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One-step template-free fabrication and capacitive properties of flower-like polyaniline in strong acidic solution

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Abstract. Three-dimensional hierarchical nanostructured polyaniline (PANI) was constructed through a simple and efficient template-free frozen polymerization of aniline in strong acid condition for fabricating high performance electrode for supercapacitor. The morphology and structure of flower-like PANI was investigated, and its charge storage ability was evaluated. The PANI electrode exhibited the specific capacitance of 428.5 F g^{-1} at a current density of 1 A g^{-1} , the capacitive retention remains 78.8% from 1 to 10 A g^{-1} , and cycling retention of 62 % after 1000 cycles, exhibiting its great potential application as the supercapacitor electrode materials.

1. Introduction

It is well known that a large specific surface area and fast ionic transport can result in a high specific capacitance of the electrode materials for supercapacitor. Apparently, the electrochemical performance of three-dimensional (3D) nanostructured PANI such as flower-like PANI can be expected to be ideal candidates for supercapacitor electrode materials owing to their large specific area and optimized ion diffusion path. The flower-like PANIs have been constructed through dilute solution polymerization [1], ethanol- and organic acid guided synthesis [2,3], polymerization in alkaline solution [4], hard template method [5]. However, These PANI had relatively weak conductivity due to dilute aniline or weak acid and even alkaline condition, implying that they could not provide high specific capacitance that came from the fast and reversible redox reactions at the electrode surface. Hence, a simple and eco-friendly one-step template-free method was presented for fabricating flower-like PANI in strong acid condition as the supercapacitor electrode materials.

2. Experimental

The aniline and ammonium persulfate as the oxidant were firstly solved in 10 ml of 1M HCl to obtain 0.2 M solution, and then two kinds of the HCl solutions placed in the culture dish with the diameter of 90 mm were frozen into the ice layers at -18°C for 12 hours, respectively. Subsequently, the aniline ice layer was took out from the culture dish and was covered on the oxidant ice layer that still stayed in another culture dish. The polymerization was carried out at 0°C by removed the dish in the ice bath. After 9 h of reaction, the product was filtered and washed by de-ionic water for several times, and finally dried in vacuum oven at 60°C overnight.

The morphology, chemical and crystal structures of as-prepared PANI were respectively investigated by FE-SEM (Hitachi S-4800), FT-IR (Nicolet 8700) and XRD (Rigaku D/Max-2550 PC). The capacitance performance was evaluated in 1 M H_2SO_4 solution on a CHI 660E electrochemical



workstation (Chenhua, China) by using a saturated Ag/AgCl with saturated KCl solution as reference electrode and a Pt plate as the counter electrode.

3. Results

3.1. Morphology and structural

As shown in figure 1, as-prepared PANI showed 3D hierarchical flower-like structure that consisted of thin sheets. The formation of flower-like structure can be attributed to the highly oxidized state of PANI appeared in the earlier stage of the polymerization and the suppressed reaction kinetics in frozen condition [3]. The characteristic peaks of PANI such as at 1563, 1481, 1296, and 1128 cm^{-1} , corresponding to the C=C stretching deformation of quinonoid and benzenoid rings, C–N stretching vibrations, and C–H in plane and out of plane deformation can be observed in its infrared spectrum [1,6], while two typical peaks for amorphous conductive PANI appeared at 2θ values of 20.8 and 25.0° in its XRD pattern [2,6].

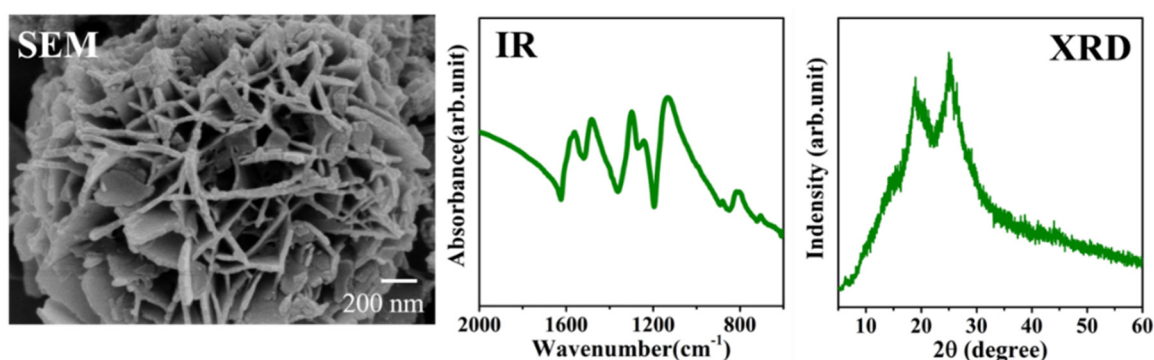


Figure 1. SEM image, infrared spectrum and XRD pattern for as-prepared PANI.

3.2. Electrochemical Performance

The capacitive behaviours of the PANI were further tested by CV, GCD and EIS measurement. As shown in figure 2a, three pairs of redox peaks can be observed at relatively scan rate, showing an excellent pseudocapacitance performance. The specific capacitance decreased from 748 to 560 F g^{-1} when the scan rate increased from 5 to 100 mV s^{-1} , exhibiting high capacitance retention is 74.8% as plotted in figure 2b. Furthermore, the nature of the electrode materials can be distinguished by analysing the capacitive vs. diffusive (battery-like behavior) contributions of the current as displayed in figure 3c. Note that the behavior of the electrode material exhibiting capacitance or battery largely depends on the nanostructure design of the counter electrode material [6]. As illustrated in figure 3d, the capacitive contribution increased from 68 % to 91 % along with the scan rate varied from 5 to 100 mV s^{-1} . The high capacitance contribution at a higher scan rate can be ascribed to the unique flower-like nanostructure of the PANI that could provide the effective transport of electrolyte during rapid charging–discharging process [6].

