Synthesis and characterization of polyaniline in CTAB/hexanol/water reversed micelle

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Template synthesis of polyaniline (PANI) has been widely developed in recent years. Microemulsion [1, 2], micelle [3, 4], anodic aluminum oxide [5], and sol-gel [6] were all used as templates to synthesize PANI. These templates provided different routes or space to polymerize aniline and the products so obtained showed good characteristics in different aspects, such as particle size, morphology, solubility, and conductivity.

In addition to the above templates, reversed micelle could also be used to synthesize PANI. As known, the reversed micelle is an isotropic, transparent, thermodynamically stable system and the "water pools" stabilized by surfactant show unique properties to solubilize various water-soluble substances, so many kinds of materials have been successfully prepared in reversed micelle and the particles so obtained were generally very fine and monodispersed [7, 8]. Ichinohe *et al.* [9] used the unique properties to synthesize PANI in reversed micelles consisting of sodium di(2-ethylhexyl)sulfosuccinate (AOT) and 2 M HCl solution in isooctane, which could be dissolved in dimethyl formanide (DMF), and N-methylpyrrolidinone (NMP). However, this article only gave primitive information about the characteristics of PANI such as chain structure, conductivity, and average molecular weight. The morphology and the size of the particles were not shown in this article and it was therefore lacking direct proof for the template synthesis of PANI using reversed micelle. Apart from this, Selvan *et al.* [2] found that when AOT was used to form water-in-oil type microemulsion, the surfactant also acted as a dopant. In this report, we selected cetyltrimethyl ammonium bromide (CTAB) as a surfactant to form reversed micelles in order to make a further study of the synthesis of PANI. More comprehensive characteristics were performed to provide valuable information of the template synthesis of PANI, and from the results we could find that CTAB was not a dopant in the above research. As far as we know, it was the first time CTAB was used as a surfactant to form reversed micelles for synthesis of PANI.

In our experiment, aniline was purified by distillation in vacuum prior to use. Ammonium peroxydisulfate (APS), CTAB, hexanol, methanol, ether, and hydrochloric acid were used as received. Deinonized water was used in all the experiments.

PANI was synthesized as follows: A reversed micellar solution was prepared by adding 10^{-6} m^3 of 4 M HCl solution to 8×10^{-5} m^3 of 0.1 M CTAB/hexanol solution and stirred for 2 hrs before 3×10^{-7} m^3 of aniline monomer was added to it. Then an aqueous solution of APS (0.75 g in 1.5×10^{-6} m^3 of 4 M HCl solution) as oxidant was dropped into the above reaction mixture to initiate the reaction which could be seen from the change of color of the solution. The mixture was stirred at 20 °C for 24 hrs. The reaction was stopped by addition of 5×10^{-5} m^3 methanol and the precipitates were collected by filtration. The precipitates were washed by methanol, ether, 4 M HCl solution, and deionized water in turn, and then dried at 60 °C under vacuum.

UV-Vis spectra were performed on 756MC UV-Vis spectrophotometer. IR spectra were measured using a Magna-IR 760 spectrophotometer (dispersed in KBr pellets). X-ray diffraction (XRD) pattern was taken with Cu K$_\alpha$ radiation using Siemens D5005 X-ray diffraction meter. The detector moved from 5 to 60° at the speed of 7°/min and the X-ray power was 40 kV and 50 mA. Electrochemical measurements were performed using a three-electrode cell at 25 ± 0.1 °C. A glass carbon working electrode (3 mm in diameter) and a Pt wire counter electrode were employed. The reference electrode was Ag/AgCl (satd). The glass carbon surface was polished with 0.3 μm α-alumina applied to a gray billiard cloth and washed with distilled water several times. Cyclic voltammograms (CVs) data were collected with LK98B Electrochemical Analyzer couple to a HP-55 Computer. Thermogravimetric analysis (TGA) was made with a Perkin-Elmer TGA-7 from 25 to 800 °C at a heating rate of 10 °C/min under N_2. PANI powders were compressed to pellets under 20 MPa pressure with a diameter of 13 mm. A standard four-probe instrument was used to measure the conductivity of the pellets at ambient temperature. The morphology was measured by a transmission electron microscope (TEM, HITACHI-600) and the samples for TEM were diffused in ethanol with ultrasonic dispersion for 5 min.

