANI is lower than that of GO/PANI, which indicates that the charge transfer resistance of the composites reduce after carboxyl-functionallization.
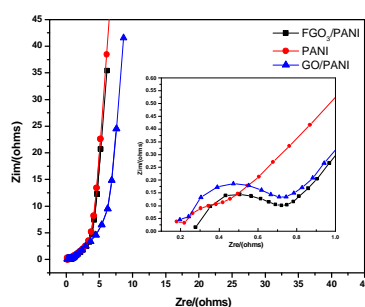

Fig. 5. Nyquist plots of PANI, GO/PANI and FGO₃/PANI

Conclusions

Carboxyl functional approach to the epoxy and hydroxyl groups in the plane of GO, then compositing with PANI, can make the PANI conductive polymers arrange orderly and uniform. GO/PANI is short rod-like and agglomerate. PANI in FGO /PANI appeares long and thin rod, and disperses uniformly. The degree of structural order of FGO/PANI is better than GO/PANI. The absorption peak at 1732 cm⁻¹ (C=O in –COOH) intenses obviously and the absorption peaks at 1383 cm⁻¹(C-OH) and 1089 cm⁻¹ (-C-O-C) decrease after carboxyl-functionalization. The specific capacitance of FGO/PANI（297 F/g）is higher than GO/PANI (226 F/g). The charge transfer resistance of composites reduces after carboxyl-functionallization.

Acknowledgments

References

[1] Z.J. Fan, Q.K. Zhao, T.Y. Li, J. Yan, Y.M. Ren, J. Feng, T. Wei:Carbon Vol. 5 (2012) , p. 1699
[2] Z.Q. Niu, J. Chen, H.H. Hng, J. Ma, X.D. Chen: Adv. Mater Vol. 24 (2012), p. 4144
[3] T. Kim, G. Jung, S. Yoo, K.S. Suh, R.S. Ruoff: ACS Nano Vol. 7 (2013), p. 6899

[4] R. Yuge, M. Zhang, M. Tomonari, T. Yoshitake, S. Iijima: ACS Nano Vol.9 (2008), p. 1865
[5] B. Chitragara, W.J. Kim, Y.D. Kim, D.S. Huh: Materials Letters Vol. 19-20 (2011), p. 3120
[6] H. Wang, Q. Hao, X. Yang, L. lu: ACS Applied Materials & Interfaces Vol 3 (2010), p. 821
[7] K. Zhang, L.L. Zhang, X. Zhao, J. Wu: Chemistry of Materials Vol 4 (2010), p. 1392