

Preparation and Characterization of Anthracenecarboxylic Acid Doped Polyaniline Thin Films*

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Abstract Doped polyaniline films were prepared with electrochemistry method. A small conjugated molecule, anthracenecarboxylic acid (2-ACA), was used as the dopant, considering its electrical activeness due to the conjugated π - π^* structure. Film morphology of doped and undoped polyaniline samples was investigated. The corresponding changes in optical and electrical properties after ACA doping were discussed. By measuring and calculating their energy level distribution, a promising application of polyaniline thin films as buffer layer in optic-electric devices is expectable.

Keywords: Electrochemistry; Polyaniline (PANI); Doping; Solar cells.

INTRODUCTION

Among the conductive polymers, polyaniline (PANI) is an attractive member due to its environmental stability, tunable electrical properties and relatively low cost. PANI found its way in various applications such as gas sensors^[1], lithium batteries^[2], light emitting diodes^[3], organic solar cells^[4–6] and so on.

The conducting PANI films applied in these devices require doping to the molecules to form conductive salt. Usually, these doped PANI films are prepared through spin coating or electrochemistry methods. In the spin coating method, the chemically oxidized PANI particles were often doped with some organic groups^[7–9] in order to increase their solubility in organic or water solvents. In comparison, electrochemical deposition of PANI films on conducting base provides an *in situ* film formation with one-step process, which is clean and easy to handle without the limitation of dopant. Electrochemical synthesis of doped PANI films was largely investigated with various dopants^[10–12].

Although doping is of great importance to form the conductive PANI films, generally the doping materials themselves are mostly insulating, which is adverse to the transportation of charges in the films. Thus, electro-active dopant should be more attractive in that it may tune the functional as well as the structural properties of the basic PANI films. In our previous research, a small molecule, 9-anthracene methyl acid (9-AMA), was used as the dopant in PANI considering its electrically active conjugated structure^[13]. Tunable structural and optical-electrical properties were obtained for its application as an anode buffer layer in organic solar cells. It was found that the doping process was much difficult due to a large space steric hindrance effect of the 9-AMA molecule chain in which the carboxylic acid is sitting on the ninth carbon atom. The doping concentration of AMA is thus affected, which causes it difficult to tune the properties of PANI films in a large scale. Here in this work, the

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PANI film morphological and opti-electrical tunability in a large scale is achieved by adopting another anthracenecarboxylic acid (ACA) that has a relatively reduced space steric effect during its participation in polymerization. The structural, optical and electrical properties of the ACA doped and undoped PANI films are investigated, which shows a feasible tunability in its morphological and optic-electric properties.

EXPERIMENTAL

Materials

Anthracenecarboxylic acid (ACA, purity > 98%) and aniline (purity > 98%) were obtained from Sigma-Aldrich. Indium-tin oxide (ITO, 12 Ω per square) glass was purchased from Wesley Tech. Co., Ltd., China. Ethanol (purity > 98%), acetone (purity > 98%) and isopropanol (purity > 98%) were obtained from Beijing Chemical Factory. All chemicals were used as received.

Preparation of PANI Films with and without ACA Doping

Specific preparation of different PANI films was as follows: first, ITO/glass substrates were precleaned by soap water followed by deionized water, and then ultrasonicated in acetone and isopropanol for 15 min respectively and finally dried in air. Next, different volume of ACA was added to a solution containing 10 mL ethanol and 0.1 mL aniline. The mole ratio (ACA:aniline) was 1:8, 1:4 and 1:2, respectively. Electro-polymerization was carried out at 1.25 V on indium-tin oxide (ITO)/glass substrate that served as the working electrode while Pt net served as the counter electrode and Ag/AgCl as the reference electrode. The reaction was allowed for different time lengths for every dopant concentration. The as-synthesized PANI films were cleaned with ethanol and dried at 60 °C in vacuum. For comparison, PANI films without ACA doping were prepared and cleaned under the same condition.

Characterization

Fourier transform infrared spectroscopy (FTIR, Varian, Excalibur-3100) was used to characterize the composition of the electrochemically deposited films. The samples for FTIR test were prepared by scratching the polymer away from the substrate and blending with potassium bromide (KBr) powder to make KBr tablets. Scanning electron microscopy (SEM) measurements were performed on a JSM-7401 ultra-resolution field emission scanning electron microscope. UV-Vis-IR absorption spectra were recorded on a Cary U-5000 model spectrophotometer (Varian). Samples obtained from the above electrochemical experiments were used directly for SEM and UV-Vis-IR tests. Cyclic voltammograms measurements were carried out on an electrochemical workstation (CHI 660E) with the PANI films coated ITO glass as the working electrode, Pt as the counter electrode and Ag/AgCl as the reference electrode.

