Fabrication and characterization of self-doped poly (aniline-co-anthranilic acid) nanorods in bundles

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Abstract

Poly(aniline-co-anthranilic acid) (PANANA) nanorods in bundles was prepared successfully in an alcohol/aqueous media without assistance of any other kinds of acids. Anthranilic acid played all roles of monomer, acid-media provider, and dopant in the reaction system, and ammonium persulfate (APS) served as the oxidant. The morphologies of PANANA nanorods in bundles were investigated by scanning electron microscopy (SEM). Influences of the monomer molar ratio on the resulting morphology were investigated. Moreover the formation mechanism of the nanstructured copolymer was proposed. FT-IR, UV–vis and X-ray diffraction (XRD) measurements were used to confirm the molecular and electrical structure of the self-doped PANANA. The intrinsic properties, such as conductivity, electrochemical redox activity and room-temperature solubility of the resulting copolymer were explored.

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1. Introduction

Conducting polymers have attracted considerable attentions due to their increasing applications in numerous fields, such as batteries, chemical sensors, electrochromic devices, light emitting diodes, etc.\cite{1–4}. Polyaniline (PANI) is a kind of electrically conducting polymers with many features that could be exploited in various applications\cite{5,6}. Furthermore, it is unique in the family of the conducting polymers due to its simple preparation and reversible doping/de-doping properties based on acid/base reactions\cite{7,8}. But the main disadvantages of polyaniline are its poor solubility and poor processability both in melt and solution due to its stiffness of the backbone\cite{9} which limited its further extensive applications in many areas. A major breakthrough in this field was the copolymerization of aniline and ramificate aniline\cite{10,11}. The self-doped polyaniline has several advantages, including better solubility as well as redox activity and conductivity over a wider pH range. A great deal of comonomers involved –SO\textsubscript{3}H, –COOH groups, etc., have been used in the preparation of self-doped polyaniline in recent years\cite{12–15}. For example, to introduce a –SO\textsubscript{3}H group into the polyaniline chain instead of the conventional inorganic acids affects the properties of the polymer without substantially sacrificing its conductivity, while the solubility of polyaniline in aqueous solution as well as most common organic solvents are greatly improved by the presence of the –SO\textsubscript{3}H groups\cite{12}.

Anthranilic acid (2-amino benzoic acid) is an important monomer and dopant for synthesizing carboxylic acid-doped polyaniline. In previous reports\cite{12,13}, it was shown that aniline and anthranilic acid monomers were almost totally copolymerized in an acid aqueous media generally due to the solubility of anthranilic acid in neutral aqueous solution. When anthranilic acid is dissolved into pure water, the solubility is so poor and the polymerization cannot be achieved under the aciidy of the system. In this work, a neutral alcohol/aqueous media was used to dissolve aniline and anthranilic acid monomers instead of inorganic acid. Actually, the anthranilic acid in alcohol/aqueous media can offer enough acidity to the copolymerization (e.g. 2.5 mmol anthranilic acid dissolved in 10 ml ethanol and 50 ml deionized water, pH 3.58) and no other kinds of acid were further required. Here, anthranilic acid plays both the roles of acid-media provider and the monomer/dopant in the reaction system. When copolymerization was carried out with proper conditions, the morphologies of the copolymer were confirmed by
SEM measurements where nanorods in bundles can be observed in large scale. For each nanobundle (∼15 μm in length), several nanorods (500–800 nm in diameter) interlaced themselves across their middles. Influences of monomer molar ratio on the morphology of the products were investigated. Furthermore, the molecular structure, crystallinity, redox activity and solubility of the products were also explored.

2. Experimental

2.1. Materials

The aniline monomer was twice distilled under reduced pressure before use. Anthranilic acid, ammonium persulfate (APS), absolute ethanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) as well as CHCl3 of analytical grade were purchased from Beijing Chemical Company and used without any purification. All aqueous solutions were prepared using ultrapure water from a UPW system.

2.2. Preparation of PANANA nanorods in bundles

A certain amount of anthranilic acid and 0.2325 g aniline monomer were dissolved into 10 ml of alcohol and 40 ml deionized water at room temperature. Twenty millilitres of APS [(NH4)2S2O8] (0.1 M) was added into this mixed solution. The mixture was ultra-sonicated for 1 min at room temperature. Then the mixture was placed into a 4 °C ambient for 24 h. The resulting precipitate was collected by centrifugal separation and was washed several times with ethanol and distilled water. Finally the product was dried under vacuum at 60 °C for 24 h.

2.3. Preparation of EB-PANI

Preparation of HCl-doped polyaniline (HCl-PANI) was done as early reported [5]. A certain amount of HCl-PANI was placed into 5% ammonium hydroxide with a constant stirring for 24 h to de-dope HCl from the polymer. Then the obtained emeraldine base (EB-PANI) was filtered, washed, dried as the same way as PANANA.

