A facile, solvent-free and scalable method to prepare poly(aniline-co-5-aminosalicylic acid) with enhanced electrochemical activity for corrosion protection

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ABSTRACT

A facile and simple route has been proposed to prepare poly(aniline-co-5-aminosalicylic acid) (PAASA) nanofibers with enhanced electrochemical activity by chemical oxidative polymerization in aqueous solution. The as-prepared PAASA copolymers were characterized by Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy. The microstructure, composition, morphology and properties of the copolymers were found to be dependent on the molar ratios of the monomers (5-aminosalicylic acid/aniline). The growth mechanism of the copolymer nanofibers is revealed to be the initial spherical soft-template aggregates of monomer-dopant salt followed by nanofiber chain-growth and elongation. The incorporation of 5-aminosalicylic acid into polyaniline backbone tuned the morphology of the resulting nanofibers as well as electrochemical activity from acid environment to wide pH environment ranging from acid to neutral environment, different from the behavior of polyaniline which become electrochemical inactive for pH ≥ 4. This work enable the conducting polyaniline nanofibers new application, especially in the area that high electrochemical activity in neutral environment is required. Nanocomposite coatings of the PAASA nanofibers (0.5 wt%) filled epoxy modified acrylate/amino baking paint (EMA/A) show significant electrochemical corrosion protection at neutral environment.

1. Introduction

Polyaniline (PANI) has received much attention in the field of conducting polymer research in recent years because of its low cost and unique properties, such as high electrical conductivity, easy doping process, good redox reversibility and excellent environmental stability as well as a good control of oxidation level [1–7]. In addition, the electrical properties of PANI can be tailored by changing the dimensionality of nanostructures, such as nanofibers, nanosheets, nanorods and nanotubes according to the requirements of various applications including electrochromic devices, light emitting diodes, biosensor and corrosion prevention [8–13]. However, its poor solubility in various solvents and the sensitive of the conductivity and redox activity of PANI to pH values remain a considerable obstacle to its widespread application, especially in which neutral and alkali solutions are required, such as rechargeable batteries [14]. For example, its electrochemically activity and conductivity is lost rapidly at pH above 4, resulting in poor stabilities and effectiveness [15].

Over the last two decades, much efforts have been dedicated to introduce pH functional groups into the PANI polymer chain to improve the pH dependence of redox activity of PANI polymers in a wide pH range [16–19]. For example Yue et al. reported that the treatment of PANI with fuming sulfuric acid successfully doped the polymers with internal sulfo-groups. Such polymers have a conductivity of $\sim 0.1\,S\,cm^{-1}$, and demonstrate independent of the solution acidity within a pH range up to 7 [18].

The copolymerization of aniline and substituted aniline with $–SO_3H$ [20,21], –OH [22–24], and –COOH [20,25] is another way to introduce pH functional groups. For example, Epstein et al. have developed a novel self-doped conducting sulfonated polyanilines with a high sulfur

to nitrogen ratio of 0.75 through chemical oxidation method. These copolymers showed good electrochemically activity in neutral solutions at pH 7 and maintained the DC conductivity unaffected by pH over the range from 0 and 14 [21]. Karyakin et al. have prepared copolymers from aniline and two substituted anilines (anthranilic acid, m-amino-benzoic acid) through electropolymerization and found that these self-doped polyanilines showed good electrochemically activity even in neutral and basic aqueous solutions up to pH 10 [20]. Mu et al. successfully prepared poly(aniline-co-5-aminosalicylic acid) (PAASA) in H_2SO_4 solution on glassy carbon electode using cyclic voltammetry. Due to the role of –OH and –COOH in adjusting pH in the vicinity of the copolymer backbone, the copolymers has a good redox activity from pH 1.0 to pH 12.0 and maintained 72% redox activity after consecutive cycles from pH 4.0 to 12.0 based on cyclic voltammograms [25]. However, all these methods are either time-consuming or not easily scalable. Also, the mechanism of these copolymerization is not totally revealed until now.

Here, a facile, solvent-free and scalable method was developed to prepare nanostructured copolymers of aniline and 5-aminosalicylic acid. The microstructure, composition, morphology and properties of the copolymer were tailored by controlling the molar ratio of the monomers, 5-aminosalicylic acid/aniline. The growth mechanism of the copolymer nanofibers was revealed and discussed. The resulting copolymer nanofibers showed enhanced electrochemical activity from acid environment to wide pH environment ranging from acid to neutral environment, different from the behavior of polyaniline which become electrochemical inactive for pH ≥ 4. Nanocomposite coatings of the PAASA nanofibers (0.5 wt%) filled epoxy modified acrylate/amino baking paint (EMA/A) showed significant electrochemical corrosion protection at neutral environment.

2. Materials and methods

2.1. Materials

Aniline (ANI) and 5-aminosalicylic acid (ASA) in a technical grade were purchased from Guangzhou Langri Chemical Co. Ltd. (China), and purified by distillation under reduced pressure before use. Sulfuric acid (H_2SO_4) and ammoniumpersulfate (APS) were purchased from Nanjing Chemical Reagent Co. and used as received without further purification.