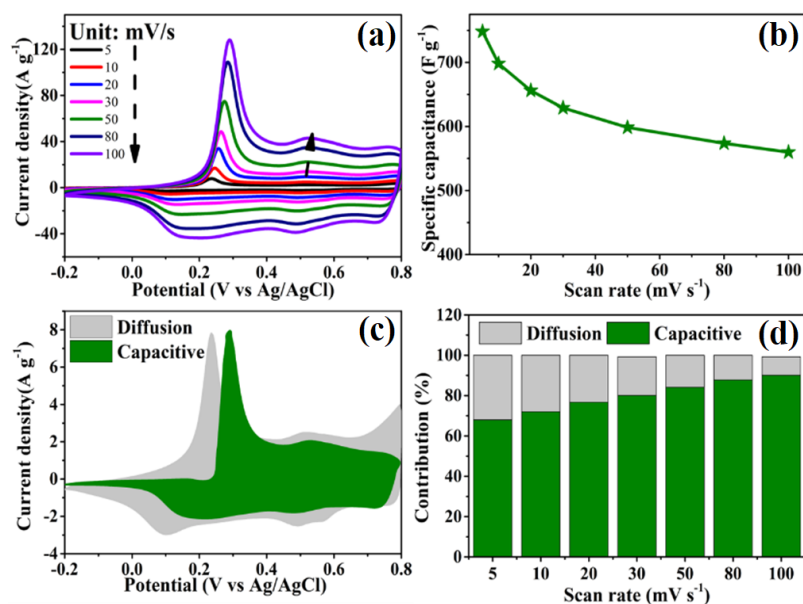


Figure 2. CV curves at various scan rate (a), specific capacitance as a function of the scan rate (b), fitting curves at 5 mV s⁻¹ (c) and the normalized contribution ratio of capacitive capacitances (d) for flower-like nanostructured PANI.

There is almost no obvious “IR drop” observed in the curves as given in figure 3a, reflecting a low internal resistance of the electrode. The discharge time decreases gradually along with the increase of the current density, and more clearly, the specific capacitance decreased from 428.5 to 337.7 F g⁻¹ once the current density raised from 1 to 10 A g⁻¹ with the capacitance retention is 78.8% as illustrated in figure 3b. High electrochemical performance can be benefited from large surface area for utilizing maximally the electroactive materials.

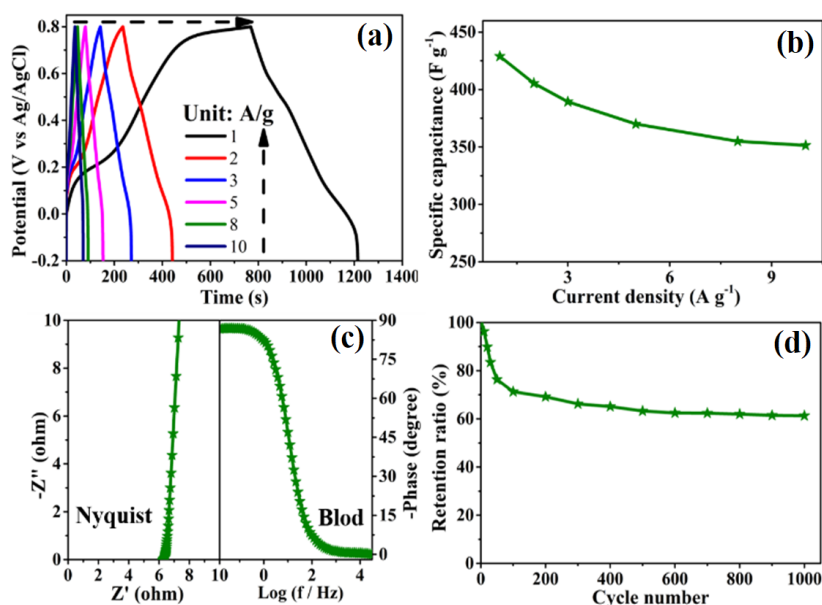


Figure 3. GCD curves at various current densities (a), specific capacitance as a function of the current density (b), Nyquist plot and Bode plot (c) and cycling stability at 5 A g⁻¹ for the flower-like PANI.

Moreover, the Nyquist plot and Bode plot were presented in figure 3c. Almost no semicircle in high frequency region implied a negligible charge transfer resistance, while a straight line near 90° in low frequency region with a small intercept at the Z' axis, more clearly, the equivalent series resistance of about $6.2\ \Omega$. Moreover, the phase angle of the PANI is -86.5° that is close to pure capacitor at low frequency, standing for the ideal capacitive behavior of electrode materials.

Finally, the cycling stability for the PANI was evaluated at $5\ \text{A g}^{-1}$. As in displayed in figure 3d, the capacitance decreased mainly in the first 200 cycles of testing, but only slightly decrease occurred in the last 800 cycles. The capacitance retention after 1000 cycles was 62 %. The results show that the flower-like PANI can provide more rapid transport of the electrolyte ions at the surface of the thin sheets, more usable surface area for capacitive behavior, and accordingly, larger specific capacitance and power capability.

4. Conclusions

The construction of flower-like PANI was achieved through one-pot template-free approach in strong acid solution by using aniline and oxidant ice layers. The flower-like PANI consisted of more thin sheets in conductive form with amorphous nature. The porous structure and large surface area of such 3D hierarchical nanostructured PANI can lead to highly efficient utilization of PANI, which eventually resulted in a large specific capacitance. This approach can be expected to provide a new strategy to promote the development of conductive polymers in the related fields including supercapacitor, rechargeable lithium-ion batteries and electrochemical sensors.

Acknowledgments

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