Mater.Phys.Mech. 4 (2001) 125-128

NANOSTRUCTURES OF POLYANILINE DOPED WITH A NOVEL DOPANT

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Received: July 3, 2001

Abstract. 4-(3-(4-((4-nitrophenyl)azo)phenyloxy)propyl)aminobenzene sulfonic acid (C3-ABSA) was designed and synthesized as a novel dopant of polyaniline (PANI). Structural characterization by FTIR, ^{1}H NMR and Second Ion Mass Spectrum (SIMS) showed that C3-ABSA has a molecular formula of $C_{21}H_{20}N_4O_6S$. Nanostructural PANI (e.g. nanorod or nanotube) was synthesized by a template-free method in the presence of C3-ABSA as a dopant. It was found that the size and room-temperature conductivity of the resulting PANI-(C3-ABSA) strongly depend on the synthetic conditions, in particular, nanotubes or nanorods with 50~300 nm in diameter and room-temperature conductivity of 1.1 S/cm were obtained when water (1.0 mL) was added before polymerization. It was proposed that C3-ABSA plays a “template-like” role in forming PANI-(C3-ABSA) nanostructures due to surfactant function of C3-ABSA. The molecular structures were characterized by FTIR, UV-Vis. absorption and X-ray diffraction, showing the main chain and electronic structure are identical to the doped PANI, but exhibit partial crystallinity.

1. INTRODUCTION

Nanotubes of conducting polymers have attracted attention at the present time because of their unique properties and application in nano-scale electronic and molecular devices. Template-synthesis [1] is an effective method for synthesizing nanotubes of conducting polymers with a controllable diameter, length and conductivity. However, it often requires a rather tedious post-synthesis process, which is required in order to remove the template. Thus, searching for a simple and self-assembly method to synthesize nanotubes of conducting polymers is a challenge project in the field of conducting polymers.

Polyaniline (PANI) has been the subject of intense investigations during the last two decades because of its desirable electrical, electrochemical and optical properties coupled with excellent environmental stability [2,3]. It has been demonstrated that the morphology and physical properties of the doped PANI could be controlled by changing the synthetic method and conditions [4,5]. Thus, it is highly expected to synthesize micro- and nanotubes or wires of the doped PANI by selecting suitable synthetic method, dopant and conditions.

In this article, 4-(3-(4-((4-nitrophenyl)azo)phenyloxy)propyl)aminobenzene sulfonic acid (C3-ABSA) was designed and synthesized as a novel dopant of PANI. Nanotubes or nanorods of PANI-(C3-ABSA) were synthesized by a template-free method in the presence of C3-ABSA as a dopant. Influence of synthetic conditions on the morphology and conductivity of the resulting PANI-(C3-ABSA) was investigated.

2. EXPERIMENTAL

4-((4-nitrophenyl)azo)phenol (A) was synthesized by a method reported by Furniss *et. al.* [6]. Then, 3-bromide-1-(4-((4-nitrophenyl)azo)phenyloxy)propane (B3) was successfully synthesized by the Williams etherification [7]. Finally, B3 reacted with sodium p-aminobenzene sulfonic acid [Na(C3-ABSA)], followed by a acidification of concentrated hydrochloric acid to form C3-ABSA. FTIR, ^{1}H NMR and Second Ion Mass Spectrum (SIMS) characterized the molecular structure of C3-ABSA, showing a molecular formula of $C_{21}H_{20}N_4O_6S$. Its melting point and decomposition temperature measured by DSC and

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Table 1. Influence of synthesis conditions on the morphology of PANI-(C3-ABSA).

