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Short communication

Facile fabrication of polyaniline with coral-like nanostructure as electrode material for supercapacitors

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ABSTRACT

Polyaniline (PANI) with coral-like nanostructure was prepared via chemical oxidative polymerization in the presence of sunset yellow (SY) as dopant and surfactant. The results showed that in comparison with the microsized bulky structure of PANI undoped with SY, the coral-like nanostructure of PANI doped with SY (PANI/SY) was observed and the diameter of coral branch decreased from 180 nm to 100 nm with the increase of feeding molar ratio of SY to aniline. Coral-like PANI/SY showed the large specific capacitance of 467 F/g and nice electrochemical stability when the feeding molar ratio of SY to aniline was 0.035:1, owning to its special coral-like nanostructure and high conductivity of 15.0 S/cm, which was essentially attributed to the synergistic effects of high doping level, ordered arrangement of PANI chain and strong π–π interaction between PANI and SY.

1. Introduction

In recent years, polyaniline (PANI) has been extensively investigated as one of the most promising conducting polymers due to its high conductivity, easy synthesis, environmental friendliness and low cost compared with other conducting polymers, as well as its various applications such as sensors, supercapacitors, fuel cells, and so on [1]. Especially, as electrode material for supercapacitors, PANI could effectively store energy by the characteristic doping-dedoping mechanism and was considered as a promising electrode material for double-layer capacitor and faradaic pseudocapacitor. Unfortunately, the severe agglomeration of neutral PANI reduced seriously the specific surface area of electrode material, which would result in the decrease of reaction site during the process of redox doping-dedoping and a small specific capacitance [2].

Up to now, PANI nanomaterials including PANI nanofiber, PANI nanotube and PANI nanowire have been prepared by many strategies [3–6]. Moreover, the template method was considered as an effective route to prepare nanostructured PANI [7]. Hu et al. explored a route to fabricate cabbage-like PANI by in-situ polymerization of aniline using the hydroxylated poly(methyl methacrylate) nanosphere as template [8]. Nevertheless, the synthetic route of template method involved omitting the template molecule by dissolution, evaporation, and so on, which resulted in a complicated post treatment and the destruction or disorder of PANI nanostructure to some extent. Recently, the template-free method for the synthesis of PANI nanomaterials has been explored, which could not only avoid obviously the complicated post treatment, but also synthesize a special structure that the template method was not easy to realize due to the fact that the size and morphology of available templates were limited [9]. Mi et al. reported the synthesis and electrochemical performance of PANI nanofiber by interfacial polymerization, which was fabricated with the aid of the organic composite fiber of methyl orange/$FeCl_3$(MO/$FeCl_3$) as seed template. In contrast with the traditional template, this MO/$FeCl_3$templatecould be automatically removed with the reduction of Fe^{3+} [10].

Anthraquinone derivatives, as the largest group of naturally present quinones, were able to bring about the fast redox reaction in aqueous solution as pseudocapacitive materials [11] and were of fundamental importance to improve the electrochemical and photoelectrical performances of polypyrrole (PPy) [12–14]. Fluorescent PPy nanosphere (PPy/CBS-X) with uniform diameter was synthesized via chemical oxidation polymerization with fluorescent brightener (CBS-X) as dopant, which simultaneously exhibited the high conductivity of 31.3 S/cm and the large specific surface area of 98.33 m^2/g. Moreover, it also possessed the large specific capacitance of 245.8 F/g at a scan rate of 5 mV/s and showed better rate capability and electrochemical stability than PPy undoped with CBS-X [15]. It was well known that the conductivity of undoped PANI was poor and the rigid molecular chain of PANI caused its poor solubility. The introduction of hydrophilic groups such as sulfonic group has been a major strategy for PANI to improve its conductivity and solubility in water [14]. However, the effect of large anthraquinone derivative containing the azo unit and sulfonate anion as

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dopant on the morphology, conductivity, specific capacitance and electrochemical stability of PANI was not investigated in detail so far.

In this paper, sunset yellow (SY), which was an anthraquinone derivative as well as an azo dye and had a large π-conjugated structure and two sulfonate anions, was used as dopant for PANI/SY synthesized by chemical oxidation polymerization for the first time. Here, SY was not only a dopant but also played the role of surfactant, which guided the growth of PANI and controlled the morphology of PANI by adjusting the feeding molar ratio of SY to aniline, leading to the improved electrochemical performance of PANI.

2. Experimental

2.1. Materials

Aniline was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and distilled under reduced pressure before use. SY of 87% purity was purchased from Aladdin reagent Co., Ltd. (Shanghai, China) without further purification. Hydrochloric acid (HCl), Ammonium persulfate (APS), N-Methylpyrrolidone (NMP), *N,N*-Dimethylformamide (DMF) and sulfuric acid (H_2SO_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. Deionized (DI) water was used throughout the experiment.