Fig. 1a gives the UV-Vis spectra of the PANI using chloroform as solvent. Two absorption bands were observed with $\lambda_{\max}$ at 320 and 600 nm in curve 2, indicating the intrinsic state of the PANI, and after being doped with HCl, these two absorption bands shifted to

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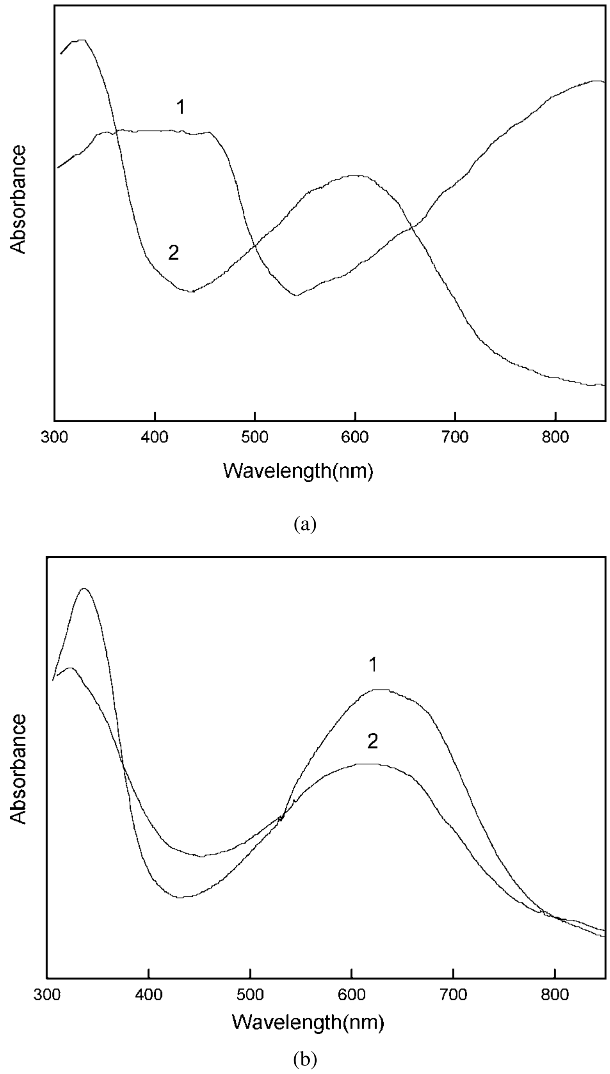

(a)

(b)

Figure 1 (a) UV-Vis spectra of PANI in chloroform: (1) doped state and (2) intrinsic state. (b) UV-Vis spectra of PANI in DMF: (1) doped state and (2) intrinsic state.

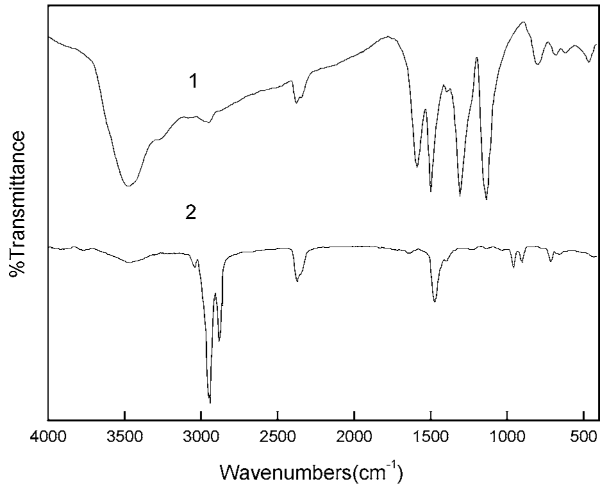

Figure 2 IR spectra of (1) PANI and (2) CTAB.