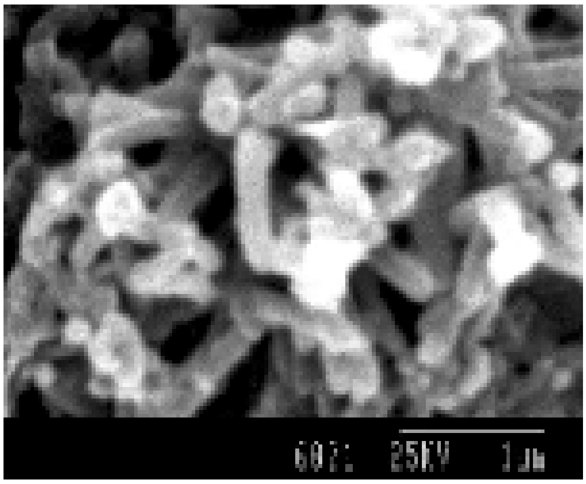
	Morphology		
Synthetic conditions	*Needle like*	*grains*	*cylinders*
Aniline (mL)	0.4-1.0	0.2	0.2
Water (mL)	Non	Non	0.2-10.0
Average diameter (μm)	1.0-4.0	0.4	0.05-0.2

C3-ABSA:5.0 mg; APS:1.0 mL (2.0 M).

TGA was about 223 °C. The nanostructures (e.g. nanorods or nanotubes) of PANI-(C3-ABSA) were synthesized by a template-free method with some modification [8].

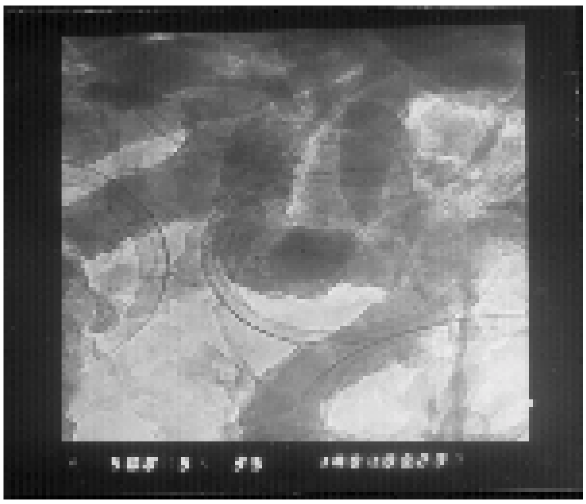
3. RESULTS AND DISCUSSION

It was found that the morphology of the resulting PANI-(C3-ABSA) was affected by the synthesis conditions. In this study, grains, needle-like and cylinders for PANI-(C3-ABSA) were observed, depending on the concentration of aniline and addition of water before polymerization as shown in Table 1. In the absence of water, the morphology of PANI-(C3-ABSA) changed from needle like to grains when the concentration of aniline decreased. On the other hand, the grains changed to cylinders when water was added before polymerization. In particular, TEM images showed that some of those cylinders are hollow (which are called tubules), but others solid (which are called nanorods) as shown in Fig. 1. C3-ABSA is expected to be a dopant with surfactant function because of having $-SO_3H$ group and alkyl group. Recently, Liu et al [9] reported that such a kind of dopant plays a template role in the reaction. This means that the "template" provides a necessary type of "local" environment when PH and charge density near the template molecules is different from that of the bulk solution. Meanwhile, this "local" environment served as a type of "nanoreactor" and is critical in anchoring, aligning, and making aniline monomer reaction, and ultimately controls what shape of PANI is obtained during reaction. Moreover, it was found that the size of PANI-(C3-ABSA) nanostructures was also affected by the synthesis conditions, especially, the diameter of the cylinders is significantly reduced from micrometers to nanom-



a)

b)



c)

Fig. 1. Typical SEM and TEM images of PANI-(C3-ABSA) nanocylinders. (a) SEM of nanotubes. (b) TEM of nanotubes (x60.0 *K*). (c) TEM of nanorods (x50.0 *K*).

eters (e.g. from 4.0 μm to 50.0 nm in diameter) when water was added before polymerization.

