Relationship between Morphology and Electrochemical Properties of Polyaniline in the Nanometer Regime

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ABSTRACT

Polyaniline (PANI) has found a wide range of applications due to its electrical properties, reversible redox behaviors and environmental stability. Here, we report the preparation of PANI nanostructures with three different aspect ratios, namely, nanospheres, nanorods, and nanofibers. A water-soluble polymer, polyvinyl alcohol is used to give a steric effect in the PANI chain growth which allows tailoring of the morphology of the resulting PANI nanostructures. The three nanostructures were prepared under the same polymerization conditions only except for the concentration of the stabilizer, and thus they present a good model system for studying the structure-property relationship of the conducting polymer in the nanometer regime. We further examine what factors strongly affect the device performance when PANI nanostructures are used as the electrode-active materials for supercapacitors. The polymerization rate became slower in the presence of the stabilizer yielding PANI nanostructures with lower aspect ratios. Accordingly, it is believed that the stabilizer sterically restricts the directional fiber growth mechanism governing PANI chain growth in aqueous solution. The oxidation/protonation levels of the three nanostructures were also investigated. The nanofibers were found to have the most outstanding oxidation/protonation level accompanied by structural ordering. The intrinsic charge-transport ability of individual nanostructures strongly influenced the electrochemical properties of the electrodes. Briefly, the nanofiber electrode had faster electrode kinetics and better capacitance than the nanorods and nanospheres. The interparticle contact resistance as an extrinsic factor also turned out to significantly influence the capacitances of the electrodes.

Keywords: Conducting polymers, Polyaniline, Supercapacitors,

1 SYNTHESIS OF PANI NANOSTRUCTURES

PANI nanostructures were fabricated with different stabilizer concentrations in aqueous solution. Aniline was first dissolved in aqueous HCl solution (70 mL), and then PVP was added to the solution. Chemical oxidation polymerization of aniline was initiated by adding APS into the above solution. All reaction steps were carried out under magnetic stirring at 25 °C. The polymerization proceeded for 2 h, and then the resulting deep green product was washed with excess ethanol and water to remove impurities such as residual monomers, stabilizer, and oxidizing agent. The desired product was finally retrieved by centrifugation and allowed to dry in a vacuum oven at 25°C.

2 RESULTS AND DISCUSSION

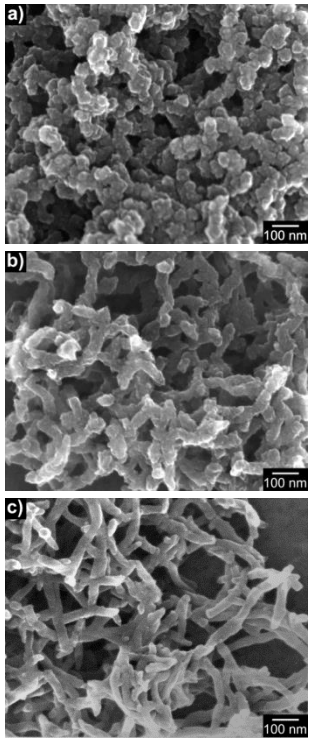

Figure 1: SEM images of PANI nanostructures: (a) nanospheres, (b) nanorods, and (c) nanofibers.

Figure 1 exhibits scanning electron microscopy (SEM) images of three PANI nanostructures synthesized with

different poly(N-vinylpyrrolidone)(PVP) concentrations at the same stirring condition. The diameters of the nanostructures were similarly found to be around 50 nm, and the lengths of the nanorods and nanofibers were about 150 and 215 nm, respectively.

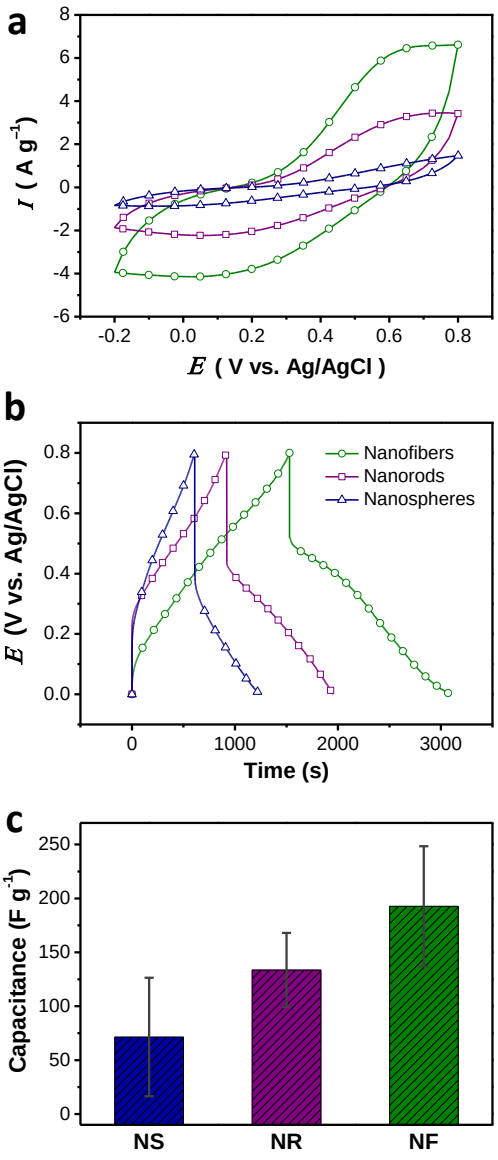

Figure 2: CV analysis of PANI nanosturctures performen in a 1 M sulfuric acid solution (a) cyclic voltammpgrams of electrodes consisting of PANI nanostrustures and the same scan rate (25 mv s^{-1}), capacitances of PANI nanostructures electrodes measured at a current density of 0.1 A g^{-1} in a three electrode cell: (b) representative galvanostatic charge/discharge curves, (c) gravimetric discharge capacotances.

In Figure 2a, the integrated areas of the CV curves, indicative of the capacitance of the electrode, clearly increased in the order of nanospheres < nanorods < nanofibers.Fonts and Spacing

PANI has been extensively used as an electrode-active material in electrochemical capacitors. The PANI nanostructures were tested first using a three-electrode configuration to obtain information on their capacitances. The specific capacitance was determined from galvanostatic charge/discharge measurements, where the potential range was chosen by taking into account the CV curves. Figure 2b displays the typical galvanostatic charge/discharge profiles of the PANI nanostructure electrodes at a current density of 0.1 A g^{-1}, allowing direct comparison between the performances of individual samples. The discharging timeincreased in the order of nanospheres < nanorods < nanofibers over the same potential range, indicating that the nanofiber electrode has the highest specific discharge capacitance. The specific capacitanceswere calculated from discharge curves to be 71, 133, and 192 F g^{-1} for nanospheres, nanorods, and nanofibers, respectively (Figure 2c). The capacitance showed higher rates of increase with decreasing aspect ratio of the nanostructures, which is consistent with the case of the internal resistance.

3 CONCLUSIONS

The use of a steric stabilizer allowed kinetic control of the anisotropic growth of PANI during chemical polymerization, making it possible to fabricate three different nanostructures, namely, nanospheres, nanorods, and nanofibers. These nanostructures with different aspect ratios offered a good opportunity to study the dependence of their main properties on the morphology. The electron transfer capability of the nanostructures was also found to increase in the order of nanospheres < nanorods < nanofibers. Furthermore, the capacitors based on the nanostructures showed morphology-dependent capacitance values, where the interparticle contact resistance was identified as a critical parameter. It is expected that the above findings may provide a new insight into tailoring nanostructures as well as an essential understanding of the parameters determining device performance.

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