2.4. Characterizations

The morphology of the resulting products was measured by a scanning electron microscope (SEM, XL 30 ESEM FEG, on Au substrate). FT-IR measurements were performed using a BRUKER Vertex 70 instrument (in a KBr pellet). UV–vis spectra (Cary 500 Scan UV/Vis–NIR Spectrophotometer, Varian, USA) of the samples dissolved in DMF medium were obtained (DMF as reference). The crystal structures of PANANA and EB-PANI samples were studied on X-ray diffraction instrument (XRD, D/max-III). Cyclic voltammograms of PANANA was recorded by using an Ag/AgCl electrode as the reference electrode. The cyclic voltammograms were obtained at room temperature on a PANANA–DMSO modified glass-carbon electrode. After the evaporation of DMSO, the glassy-carbon electrode was put into a 0.5 M H2SO4 aqueous solution and run the potential scanning between −0.4 and 1.0 V at different scanning rate. Room-temperature solubility of the product in different organic solvents was examined as following: a certain quality of dry sample was placed into 2 ml of organic solvents with ultrasonication for 10 min, then centrifugally separated and washed with deionized water for several times before drying under vacuum at 60 °C for 24 h, finally weighed and calculated.

3. Results and discussion

3.1. Morphology of PANANA and their formation mechanism

SEM images show that morphology of the copolymer products changed with different molar ratio of the mixed monomers. Fig. 1 presents the SEM images of the PANANA synthesized with different aniline/anthranilic acid molar ratios: (a) 2:1, (b) 1:1 and (c) 1:2.

![SEM images of PANANA synthesized with different aniline/anthranilic acid molar ratios: (a) 2:1, (b) 1:1 and (c) 1:2.](image-url)
in the diameter of 500–800 nm and interlaced themselves across their middles to form a nanobundle with a length of ca. 15 μm. It can also be observed that surface of the nanorods are not smooth as well. High magnification SEM image (Fig. 2c) further reveals that, a single rod in the bundles consists of a series of orientated nanoparticles–nanorods with a diameter of ca. 50 nm.

The possible formation mechanism for the prepared bundle-structured PANANA nanorods is depicted in Fig. 3. Since anthranilic acid dissolved in the alcohol/aqueous solution can provide enough acidity (pH 3.58) for the copolymerization, in this system, aniline and anthranilic acid monomers were first oxidized by APS into copolymer nanoparticles. Then these nanoparticles might assemble themselves into a rod-like structure via a self-assembly process. At the same time, free aniline and anthranilic acid molecules adsorbed upon the nanorod can be oxidized by APS continuously and evolved into a multi-strips nanorod. With the proceeding of polymerization, the subsequently formed nanorods deviated from the previous one into other directions probably due to special resistance between each other. However, more detailed formation process of the copolymerization is much dependent on further investigations.

SEM images obtained at room temperature revealed that large scale of bundle-structured PANANA nanorods can also be obtained in a relatively wide temperature range. The result indicates that reaction temperature can hardly affects on the copolymerization. However, when the reaction system was ultrasonically vibrated or disturbed instead of static state, no bundle-structured nanorods can be obtained, which is revealed by an optical observation (400 times magnification).

3.2. Structure characterization

The FT-IR, UV–vis and X-ray diffraction measurements were used to characterize the structure of the self-doped PANANA. Fig. 4 shows the spectra of PANANA (a) and EB-PANI (b). In curve a, the absorption bands at 1504 and 1571 cm\(^{-1}\) are derived from typical quinoid and benzenoid moieties, respectively [16]. It is consistent with those characteristic peaks of EB-PANI (curve b). And the peaks at 1685 and 1448 cm\(^{-1}\) are corresponding to the C=O and C–O stretching vibrations of the carboxyl group [17]. It confirmed that –COOH and/or
Fig. 5. UV–vis spectra of PANANA in DMF: (a) fresh solution and (b) stale solution set for 2 weeks.

–COO\(^{-}\) groups are involved in the resulting polymer chain, and the copolymer was successfully self-doped by anthranilic acid.

UV–vis measurements of PANANA nanorods in bundles were carried out in DMF solution. Fig. 5 shows the corresponding UV–vis spectrum. In either curve a (fresh solution) or curve b (the same solution which was set for 2 weeks without disturbance), there are two main absorption peaks at ca. 385 and 550 nm. The peak observed at 550 nm corresponds to exciton-like transition in quinoid diimino units [18]. And the other peaks appear at 385 nm is attributed to /H9266 –H9266*/ transition in benzenoid units of the polymer chain. Compared with the same characteristic absorption peak of EB-PANI [19], it shifts ca. 60 nm to the long wave direction, which indicates that the conjugate conjunction of PANANA decreased compared with EB-PANI. It may be caused by the following reasons: (a) –COOH groups doped into the backbone of the polymer chain are strongly attracting electron radicals which intensively decreased the electron cloud density of aromatic rings; (b) due to the special resistance effect of –COOH groups, the planar conjugate conjunction of aromatic rings decreased. Therefore, the together cooperation caused the reducing of the conjugate conjunction around the whole polymer chain. In addition, curve b is similar to curve a except for a little weakness in intensity of each characteristic peak which suggests the stability of the resulting copolymer.

