Electrochimica Acta 125 (2014) 630–636

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Well-defined aniline-triphenylamine copolymer nanotubes: Preparation, photoluminescent, and electrochemical properties

Xue Wang, Haidong Li, Peng Liu*

State Key Laboratory of Applied Organic Chemistry, and Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China

ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form 3 February 2014
Accepted 3 February 2014
Available online 16 February 2014

Keywords:
Conducting polymers
Copolymerization
Nanotubes
Photoluminescence
Electrochemical properties

ABSTRACT

As electrode material for pseudocapacitors, polyaniline (PANI) can be subject to irreversible oxidation and volume changes during the ion insertion-deinsertion process in the charge-discharge procedure that reduces cycle life and electrode capacity, thus, limiting its widespread application. Here, triphenylamine (TPA) was copolymerized with aniline via the facile chemical oxidative polymerization. TEM analysis showed that the products were well-defined nanotubes, and their lengths and diameters increased with increasing the feeding ratio of TPA. By introducing TPA units, the copolymer P(ANI-TPA) nanotubes exhibited photofluorescence and the fluorescence emission intensity at 430 nm decreased with decreasing the media pH values. Their specific capacitance and electrochemical cyclic stability were enhanced when being used as the electrode materials for supercapacitors, compared with the homopolymer PANI. The copolymer P(ANI-TPA) nanotubes with unique morphology developed in the present work strengthen the applications of conductive polymer nanomaterials as supercapacitors, photoluminescence devices and pH sensors.

1. Introduction

Based on the increasing demand for high energy density resources, supercapacitors have attracted great research interest over the past decades as a new kind of energy storage device with high power density, low maintenance cost and long durability [1]. Conducting polymers have been considered as promising electrode materials for supercapacitors and received a significant amount of attention. Among numerous conducting polymers, polyaniline (PANI) has attracted great interest in nanoscale devices owing to its remarkable properties including low cost of aniline monomers, easy-to-handle synthesis, high level of doping, high electrical conductivity, good redox characteristics, environment stability and high specific pseudocapacitance, associated with its highly π-conjugated polymer chains and multiple redox states [2–4].

However, besides the irreversible oxidation [5], the swelling/shrinking of PANI causes volume changes and destroys the backbone of polymer during the insertion/deinsertion process of the counter ions [6], which seriously diminishes its charge–discharge cycle life and electrode capacity, and consequently hinders its application in supercapacitors. Therefore, many approaches have been developed to improve the stability of the PANI electrodes, such as stabilizing with polyacid [5], and immobilizing onto various inorganic nanomaterials (graphene [7], carbon nanotubes [8], carbon nanocoils [9], metals [10,11] and oxide nanoparticles [12], nanotubes [13], nanowires [10], or nanosheets [14]) in the form of nanocomposites.

Copolymerization with other monomers has been realized as a potential way to tailor the properties of the conductive polymers [15]. The morphology and size [16–22], solubility [23], electrical conductivity [18–23], electrochromic behavior [19,24], and electrochemical property [24] could be enhanced notably via the copolymerization of aniline with other monomers. It was also interesting to note that the copolymerization of aniline with the functional aniline derivatives (such as *m*-aminophenol and 2,4-diaminophenol [20], nitroaniline [25], *m*-phenylenediamine [26] or *p*-phenylenediamine [27]) as the comonomers could improve the cycling performance and the structure stability of the conductive polymer electrodes when being used in fuel cells, Na-ion battery [25], and supercapacitors [26].

Triphenylamine (TPA) and its derivatives have been widely used in the organic light-emitting diode (OLED) devices [28,29], solar cells [30,31], and polymeric memory devices [32,33], due

---

* Corresponding author. State Key Laboratory of Applied Organic Chemistry, and Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China. Fax: +86 931 8912582.
E-mail address: pliu@lzu.edu.cn (P. Liu).

http://dx.doi.org/10.1016/j.electacta.2014.02.015
0013-4686/© 2014 Elsevier Ltd. All rights reserved.

to unique structure, stability, hole-transporting and electroluminescence [34]. TPA had been also used as the crosslinkers in the copolymerization of aniline and *p*-phenylenediamine for crosslinked polyaniline with enhanced conductivity [35,36]. By now, there is no report on the photofluorescence or electrochemical properties of its copolymer with aniline.

In the present work, TPA was used as the comonomer to be copolymerized with aniline by the facile chemical oxidative polymerization at room temperature (Table 1). The electrochemical performance of the P(ANI-TPA) nanotubes was evaluated by cyclic voltammetry and galvanostatic charge-discharge techniques with different current collectors in different electrolytes.

2. Experimental

2.1. Materials and reagents

Aniline (Tianjin Fuchen Chemical Reagent Co., Tianjin, China) was distilled under reduced pressure before use. Analytical reagent grade ammonium peroxodisulfate (APS) (Tianjin Chemical Reagent Co., Tianjin, China) and triphenylamine (TPA) (Gracia Chemical Technology Co., Ltd, Chengdu, China) were used as received. Hydrochloric acid, ethanol, N, N- dimethylformamide (DMF) and other reagents were analytical reagent grade and used without further purification. Deionized water was used throughout.

