

SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF PANI/CARBON NANOSTRUCTURE COMPOSITE

Guangmin Zhou¹, Dawei Wang², Hui-ming Cheng¹, Feng Li¹

¹Shenyang National Laboratory for Materials Science Institute of Metal Research, Chinese Academy of Sciences 72 Wenhua Road, Shenyang 110016, P. R. China

²ARC Centre of Excellence for Functional Nanomaterials, AIBN, The University of Queensland, St Lucia, Brisbane 4072, Australia

Introduction

Recent, supercapacitors are a new energy storage devices, which has aroused extensive attention because of the performance range between traditional capacitors and batteries with high energy density, high power density, long cycle life, less pollution [1-2]. Under the principle of energy storage, supercapacitors can be divided into double-layer capacitance and Faraday capacitance. The storage charge of double-layer capacitor rely on interface between electrode and electrolyte. The stored energy of Faraday capacitor are based on redox reactions between electrode material and electrolyte [3]. The electrode materials include carbon-based materials, metal oxides and conductive polymers. Carbon-based materials has high specific surface area and the cycle stability, rich pore structure, but less than capacitance. The conductive polymer are easy synthesis, low cost and high capacity, but low electrical conductivity and poor cycling stability [1, 4-5]. Therefore, combining the virtues of the carbon-based / polymer composites as electrode materials for supercapacitor is an important research direction, which can be combined with carbon materials with electric double layer energy storage and conductive polymers with Faraday process to have completed high energy storage.

In this study, we chose three different dimensions of typical carbon (0 D conductive carbon black(CB), 1 D carbon nanotubes(CNTs) and 2D graphene nanosheet (GNS)) as a substrate in situ chemical polymerization of polyaniline (PANI), we can obtain the CB/PANI, CNT/PANI and GNS/PANI. Three kinds carbon matrix / PANI composite electrode materials were prepared and explored their electrochemical properties of the difference.

Experimental

All the composites were prepared by *in situ* polymerization as following process: 200 mg of different nanostructure carbon powers (GNS, CNTs and CB) were firstly dispersed into 100 ml of 1 M hydrochloric acid (HCl) aqueous solution respectively and ultrasonicated for 30 min to form different nanocarbons dispersion, followed by mixing with 200 mg (2.2 mmol) aniline monomer dissolved in 50mL of 1M HCl aqueous solution. After that, an ammonium persulfate (APS, (NH₄)₂S₂O₈) solution containing 50 ml of 1M HCl and 0.5g (2.2mmol) of APS was added dropwise while

maintaining vigorous stirring, allowing the in situ polymerization for a further 24h at an ice-cooled temperature (0 °C). The precipitated polymer was filtered and washed repeatedly with ethanol and de-ionized water, respectively. The yield of PANI calculated from the weight of different dimensions of nanocarbons before and after polymerization were 90%, 81%, 69% for GNS/PANI, CB/PANI and CNTs/PANI, respectively. The pure PANI powders were also synthesized through the above-mentioned chemical process without adding carbon materials for the sake of comparison.

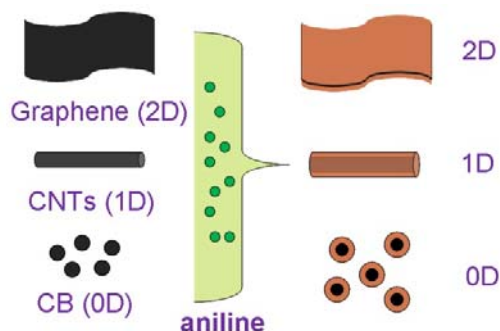


Fig.1 Schematic illustration for the synthesis of different carbon matrix/PANI composites by *in-situ* chemical polymerization

Results and Discussion

The yield of PANI calculated from the weight of different dimensions of nanocarbons before and after polymerization were 90%, 81%, 69% for GNS/PANI, CB/PANI and CNT/PANI, respectively. By scanning electron microscopy (Figure 2) and Raman characterization, the carbon materials are uniformly deposited on the polyaniline. The graphene with unique two-dimensional plane structure makes the surface of polyaniline effectively and polymerization between the layers. With respect to CNTs and CB, the PANI layers were uniform and tightly coated on the surface of CNTs or CB to form a core-shell structure consisted of polyaniline shell and CNTs or CB core in Figures 2e, f and Figures 3b, c.

The higher yield and the uniform dispersion of PANI on GNS are favorable for the enhancement of the electrochemical performance for supercapacitors. The performance of pure PANI and the nanocarbons/PANI composites as electrodes for supercapacitors were evaluated by CV, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) tests in three electrode systems. Figure 4a illustrates the CV of PANI and compares it with different dimension of nanocarbons/PANI composites at a scan rate of 50 mV s⁻¹. It is obviously observed that there are two couples of redox peaks (C₁/A₁, C₂/A₂) for all the samples which are attributed to the redox reaction of PANI, corresponding to the redox transitions between a semiconducting state (leucoemeraldine form)/a conducting state (polaronic emeraldine form) and the Faradaic transformation of emeraldine/pernigraniline, respectively. In addition, the larger integrated areas of all the composites

means higher specific capacitance compared with PANI indicating the synergistic effect between different nanocarbons and polyaniline, among which the GNS/PANI composite shows the highest specific capacitance.

