Electrochemical preparation of self-doped poly(o-aminobenzenesulfonic acid-co-aniline) microflowers

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Abstract

Self-doped poly(o-aminobenzenesulfonic acid-co-aniline) (abbr. p(oASA-co-Ani)) nanoflowers were prepared by an electrochemical preparation without any other supporting electrolytes. The images of scanning electron microscope show that the nanoflowers are uniform. In addition, the results obtained from the cyclic voltammetry indicate that it exhibits a remarkable electroactivity at an extended pH range from 3 to 13.5.

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1. Introduction

Polyaniline, one of the most promising intrinsically conducting polymers, has received considerable attention in recent years due to its ease of polymerization, chemical stability, relatively high conductivity, and potential applications in electronic devices, batteries, and sensors [1]. A major breakthrough in this field is the discovery of self-doped polyaniline (SPAN) due to its desirable properties in practices [2,3]. For example, the self-doped form of polyaniline takes various advantages, such as better solubility, well redox activity, and excellent conductivity over a wider pH range [4], which make them more promising in a broad field of applications, such as energy conversion devices, sensors, electrochromic devices, electromagnetic interference shielding, electronic circuits, etc. [5,6]. SPAN can be easily prepared chemically or electrochemically [7]. Electrochemical preparation is preferred in many ways due to easy controllability of experimental conditions, which affects stability of the polymers, as well as chemical, electrical and electrochemical properties [8]. Size, shape and dimensionality strongly affect the properties of such materials. The nanotubular [9] and dendritic [10] SPAN have been prepared by copolymerization and electrosynthesis, respectively. As far as we know, only inorganic oxide nanoflowers has been obtained to produce super-hydrophobic flowers [12], and there is no any report on a flower-like self-doped polyaniline at moment. In this work, we first communicate the synthesis of hydrophilic SPAN microflowers by electrochemical polymerization of o-aminobenzenesulfonic acid (oASA) in the presence of aniline without any other supporting electrolytes.

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2. Experimental procedure

2.1. Chemicals and reagents

\(\text{o-}\)Aminobenzenesulfonic acid (Aldrich) was used as received, except for aniline (Beijing) which was distilled under a nitrogen atmosphere at reduced pressure and kept below 0 °C. Other chemicals were analytical pure. All aqueous solutions were prepared with ultra pure water obtained from Millipore System (>18 MΩ cm). And all experiments were carried out at room temperature (25 °C).

2.2. Apparatus

The ESEM images were obtained on PHILIPS XL-30 ESEM. Electropolymerization and electrochemical characterizations were carried out with a CHI660 (CHI Instruments, Austin, TX, USA). In these experiments, a conventional three-electrode cell was employed with a gold electrode or Pt/Si, a KCl-saturated silver–silver chloride (Ag|AgCl), and platinum wire as the working electrode, reference electrode, and counter electrode, respectively. All potential values reported refer to this reference electrode. Before the electropolymerization, the gold electrode was mechanically polished with 0.03 µm alumina powder to a mirror finish. Silicon wafers were cleaned in acetone for 5 min and then in ethyl alcohol for 5 min. After rinsing them in ultra pure water, they were dipped into a hot Piranha solution (3:1 mixture of H₂SO₄:H₂O₂) for 30 min. Then, they were rinsed in acetone and ultra pure water, and finally dried in nitrogen flow.

2.3. Procedure

The cleaned silicon wafer was sputtered with Pt, and then it was placed in a solution containing 17 mM aniline and 85 mM \(\text{o-}\)aminobenzenesulfonic acid. The potential was scanned between −0.1 and +0.9 V in an unstirred solution at a scan rate of 50 mV s⁻¹, and followingly rinsed in ultra pure water and dried in nitrogen flow. Then, chronocoulometry was carried out between 1.1 and −0.2 V with a pulse width of 5 s. The area of the electrode is 0.25 cm².
3. Results and discussion

3.1. SEM image of films

The films (abbr. p(oASA-co-Ani)) prepared by the method mentioned above appear to be fairly uniform. The morphology of the film was examined under a field emission-scanning electron microscope (SEM). A large number of polymer microflowers are seen at a low magnification (Fig. 1(a)). At a higher magnification (Fig. 1(b)), more distinct morphology of such flower-like micro-structures can be observed. More details of the flower-like micro-structures are shown in Figs. 1 (c) and (d). Two different types of flowers are shown and every individual flower possesses many radically out-extending thin pedals. And the size of those two different flowers exhibits a narrow distribution of ca. 6–8 and 3–4 μm, respectively. It seems that almost certainly a two-dimensional growth is part of the mechanism as had been put forward in [13].

3.2. Electrochemical properties of films

Cyclic voltammetry (CV) was used to investigate the electroactivity of p(oASA-co-Ani). Fig. 2 shows CV curves of the p(oASA-co-Ani) modified gold electrode in various BR buffer solutions. At pH 3, cyclic voltammogram exhibits three sets of redox waves. Two of these waves observed at 0.16 V ($E'_0$) and 0.54 V ($E'_0$) correspond to leucoemeraldine/emeraldine ($E'_0 \sim 0.158$ V) and emeraldine/pernigraniline ($E'_0 \sim 0.536$ V) transformations (as shown in Scheme 1), and the second redox peaks with maximum anodic/cathodic current is considered to be originated from the presence of cross-linking units or degradation products [11]. In addition, the results obtained indicate the remarkable extension of the redox activity of the processible p(oASA-co-Ani) material up to pH 13.5, which is consistent with the previous report [7].

The wetting properties of the microflowers are also investigated further. The contact angle of water is 68°, which suggests that p(oASA-co-Ani) is much hydrophilic. This should be originated from the sulfonate groups in the polymer matrix [11].

The mechanism how the flowers are formed is not clear at moment. We consider that the nanoflowers grew by three continuous steps: first, films could be built during the CV scanning, and then the film became loosen at such high applied potential (1.1 V), finally those flowers were formed with the help of nitrogen flow.

In summary, flower-like p(oASA-co-Ani) was successfully synthesized in this study. The electroactivity is kept at very wide pH range, which is quite desirable for sensor design, especially in pH-neutral and -base solutions.

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References