

Seed polymerization and capacitive performances of polyaniline nanofibers

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Abstract. Polyaniline (PANI) nanofibers have great potential application as a lightweight and high-performance pseudocapacitive material for supercapacitors. In this work, aniline oligomers as the seeds are produced in weak acidic solution of phosphoric acid through dilution polymerization, then these seeds were used to promote the grow of PANI nanofibers in the condition of hydrochloric strong acidic by adding more aniline monomers again. The microstructure and capacitance performances of PANI nanofibers were investigated by SEM, FT-IR, XRD and electrochemical measurements. When the current density is 1 A g^{-1} , the specific capacitance could be as high as 442.9 F g^{-1} . This work provides a route for the simple and efficient preparation of electrode materials with excellent performance.

1 Introduction

Recently, there has been increased focus on developing high-performance and lightweight electrodes for energy storage devices [1]. PANI plays a big role among conductive polymers for flexible supercapacitor with high energy density due to its facile fabrication, reversible redox properties and ultra-high theoretical specific capacitance [2]. Especially, PANI nanofibers could provide remarkable surface area and high charge transport ability, therefore more methods have been developed to fabricate high quality PANI nanofibers. Among them, seed polymerization has been demonstrated to be one kind of highly efficient approaches for preparing high performance PANI nanofibers [3]. Generally, aniline oligomers as the seeds are synthesized in neutral and even alkaline environment [4,5]. In this work, we prepared polyaniline nanofibers by seed polymerization. The aniline oligomers would be produced in weak acidic solution of phosphoric acid, and then seed polymerization would be carried out in 1 M hydrochloric acid aqueous solution by adding more aniline monomers again to form highly conductive PANI nanofibers [6]. The microstructure and capacitance performances would be investigated in detail. It is believed that as-prepared PANI nanofibers could prove its potential in energy storage materials.

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2 Experimental

The aniline oligomers were prepared in weak acidic medium of phosphoric acid (pH=3) by using 0.05 M aniline for 0.5 h, and then the PANI nanofibers were formed based on oligomers in 1 M hydrochloric acid solution by using 0.1 M aniline for 5.5 h. The molar concentrations of aniline monomer and oxidant are the same. The product was dispersed and filtered repeatedly, and at last put it in the vacuum for 24 h at about 60 °C.

The morphologies of seeds and nanofibers were observed by field emission scanning electron microscopy (HITACHI S-4800). The microstructure of PANI nanofibers was characterized by FTIR spectrometer (Nicolet 8700) and X-ray diffraction spectrometer (D2 phaser). A series of electrochemical tests were performed by electrochemical workstation (CHI 660D) using a three-electrode system.

3 Results

3.1 Morphology and microstructure

As displayed as the **Figure 1**, the SEM images of aniline oligomer seeds and PANI nanofibers. Generally, irregularly shaped products tend to form at higher monomer concentrations due to the secondary formation of nucleation centers. However, when aniline oligomers generated in weak acidic solution of phosphoric acid through dilution polymerization were used as efficient nanofibrous seeds, the PANI nanofiber structure can also be formed under the condition of higher monomer concentration [7]. The length of the nanofibers was 383 ± 45 nm, and the diameter was 45.5 ± 7 nm. It is obvious that electrochemical behaviours of PANI strongly depended on the electrochemically active surface area and the rate of ion diffusion and charge transport along the nanofibers.

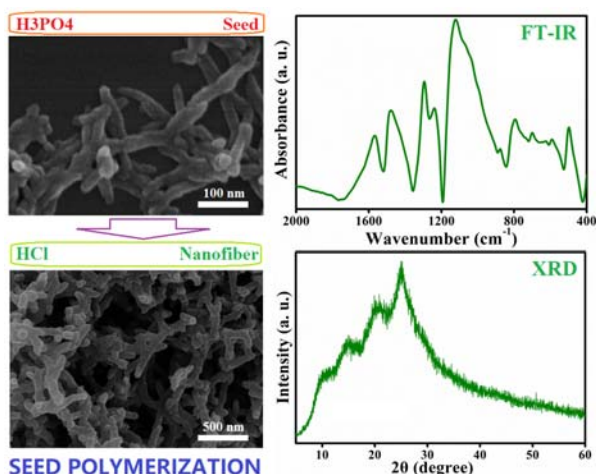


Fig. 1 SEM images of the seed produced in phosphoric acid solution and nanofibers formed in hydrochloric acid solution, and infrared spectrum and X-ray diffraction pattern for as-prepared PANI nanofibers.