2.2. Synthesis of PANI/SY

PANI/SY was synthesized by chemical oxidative polymerization and the feeding molar ratio of SY to aniline was varied as 0.0087:1, 0.017:1, 0.035:1, 0.052:1 and 0.087:1. A certain amount of SY was added to 100 mL of 1 mol/L HCl in a 250 mL round-bottom flask and stirred for 30 min 0.01 mol aniline was added to the above solution and the mixture was stirred in ice-water bath for 1 h 20 mL aqueous solution containing 0.01 mol APS was added drop by drop to the above mixture and the mixture continued to be stirred in ice-water bath for 12 h. PANI/SY sample was filtered and washed repeatedly with ethanol, acetone and DI water to remove residual chemical agents and oligomers until the filtrate was colorless, and then dried under vacuum at 60 °C for 24 h. For comparison, PANI without SY was synthesized under the same reactionI/SY sample was filtered and washed repeatedly with ethanol, acetone and DI water to remove residual chemical agents and oligomers until the filtrate was colorless, and then dried under vacuum at 60 °C for 24 h. For comparison, PANI without SY was synthesized under the same reaction conditions. For the convenience of discussion, the resulting PANI/SY samples were designated as PS-1, PS-2, PS-3, PS-4 and PS-5 with the increase of feeding molar ratio of SY to aniline.

2.3. Measurements

Fourier transform infrared (FT-IR) spectrum and UV–vis absorption spectrum were recorded by Nicolet 5700 fourier transform infrared spectrometer and Hitachi U-2001 UV–vis spectrometer, respectively. SEM analysis was taken using a Zeiss SUPRA 55 scanning electron microscopy at an accelerating voltage of 3 kV. The conductivity was recorded using a RTS-2 four-point probe conductivity tester at room temperature and the pellet was obtained by subjecting the powder sample to a pressure of 20 MPa. Each provided value was an average of three measurements.

All the electrochemical experiments were carried out in a three-electrode system with a working electrode, a platinum counter electrode and a standard calomel reference electrode (SCE). For the preparation of working electrode, the active material (PANI or PANI/SY), carbon black and polyvinylidenedifuoride (PVDF) were mixed in a mass ratio of 80:15:5 [10,16] and dispersed in NMP to form uniform slurry. Carbon black and PVDF were used as conductive agent and binder, respectively. Then the slurry was coated onto the stainless steel (SS) substrate (1 cm × 1 cm) and dried in an oven at 60 °C for 24 h. Finally, the working electrode was obtained by subjecting the SS substrate after coating to a pressure of 10 MPa. The mass loading of material on the SS substrate was obtained by measuring the weight difference before and after coating using a microbalance, eighty percent of which was the weight of active material. The weight of active material loaded on the SS substrate was about 4 mg and the thickness of working electrode was about 0.5 mm. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed on a CHI660D electrochemical workstation in a 1 mol/L H_2SO_4 aqueous solution. The potential range for CV and GCD tests was −0.2–0.8 V. EIS test was carried out in the frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 5 mV.

The specific capacitances (C) were calculated from the CV curves and the GCD curves, respectively, according to the following equations [17,18].

$$C_{CV} = \frac{1}{2m\Delta V\upsilon}\int I(V)dV \tag{1}$$

$$C_{GCD} = \frac{I\Delta t}{m\Delta V} \tag{2}$$

Where *I*, *Δt*, *ΔV*, *ν* and *m* were the constant current, the discharge time, the total potential deviation, the scanning rate and the weight of active material, respectively.

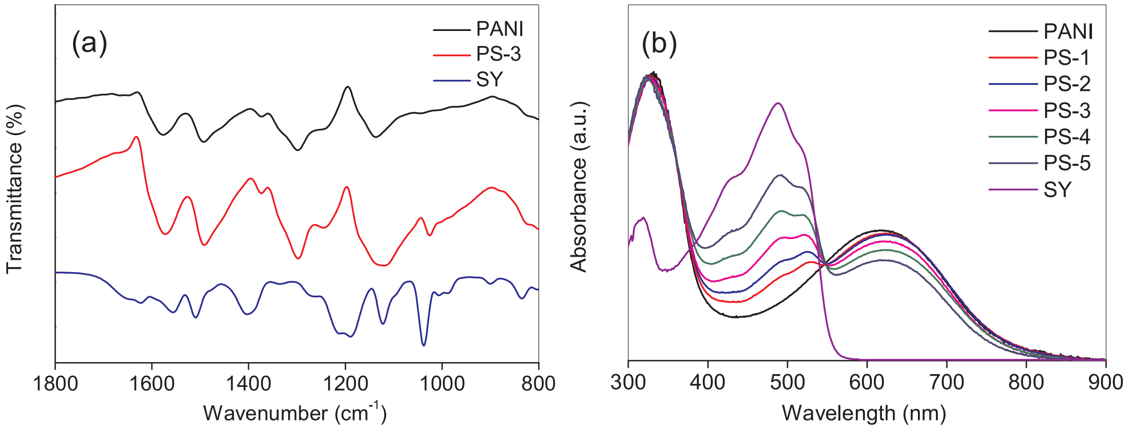

Fig. 1. (a) FT-IR spectra of PANI, PS-3and SY and (b) UV–vis absorption spectra of PANI, PANI/SY and SY.