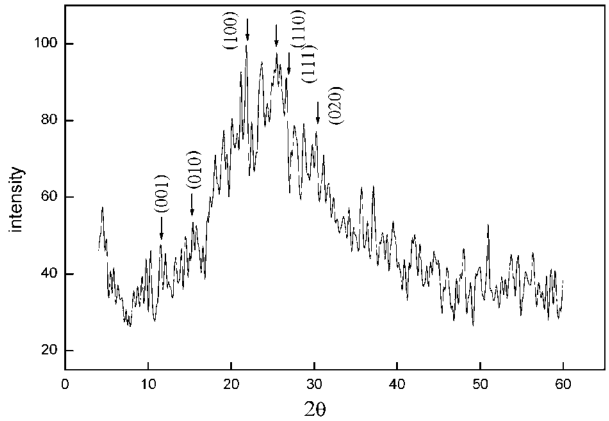

Figure 3 XRD pattern of PANI.

340–420 nm as a platform and 800 nm as the maximum peak respectively (curve 1). The plateau is combined by the two absorption bands of 320–360 nm and 400–420 nm wavelength; the first of these bands arises from π-π^* electron transition within benzenoid segments and the second band, accompanied by the 780–820 nm absorption band, is related to the doping level and formation of polaron [3]. However, the same phenomenon could not be found in Fig. 1b when using DMF as solvent. It was considered to be due to the interaction between the solvent and the doped PANI and hence the consequent formation of the deprotonation [10].

IR spetra of doped PANI is shown in Fig. 2 (curve 1). The main peaks of the PANI have been assigned as follows: 1590 and 1497 cm^{-1} as quinone (Q) and benzene ring (B) deformation and 1140 cm^{-1} relating to the doped structure from 1160 cm^{-1} as the intrinsic structure representing the vibrational mode of $N = Q = N$ [11]. The ratio of the relative intensity of 1584 to 1497 cm^{-1} was 1.08, which represented the Q/B ratio. It indicated that similar nitrogen quinone and benzoid ring structures existed in the PANI chain [11]. Compared with curve 2, the IR spectrum of CTAB, it was found that the structure of the surfactant was hardly present in the PANI structure, indicating that CTAB only played the part of a template by forming the reversed micelle to provide synthesis place for the polymerization of aniline, which was different with the PANI synthesized in dodecylsulfate (SDS) and dodecyl benzenesulfonic acid (DBSA) micelle systems [3, 4]· The latter showed that the surfactants were used both as surfactant and dopant, but in our experiment the CTAB just took part in the template synthesis of PANI and did not alter the structure of the HCl doped PANI.

The X-ray diffraction pattern of PANI is presented in Fig. 3 and the main diffraction peaks of the particles are indicated with arrows and some of them are indexed, which is consistent with the characteristic diffraction pattern of PANI doped with HCl [12]. Because the reaction is performed in the "water pools" [9], which is similar to the polymerization in common aqueous solution, and the CTAB only acts as surfactant, the obtained PANI has not got a high crystalline quality like those with SDS and DBSA used both as surfactant and dopant [3, 4].

Fig. 4 shows the CVs of PANI in DMF. By increasing the number of potential cycles, the peak current increased. The curves show that the PANI has the ability to form a film. It shows that PANI has a high electrical activity in DMF, a widely used solvent for PANI.

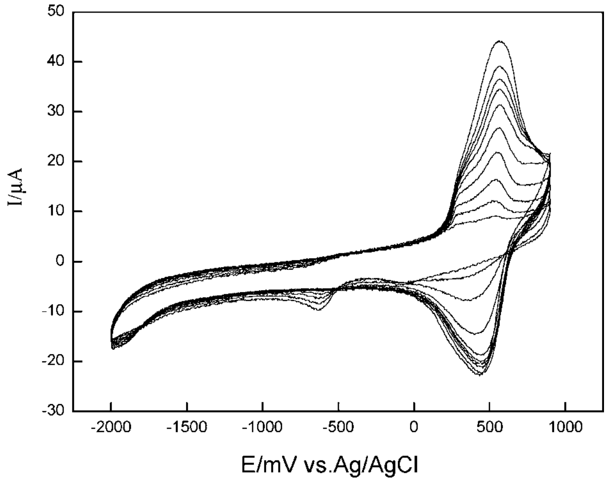

Figure 4 CVs of PANI in DMF (10 times).