PANI nanofibers exhibited five characteristic infrared bands at 1590, 1486, 1305, 1238 and 1153 cm^{-1} as shown in **Fig. 1**, which prove the electrical conductivity formation of emerald salts. The intensities of the absorption peaks at 1590 and 1486 cm^{-1} are related to the C=C stretching vibrations of the quinone (Q) ring and the benzene (B) ring. Relatively

large intensity ratio of the IQ/IB could be observed, implying high conductivity of PANI [8]. Furthermore, the appearance of three distinct and stronger peaks at 15°, 20° and 25° showed that PANI nanofibers had more regular and oriented structures, which would be beneficial to improve the charge carrier transport capability.

3.2 Capacitance Performance

The electrochemical properties of PANI nanofibers including CV, GCD and EIS can be tested in 1.0 M H₂SO₄ electrolyte. **Fig. 2 (a)** presents CV curves at different scan rates for PANI nanofibers. PANI nanofibers exhibited large redox peaks due to their reversible doping and de-doping state changes, in which the capacitance also came from Faraday redox [8]. The apparent reduction and oxidation peaks indicate that the electrode exhibits sufficient redox reactions. As the scan rate increases, as shown in **Fig. 2 (b)**, the specific capacitance of the PANI electrode decreased from 774.3 to 689.3 F g⁻¹, and its capacitance retention could be as high as 89 %. Furthermore, the principle of charge storage of PANI nanofibers could be evaluated from the CV curves. The equation of $i = k_1v + k_2v^{1/2}$ was used to quantitatively distinguish the capacitive and diffusion contributions of the electrochemical process, where k_1 and k_2 are constants representing the capacitive and diffusion contributions, respectively. Shown as the **Fig. 2 (c)**, it was the fitted curve of the PANI capacitance contribution when the scan rate is 10 mV s⁻¹, and as the scan rate increasing to 100 mV s⁻¹, as shown in **Fig. 2 (d)**, the capacitance contribution increased from 76.9 % to 90.4 %. At high scan rates, the reduction in diffusion time results in a high capacitive contribution. It is commonly known that PANI nanofibers can provide more efficient electrolyte transport during fast charging and discharging.

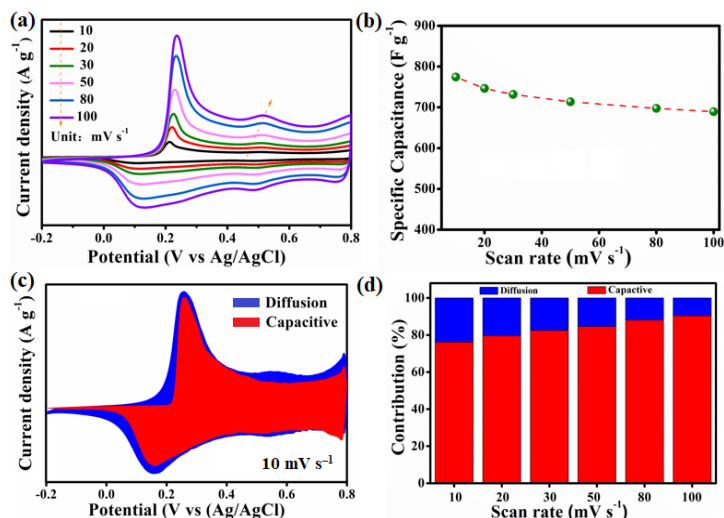


Fig. 2 (a) CV curve, (b) specific capacitance change curve, (c) fitted curve of capacitance contribution and (d) capacitance contribution rate at different scan rates for as-prepared PANI nanofibers.