2.2. Copolymerization of aniline and ASA

1.86 g aniline (0.02 mol), various amounts of 5-aminosalicylic acid (0–0.02 mol) (Total molar of aniline and ASA is fixed to 0.02 mol) and 5.88 g sulfuric acid (98 wt%) were dissolved in deionized water (50 mL) and stirred magnetically at room temperature for 0.5 h to form a uniform solution. After 10 mL APS aqueous solution (2 mol/L) was added dropwise into the above solution at 0–5 °C, the mixture was allowed to react for 18 h at 0–5 °C. The precipitate was washed alternately with water and ethanol for six times, and then dried in vacuum oven at room temperature for 24 h.

Polymerization yield (%) = Weight of resulting polymers/Weight of monomers

The fraction of ASA in the copolymers was measured by XPS with element analysis after polymerization for 30 min, washing alternately with water and ethanol for six times, and then drying in vacuum oven at room temperature for 24 h.

2.3. Preparation of aqueous epoxy modified acrylate/amino (EMA/A) baking paint with PAASA nanofibers

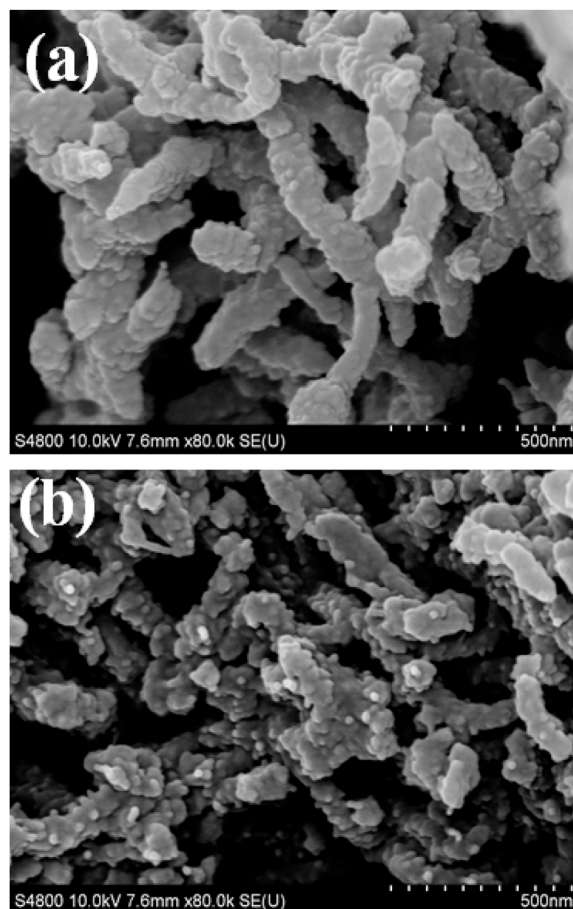PAASA nanofibers were surface modified with surface active agent

Fig 1. SEM images of (a) PANI and (b) PAASA (f_{ASA}: 5 mol%) after polymerization for 0.5 h.

(PT-04) and dispersed in EMA/A baking paint by stirring with a 500 r/min for 60 min to obtain the PAASA filled nano-paint. The nano-paint was solidified at 120 °C for 30 min. The thickness of the coating was 70 nm.

2.4. Characterization

The morphologies of the nanofibers were imaged with a TE CHAI-12 (Philips) transmission electron microscope and a S-4800 II (HITACHI) scanning electron microscope. The molecular structure of the nanofibers was characterized using a Cary 5000 UV–vis spectroscopy (Agilent, Australia) with a sample dissolved in N-Methyl pyrrolidone (NMP) and FTIR spectroscopy (Bruker Tensor 22). The doping degree was measured by XPS (Thermo Scientific ESCALAB 250Xi). The room-temperature conductivity of the compressed PANI pellets was measured using a standard four-probe method with a Keithley 196 System DMM digital multimeter and an Advantest R1642 programmable dc voltage/current generator as the current source. Cyclic voltammetry (CV) and Tafel test measurements were performed on CHI 84013 electrochemical work station. The polymer served as the working electrode while an overcapacitive YP-50F electrode was the counter and Ag/AgCl was the reference electrode. Electron Paramagnetic Resonance (EPR) measurements were performed using Bruker A300 spectrometer in *X*-band (9.862 GHz) at 25 °C. The microwave power for ESR measurements of polyaniline/PAASA sample was set 20.1 mW (the sample powder was put into the quartz tube with a diameter of 3 mm, and then the quartz tube was inserted vertically in the cavity). The modulation amplitude was set at 1.0 G, The sample direction was ⊥G (perpendicular to the magnetic field). The ESR spectra (polyaniline, PAASA, deprotonated polyaniline, and deprotonated PAASA) were recorded every 90 s, which