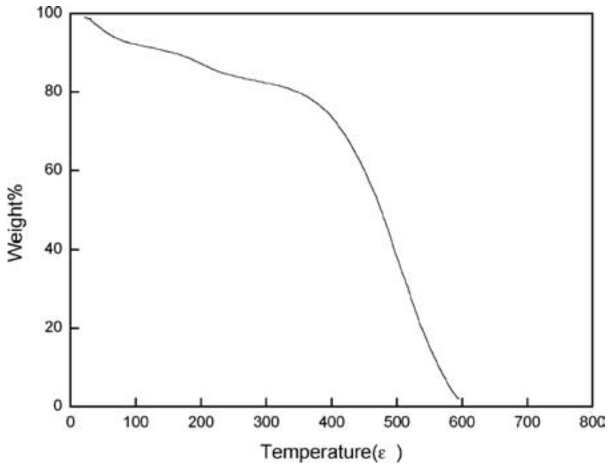

Figure 5 TGA curve of PANI.

Fig. 5 gives the TGA results for the PANI. The thermogram presents a typical three-step weight loss behavior. The first step showed 8% weight loss at temperatures up to 95 °C. This step could be attributed to loss of moisture present in the product. The second step exhibited a weight loss around 10% in the temperature range of 95–250 °C. This may be due to the loss of dopant in the sample. The third step began at 300 °C and became fast after 387 °C up to 600 °C, resulting in total weight loss, which indicates thermal degradation of PANI.

The conductivity of the sample was 1.4 S/cm, which was similar to the HCl doped PANI prepared by common polymerization in aqueous solution [9]. However, the dosage of the HCl here was just 1/20 of the amount reported in the literature [9], from which it is concluded to some degree that the reversed micelle located the HCl in a microenvironment with a high concentration and led to a high doping ratio.

The TEM image of PANI is given in Fig. 6. It shows that the PANI is ellipsoidal in shape with a diameter of ca. 50 nm and length of ca. 400 nm. We assume that the ellipsoidal PANI is composed of smaller globular particles because of some interaction of the surfactants, aniline and PANI particles, but the exact reason is not clear. From the hypothesis for the mechanism of nanoparticles formation in reversed micelles [13], we think surfactant CTAB first constructs reversed micelles in hexanol by dropping small amounts of aniline-HCl salt aqueous solution and small amounts of "water pools" are formed. After the oxidant is added into the system, APS accesses the "water pools" by diffusion and initiates the reaction. Then PANI precipitates in the "water pools" because of its insolubility in water. But the reversed micelle is not a static system and the "water pools" are undergoing a process of continuous formation and destruction. The surfactant will definitely have effects on the morphology of the preformed PANI particles, besides which the aniline-HCl salts and the preformed PANI particles themselves can interact with each other and finally lead to the ellipsoidal products. Furthermore, many factors such as the concentration of the aniline monomer, the kind of the surfactant, water content, and such factors influenced the morphologies of the PANI. Research in this field is still in progress.

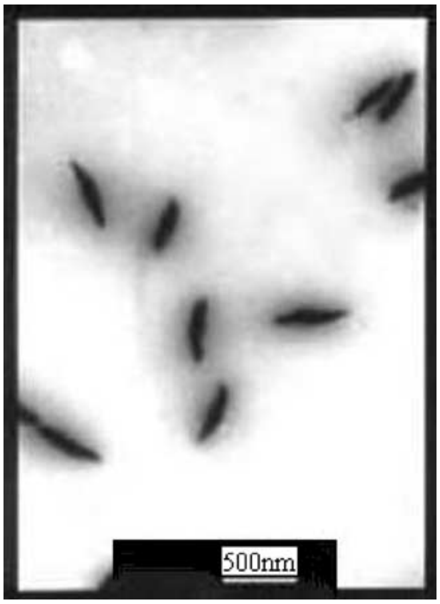

Figure 6 TEM picture of PANI.

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