The current density range of the GCD test varied from 1 to 10 A g⁻¹, while the cycle stability test was repeated 2000 times at a current density of 10 A g⁻¹. According to **Fig. 3 (a)**, all GCD curves retain similar triangle and symmetrical profiles with tiny IR drops as the increasing of current density, showing that PANI could deliver characteristic pseudocapacitive behaviour [9]. When the current density was 1 A g⁻¹, the PANI nanofibers exhibited a specific capacitance of 442.9 F g⁻¹. As plotted in **Fig. 3 (a)**, with the increasing

of current density, specific capacitance of the nanofibers gradually decreased from 442.9 to 428.7 F g⁻¹. The capacity decrease is due to the limitation of the ion transfer of electrolytes at a high current density, that is to say, the decreased utilization efficiency of active materials at higher current densities [9]. The PANI nanofibers could retain the initial capacity of 52 % after 2000 cycles as displayed in **Fig. 3 (c)**. It could be found that the decrease in specific capacitance is mainly reflected in the first 400 cycles, while the capacitance only decreases a little in the latter cycles. The well-orientated nanofibers could provide low internal resistance and larger specific surface area, which help to reduce the damage degree of PANI chains due to expansion or contraction during charge-discharge cycling [10].

Figure 3(d) displays the Nyquist plot of PANI nanofibers, which the frequency range is from 0.01 Hz to 100 M Hz. The almost absence of semicircles in the high frequency region means that the charge transfer resistance is negligible [10], while a nearly vertical straight line can be observed in the low frequency region, which indicates a fast ionic diffusion rate between the nanofibers and the electrolyte. Furthermore, the relaxation time can be calculated to characterize the discharge rate, according to the equation [11]: $\tau_0 = 1/2\pi f_0$, where f_0 can be derived from the capacitance plot as shown in the insert in **Fig. 3 (d)**. The relaxation time constant (τ) is about 13.6 ms. Apparently, PANI nanofibers in this work could exhibited faster ion transport rate and larger specific surface area, which further explained the larger specific capacitance and better electrochemical performance.

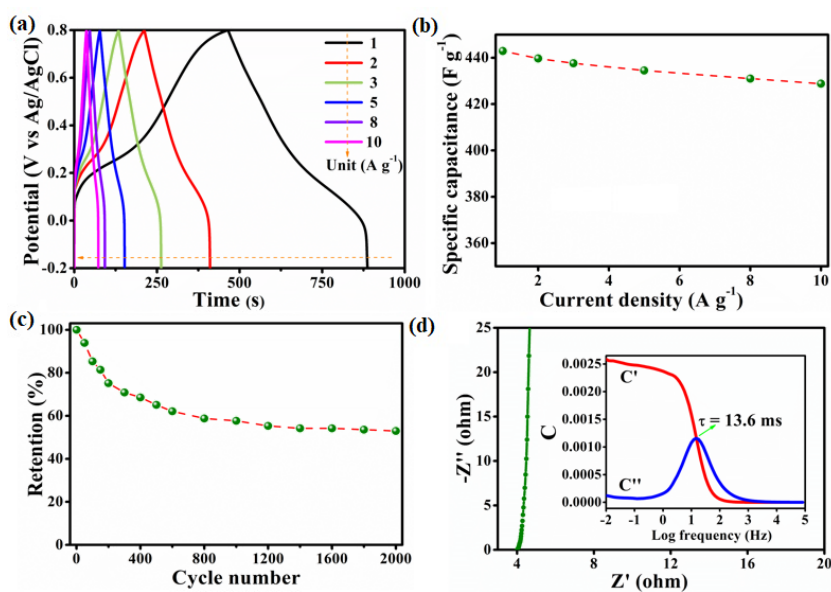


Fig. 3. (a) GCD curve, (b) specific capacitance change curve, (c) cycling stability, and (d) Nyquist plot (inset illustration of relaxation time calculation) for the as-prepared PANI nanofibers.

4 Conclusion

The seed polymerization was proposed as a green and environment-friendly method for preparing high-quality polyaniline in all aqueous phase, which requiring without any additives. As-prepared PANI nanofibers had relatively large aspect ratio, long conjugation length and high chain orientation. As one kind of highly performance electrode materials, the capacitance of PANI nanofibers reaches 442.9 F g⁻¹ at a current density of 1A g⁻¹, while

the cycle stability of 52 % can be achieved after 2000 cycles. These results demonstrate that the seed polymerization method proposed in this work is a facile and scalable method for the synthesis of high-performance polyaniline nanofibers, which provides an efficient route to realize the application of conducting polymers in supercapacitors.

The seed polymerization method is also expected to be an effective way for large-scale preparation. In the future, we should focus on how to apply the seed polymerization method to control the structure of polyaniline nanofibers to obtain higher performance polyaniline.

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