Nickel foam (pore density: 110 ppi) and stainless steel mesh (150 mesh) were rinsed with acetone and hydrochloric acid to clean the metal surface prior to prepare the electrodes of the homopolymer PANI and the P(ANI-TPA) copolymer.

2.2. Synthesis of P(ANI-TPA) nanotubes

The P(ANI-TPA) nanotubes were synthesized by chemical oxidative copolymerization at room temperature. Firstly, 0.01 mol of aniline and a certain amount of TPA were dissolved into 100 ml of 0.10 M HCl aqueous solution. Then 100 ml of 0.10 M HCl aqueous solution containing a certain amount of APS was added into the above solutions at room temperature; the copolymerization started immediately. After being stirred overnight, the resulting precipitates were filtered, and washed with 0.10 M HCl aqueous solutions and ethanol, and dried under vacuum finally.

For comparison, the homopolymer polyaniline (PANI) was also synthesized by the same procedure without TPA. The copolymerization conditions are summarized in Table 1.

2.3. Characterizations and testing

Transmission electron microscopy (TEM) measurements were carried out on a JEM-1230 transmission electron microscope (JEOL, Tokyo, Japan) operating at an accelerating voltage of 100 kV. The samples were dispersed in water and dropped onto the Cu grids covered with a perforated carbon film, followed by solvent evaporation in air at room temperature.

Fourier transform infrared (FT-IR) measurements (Impact 400, Nicolet, Waltham, MA) were carried out in the range of 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1} with the KBr pellet method.

Ultraviolet-visible spectra (UV-vis) were performed using an UV-vis spectrometer (TU-1901, Beijing Purkinje General Instrument, Co., Ltd, Beijing, China).

Photoluminescence (PL) spectra were measured with a Perkin Elmer LS55 Luminescence Spectrometer (Perkin-Elmer Ltd, Beaconsfield, England).

Elemental analysis of the copolymer samples was conducted with Elementar vario EL instrument (Elementar Analysen systeme GmbH, Munich, Germany).

The electrical conductivity of the (co)polymer samples was measured using a RTS-2 four-point probe conductivity tester (Guangzhou four-point probe Technology Co., Ltd, Guangdong, China) at ambient temperature. The pellet was obtained by subjecting the powder to a pressure of about 20 MPa. The values represent the averages of at least three measurements.

Electrochemical measurements on the (co)polymer samples were performed with CHI660B Electrochemical Workstation (CH Instruments, USA) in a conventional three-electrode cell with a platinum counter electrode, a working electrode and a standard calomel reference electrode (SCE). The working electrodes were fabricated as follows. The homogeneous slurries were prepared by mixing the active materials (the copolymers P(ANI-TPA) or the homopolymer PANI), carbon black, and polyvinylidenefluoride (PVDF) with mass ratio of 80:15:5 in N, N- dimethylformamide (DMF). Then the slurry was uniformly laid on the Ni foam or stainless steel mesh as a current collector and then dried at 50 °C for 24 h. The Ni foam or stainless steel mesh coated with the active materials was pressed for 1 min under 1.0 MPa to obtain the working electrodes. The measurements of the Ni foam or stainless steel mesh based electrodes were carried out in a 1.0 M $NaNO_3$ and 1.0 M H_2SO_4 aqueous electrolyte at room temperature, respectively. The working electrodes based the Ni foam with mass loadings of about 2 mg were comparable with the electrodes based the stainless steel mesh with mass loadings of about 0.5 mg.

The specific capacitance (*Cm*) of the electrodes of the PANI and the copolymers could be obtained from the CV and galvanostatic charge/discharge curves, and be calculated according to the equation (1) following:

$$C_m = \left(\int IdV \right) / (mV\upsilon) \tag{1}$$

where *Cm* is the specific capacitance, *I* is the response current density, *V* is the potential window, υ is the potential scan rate, and *m* is the mass of active material in the electrode. The electrodes were characterized successively by CV, galvanostatic charge/discharge, and cycling stability measurements.

3. Results and discussions

3.1. Morphological analysis

The morphology of the P(ANI-TPA) copolymers was compared with the homopolymer PANI by TEM (Fig. 1). All the four copolymer samples were tubular (Fig. 1 (b, c, d and e)), obviously different from the irregular shape of the PANI (Fig. 1 (a)). With increasing the feeding ratio of TPA from 0.5% to 5%, the length of the nanotubes increased from about 700 nm to 2.8 μm, and the inner diameter increased from about 20 nm to 80 nm, respectively. So it could be concluded that the tubular morphologies of the copolymers might be resulted from the “templating effect” of the TPA molecules due to its poor solubility [22]. With increasing the feeding ratio of TPA, the rod-shaped template formed by the TPA molecules grew up. So the length and the inner diameter of the copolymer nanotubes increased [2]. With the higher mole feeding ratio of TPA of 2% and 5% added, some irregular nano-structured products and their aggregates appeared.

Furthermore, the reaction temperature during the polymerization process had been monitored. The temperature changes (T_{delta}) of the different samples with TPA feeding ratios during the chemical oxidative copolymerization in 1.0 M hydrochloric acid were recorded as shown in Fig. 2. It can be observed that the reaction temperature increased at first with the increase of the reaction time for all the four copolymer samples, and then decreased. And the temperature of all the reaction system increased for 3-3.5 °C