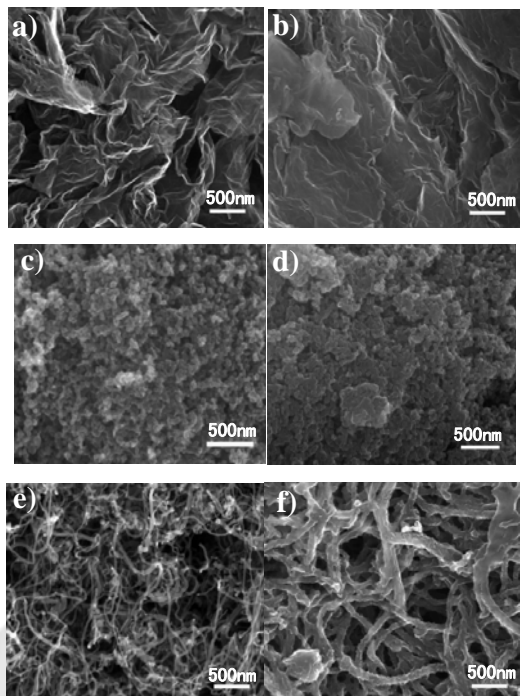


Fig. 2 SEM images of (a) graphene, (b) graphene/PANI, (c) CB, (d) CB/PANI, (e) CNT, (f) CNT/PANI

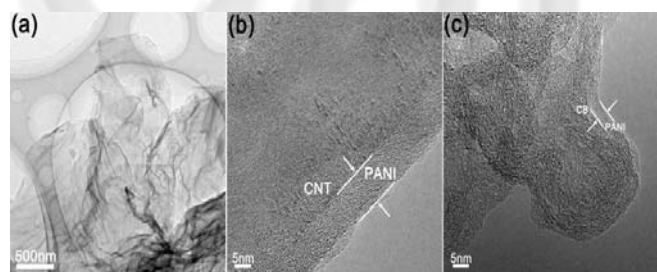


Fig. 3 Typical TEM image of (a) GNS/PANI composite and HRTEM images of (b) CNT/PANI and (c) CB/PANI composites.

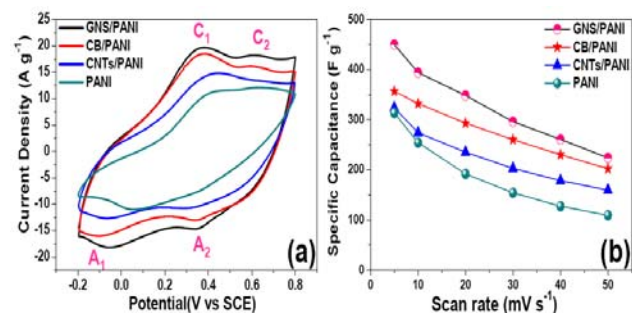


Fig. 4 (a) CV curves of PANI and GNS/PANI, CB/PANI, CNTs/PANI composites at 50 mV s^{-1} . (b) Specific capacitance of PANI and GNS/PANI, CB/PANI, CNTs/PANI composites at different scan rates.

Conclusions

In summary, the different dimensions of nanocarbons/polyaniline composites were prepared by in situ polymerization. The 2D GNS/PANI composite showed higher yield (about 90%), higher specific capacitance (450 F g^{-1} at 5 mV s^{-1}), higher energy density (5.6 W h kg^{-1}) at a power density of 8070 W kg^{-1} , lower equivalent series resistance (0.79Ω) and redox reaction resistance (1.62Ω) as well as enhanced cycling stability ($\sim 90\%$ after 1000 cycles) and rate capability compared with CB/PANI, CNT/PANI and PANI. The better performance can be attributed to the 2D GNS which provide much larger surface areas for homogeneous nucleation of PANI and more active sites for electrode-electrolyte accessibility for redox reaction, act as an excellent conductive agent to provide express ways of electron transfer and play a “flexible confinement” function for preventing the desquamation of PANI from substrate and tolerate the mechanical changes (swelling and shrinkage) of PANI during cycling. These findings highlight the advantages of 2D planar structure GNS/PANI composite for better utilization of electroactive PANI and GNS for energy storage applications in high performance supercapacitors. Furthermore, the results are useful for depositing other film or planting on 2D GNS with expected properties for many other applications such as lithium ion batteries, sensors, solar cells and so on.

Acknowledgment. This work was supported by Ministry of Science and Technology of China (No. 2009AA03Z337), National Science Foundation of China (No.50921004 and 50632040) and K.C Wong Education Foundaion, Hong Kong.

References

- [1] Conway BE. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications. New York: Plenum Publishers. 1999, 11-32.
- [2] Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nat Mater, 2008; 7: 845- 854.
- [3] Frackowiak E, Beguin F. Carbon materials for the electrochemical storage of energy in capacitors. Carbon, 2001; 6: 937-950.
- [4] Wang DW, Li F, Zhao JP, Ren WC, Chen ZG, Tan J, Wu ZS, Gentle I, Lu GQ, Cheng HM. Fabrication of Graphene/Polyaniline Composite Paper via In Situ Anodic Electropolymerization for High-Performance Flexible Electrode. ACS NANO, 2009; 3: 1745-1752.
- [5] Wang YG, Li H Q, Xia YY. Ordered Whiskerlike Polyaniline Grown on the Surface of Mesoporous Carbon and its Electrochemical Capacitance Performance. Adv. Mater, 2006; 18: 2619-2623.