

Original Research

Polyaniline nanostructures tuning with oxidants in interfacial polymerization system

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Abstract

Three kinds of nanostructured polyanilines (PANIs) were prepared through interfacial polymerization by using ammonium persulfate (APS) as a single oxidant, and APS/FeCl₃, APS/K₂Cr₂O₇ as composite oxidants, respectively. It is observed that faster formation process and higher yield of nanostructured PANIs could be achieved in the presence of FeCl₃ and K₂Cr₂O₇. The as-prepared PANIs were characterized by field emission scanning electron microscopy, ultraviolet–visible absorption spectroscopy, Fourier transform infrared and Raman spectroscopy, X-ray diffraction analysis and electrochemical measurements including cyclic voltammetry and galvanostatic charge/discharge measurement. The influence of composite oxidants on the morphology, microstructure, and electrical and electrochemical properties of PANIs was discussed. Interestingly, when APS/K₂Cr₂O₇ was used as the composite oxidants, PANI exhibited petal-like structure with high yield of 57.35% instead of general nanofibrous morphology formed in interfacial polymerization. Compared with those nanofibrous PANIs obtained by using APS as a single oxidant or APS/FeCl₃ as composite oxidants, petal-like PANIs exhibited the largest specific capacitance (692.4 F/g at scan rate of 5 mV/s) and highest cycle stability among them. It provides a new insight into the control of PANI nanostructures with high yield and energy storage ability by simply selecting suitable composite oxidants in interfacial polymerization.

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1. Introduction

Nanostructured conducting polymers have received great attention due to their remarkable properties and promising applications in nanomaterials and nanodevices. Among them, polyaniline (PANI) has been extensively studied owing to its mild reaction condition in the synthesis, excellent chemical stability, appropriate conductivity, and unique proton doping–dedoping properties [1–3]. Recently, PANI has been designed to a variety of nanostructures, such as nanofibers, nanospheres, hollow nanocapsules, nanosheets, nanorods and nanotubes [1,4–7]. Because of the peculiar small size effect, the nanostructured

PANIs have been promising in widely potential applications, such as electrochemical supercapacitors, batteries, metallic anti-corrosion coatings, sensors, electrochromic devices, light emitting diodes and so on [1,2,6]. These nanostructured PANIs can be prepared by electrochemical polymerization, hard or soft-template polymerization, rapid-mixing and dilute solution routes and radiolytic synthesis, as well as interfacial polymerization [1,3]. Among these methods, interfacial polymerization is one of the most effective approaches, which produces high-quality PANI nanofibers in large quantities [7–13].

Previously work about interfacial polymerization has been expended toward the effect of doping acids, solvents, polymerization temperature, and monomer concentration on the morphology of nanostructured PANIs. However, less attention has been paid to the effect of the oxidant especially composite

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oxidants on the morphology, microstructure and electrochemical properties of PANIs. In traditional chemical system, the oxidant can only affect the yield and conductivity of PANI owing to the bulk reaction where aniline monomer and oxidant are completely contacted. However, during the process in interfacial polymerization, the reaction between monomer and oxidant only occurs where they encounter. Moreover, the morphology and dimension of nanostructured PANIs can be efficiently controlled by just adjusting the redox potential of the oxidants [14]. It has been reported that ammonium persulfate (APS), ferric chloride (FeCl_3), potassium permanganate (KMnO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), as well as some composites such as Fe^{3+} /hydrogen peroxide (H_2O_2) and $\text{Cu}^{2+}/\text{O}_2$ could be used as the efficient oxidants for the synthesis of PANI [2,11,15–20]. Furthermore, when $\text{K}_2\text{Cr}_2\text{O}_7$ or FeCl_3 was used as oxidant for aniline polymerization, the conversion was very low. Fortunately, when they were used with APS as a composite oxidant, higher conversion was obtained. However, in interfacial polymerization system, the composite oxidants especially that with the most common used oxidant, APS, as one of the component was scarcely studied. Meanwhile the adjustment on the morphology and property of final products is limited to some degree when the single oxidant would be designated oxidizability. Fortunately, the composite oxidants system can exhibit more widely controllable oxidizability depending on the nature and amount of the second component of the oxidants, which can be expected to obtain more complicated nanostructures of PANIs [15,21,22].