X-ray diffraction patterns were taken to compare the crystallizability of PANANA and EB-PANI. In Fig. 6b, a broad peak around \(2\theta = 19.90^\circ\) (0 0 1) can be distinctly observed [20] which was characteristic peak of amorphous emeraldine base form of PANI [21]. While PANANA (Fig. 6a) shows a peak not only at 20.46\(^\circ\), but also at 13.52\(^\circ\), 15.42\(^\circ\), 17.72\(^\circ\), 18.38\(^\circ\), 23.40\(^\circ\), 25.52\(^\circ\), 27.04\(^\circ\), 27.93\(^\circ\), etc. Among these peaks, the peak at 25.52\(^\circ\) (1 1 0) [20] may be ascribed to periodicity perpendicular to the polymer chain. And the other peaks may be caused by the groups doped into the polymer chains in various directions. From the XRD results, it suggests that PANANA has a better crystallizability than EB-PANI.

3.3. Instinctive properties of PANANA

The electrochemical behavior of PANANA film on glassy-carbon electrode was tested through cyclic voltammetric measurements in an acidic electrolyte. Fig. 7a depicts the oxidation/reduction process of PANANA film on glassy-carbon electrode. Unlike polyaniline and many of its substituted forms, PANANA film does not show well-defined redox peaks in the potential range from −0.4 to 1.0 V. Only two pairs of relatively weak current peaks at 0.233 V/0.003 V and 0.577 V/0.450 V can be observed which were corresponding to leucomeraldine/emeraldine and emeraldine/pernigraniline reversible transition, respectively. Different scanning rates were used to examine the dynamic property of PANANA during the redox process (Fig. 7b). As is shown in Fig. 7c, the peak current is directly proportional to the scan rates, suggesting an electric charge-transfer controlled process.

Finally, room-temperature solubilities of the copolymer PANANA in several organic solvents such as DMSO, THF, DMF as well as CHCl\(_3\) were examined, and the results were shown in Table 1. In order to compare the solubility of PANANA and the measurements in an acidic electrolyte. Fig. 7a depicts the oxidation/reduction process of PANANA film on glassy-carbon electrode. Unlike polyaniline and many of its substituted forms, PANANA film does not show well-defined redox peaks in the potential range from −0.4 to 1.0 V. Only two pairs of relatively weak current peaks at 0.233 V/0.003 V and 0.577 V/0.450 V can be observed which were corresponding to leucomeraldine/emeraldine and emeraldine/pernigraniline reversible transition, respectively. Different scanning rates were used to examine the dynamic property of PANANA during the redox process (Fig. 7b). As is shown in Fig. 7c, the peak current is directly proportional to the scan rates, suggesting an electric charge-transfer controlled process.

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Table 1
The solubility of PANANA in several solvents (mg ml$^{-1}$)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DMF</th>
<th>DMSO</th>
<th>THF</th>
<th>CHCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANANA</td>
<td>4.40</td>
<td>11.75</td>
<td>5.70</td>
<td>2.80</td>
</tr>
<tr>
<td>HCl-PANI</td>
<td>2.12</td>
<td>2.96</td>
<td>2.45</td>
<td>2.22</td>
</tr>
</tbody>
</table>

conventional polyaniline doped with inorganic acid, for example, HCl, some relative data were collected and listed in the table [19]. It can be obviously seen from this table that PANANA has a relatively higher solubility in all the above solvents, especially in DMSO, it reaches 11.75 mg ml$^{-1}$. It reveals that the solubility of the resulting product in most organic solvents can be extensively improved by introducing –COOH groups into the backbone of polyaniline chain.

4. Conclusions

In conclusion, bundle-structured nanorod of poly(aniline-co-anthranilic acid) has been successfully fabricated via an aqueous/ethanol medium without participant of any other acids. Anthranilic acid plays both the roles of acid-media provider and the monomer/dopant in the reaction. It can be considered as a real-content fabrication of self-doped copolymer of aniline and anthranilic acid. Optimal reaction conditions were investigated, discussed and the possible formation mechanisms were also proposed. The molar ratio of monomers and the reaction mode (stirring/static state) affect significantly on the morphology of the copolymer. FT-IR, UV–vis and XRD measurements show that the main chain structure and electrical structure of the synthesized copolymer are identical to those previous investigations, and also confirmed the existence of –COOH groups. Finally, some instinctive properties involved oxidation/reduction behavior and room-temperature solubility of PANANA in several organic solvents were examined.

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