The molecular structure of PANI-(C3-ABSA) was characterized by FTIR, UV-Vis. spectra and X-ray diffraction. FTIR spectra showed that the main chain of PANI-(C3-ABSA) is identical to that of PANI synthesized by a common method [10]. However, the position of the benzene ring at 1578-1590 cm^{-1} and the doping bands at 1123-1142 cm^{-1} were slightly affected by the oxidation state.

It was found that UV-Vis. absorption of PANI-(C3-ABSA) is dependent upon the solvent. The UV-Vis. absorption of PANI-(C3-ABSA) dissolved in NMP solvent is identical to the emeraldine base form of PANI [11] due to dedoping. But it exhibits behavior of the emeraldine salt form of PANI when it dissolved in *m*-cresol.

Furthermore, the crystallinity of the PANI-(C3-ABSA) significantly depends on the oxidation state. In particular, a sharp peak at $2\theta=9.8$ assigned as the repeat unit parallel to the PANI chain [12] was observed when the oxidation state was high (e.g. APS/aniline=1.0), indicating a long range order in the polymer chain of PANI-(C3-ABSA). In addition, it was found that the conductivity of PANI-(C3-ABSA) at room temperature depends on the synthesis condition, namely it increases with increasing addition of water as shown in Fig. 2. The maximum conductivity of 1.1 S/cm at room temperature could be achieved when 1.0 mL of water was added before polymerization.

In summary, C3-ABSA designed and synthesized by us is a novel dopant for self-assembled PANI nanostructures. The size of PANI-(C3-ABSA) cylinders strongly depends on the synthesis conditions, in particular, nanotubules or nanorods with 50-300 nm in diameter and conductivity of 1.1 S/cm at room temperature could be obtained when water was added before polymerization. The main chain of PANI-(C3-ABSA) nanostructures is identical to that of PANI synthesized by a common method, while the electronic structures are dependent upon the acidic / basic behavior of the solvent used. X-ray scattering patterns show amorphous with partial crystallinity depending on the oxidation state of PANI.

ACKNOWLEDGEMENTS

This project was supported by 973 program of China (No. G 1999064504), National Natural Science Foundation (No. 29974037), and Chinese Academy of Sciences.

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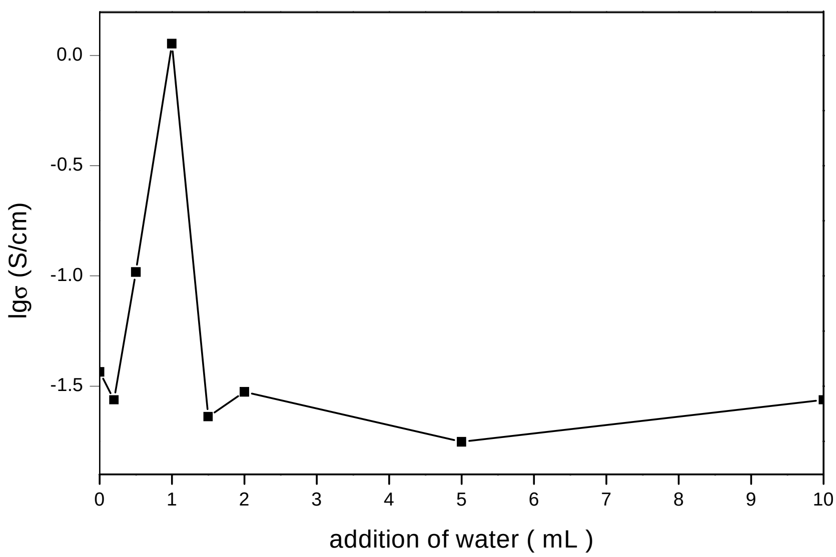

Fig. 2. Influence of the addition of water prior to polymerization on the room-temperature conductivity of PANI-(C3-ABSA) nanocylinders; Aniline / C3-ABSA / APS: 0.2 mL / 5.0 mg / 1.0 mL(2.0 mol/L). The conductivity was measured by the probe method.

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