Since the oxidants play an important role in controlling the formation of PANIs, it is necessary to study the effects of the oxidants especially the composite oxidants to prepare high-quality nanostructured PANIs. In this article, three kinds of nanostructured PANIs were prepared through interfacial polymerization by using APS and APS-based composite oxidants. The influence of composite oxidants on the morphological structure, chain structure, crystallinity, and electrical and electrochemical properties were investigated.

2. Experimental

2.1. Materials

Aniline monomers with an average molecular weight of 93 g/mol, APS, FeCl_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, carbon tetrachloride (CCl_4) and hydrochloric acid (HCl) were purchased by Sinopharm Chemical Reagent Co., Ltd. and used without further purification. The deionized water was used for all the experiment.

2.2. Preparation

The typical procedure for the synthesis of PANI via interfacial polymerization was carried out as follows: aniline monomers were dissolved in 100 mL CCl_4 and various oxidants including APS, APS/ FeCl_3 (molar ratio of 2:1) and APS/ $\text{K}_2\text{Cr}_2\text{O}_7$ (molar ratio of 1:1) were dissolved in 100 mL 1 M HCl solution, respectively. The molar ratio of aniline monomer to oxidant was 4:1, 1:3 and 2:1 for APS, APS/ FeCl_3 and APS/

$\text{K}_2\text{Cr}_2\text{O}_7$, respectively. Then aniline monomer and oxidant solutions were carefully transferred to a 250 mL beaker to form a static interface of the two phases. After reaction for 12 h at room temperature, the resulting precipitates were filtered and rinsed with deionized water for several times, and the products were dried under vacuum at 60 °C for 24 h.

2.3. Characterization

Field emission scanning electron microscopy (HITACHI S-4800, Tokyo, Japan) was employed to observe the morphology of as-prepared PANIs. Ultraviolet–visible spectra (UV–vis) were recorded on a Shimadzu UV-2550 ultraviolet–visible spectrophotometer in the wavelength region of 200–900 nm with a scan rate of 100 nm/min. Fourier transform infrared spectra (FT-IR) were recorded from KBr sample pellets using a Nicolet 8700 FT-IR spectrometer over a wavenumber range of 2000–400 cm^{-1} with a resolution of 4 cm^{-1} at room temperature, and Raman spectra on a Renishaw inVia-Refle micro-Raman Spectroscopy System using a 532 nm Nd:YAG laser with the output power of 20 mW. X-ray diffraction (XRD) patterns were obtained by a Philips PX1500 X-ray diffractometer by using Cu $\text{K}\alpha$ X-rays with a voltage of 40 kV and a current of 30 mA.

The electrical conductivity of compressed PANI pellets was measured by a two-point probe method at room temperature by using an Agilent 34401A digital multi-meter linked to the computer. The electrochemical measurements were tested on CHI 660D workstation (Chenhua, Shanghai, China) by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements in 1.0 M H_2SO_4 electrolyte. The experiments were carried out on a three-electrode mode with platinum wire as counter electrode, Ag/AgCl as reference electrode and glassy carbon electrode as working electrode, respectively. The working electrode was prepared by dropping a concentrated PANI onto a glassy carbon electrode with a diameter of 3 mm. Typically 2 mg of the product was ultrasonically dispersed in 1 mL deionized water to form a uniform concentrated solution. Finally, 10 μL of the above solution was dropped onto the glassy carbon electrode using a pipet gun and dried at room temperature. The typical CV measurements were carried out at the scan rate of 5, 10, 20, 30, 50, 80 and 100 mV/s within the potential window of -0.2 – 0.8 V. Subsequently, the GCD plots were measured in the potential range of -0.2 – 0.8 V at a current density of 0.5, 1 and 2 A/g. Furthermore, the long-term cycle stability was evaluated by repeating the cyclic voltammetry at a scan rate of 5 mV/s for 1000 cycles.

3. Results and discussion

3.1. Formation process

PANI is typically synthesized by oxidative polymerization of aniline in strong acidic solution using APS as oxidant via a variety of approaches. The reaction is characterized by an induction period followed by bulk precipitation of a dark-green electrical conducting powder called emeraldine salt. In interfacial polymerization, it is believed that the self-assembly of aniline

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