RESULTS AND DISCUSSION

The infrared spectra of the PANI films with and without ACA doping are shown in Fig. 1. Generally, similar infrared signals are observed for all the PANI samples. The two peaks locating between 1400 cm^{-1} and 1600 cm^{-1} are characteristics of the C=C bond vibration with the quinonoid ring at 1490 cm^{-1} and the benzenoid ring at 1580 cm^{-1} respectively. The characteristic peaks of the bonded —COO— group in the ACA doped polyaniline salts cannot be individually detected. This is due to its overlapping with the strong vibration signals of the PANI bone. Specifically, compared with the undoped PANI, the doped samples exhibit broadened infrared signal at 1580 cm^{-1} , which is attributed to the mergence of the vibration band of COO— into the C=C bond vibration peak. Similar behavior happens at the peak of 1250 cm^{-1} that is due to the overlapping of C—O stretching with the C—N stretching. Furthermore, the comparative peak intensity of quinonoid ring at 1490 cm^{-1} and the benzenoid ring at 1580 cm^{-1} is broadened after the ACA doping, suggesting that the oxidation state of the PANI is slightly affected by the ACA dopant. This is caused by the electron withdrawing property of carboxyl group in the ACA, which influences the electron density in the C=C bones^[14, 15].

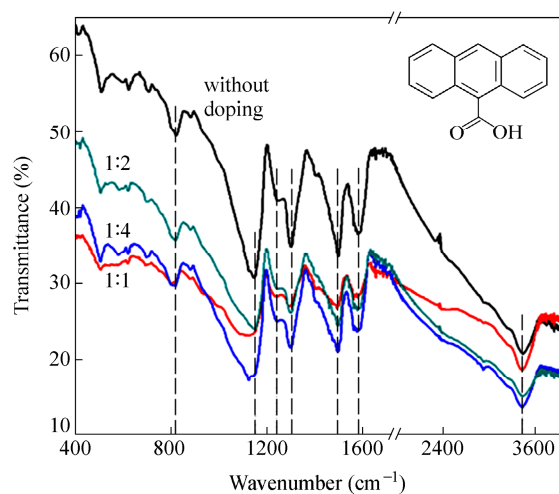


Fig. 1 FTIR spectra of ACA doped and undoped PANI materials (Reaction time 180 s)
The insert shows the molecule structure of 2-ACA used in this work.

The film morphology of PANI without ACA doping is shown in Fig. 2. It can be seen that, despite the deposition time, nano-sized particles exist on surface. The presence of this kind of morphology has been discussed as a mechanism dominated by preferential nucleation-growth process^[6] although blended ethanol and water solvents are used here. Comparing with the film deposited for 90 s, the film for 180 s has enlarged nanoparticle density on surface.

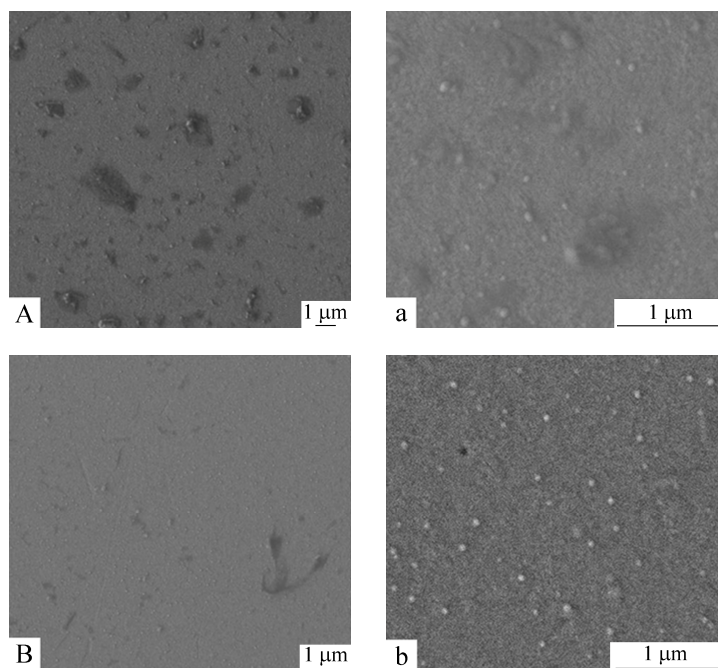


Fig. 2 Surface morphology of undoped PANI films at different deposition time:
(A) 90 s, (a) 90 s, (B) 180 s and (b) 180 s

Figure 3 shows the SEM images of ACA doped PANI films at different reaction time lengths and doping concentrations. Comparing with the undoped PANI films in Fig. 2, the surface of ACA doped PANI films at initial deposition (Fig. 3a and 3b) comprises two distinct nano-structures; one is nano-particles that can also be

seen in the undoped sample and the other one is large knolls well dispersed surrounding the nano-particles. Along with the deposition time of the doped PANI films, the knolls are gradually enlarged in size and density and connected with each other to bury the nano-particles and form the film surface (Figs. 3c and 3d)). Besides, at a smaller doping ratio, the size of the interconnected knolls is smaller and the film surface is completely covered by them (Fig. 3e) while at a larger doping ratio, the knolls become much larger and completely form the surface of the film (Fig. 3f). The nano-particles on both the doped and undoped PANI samples are pure PANI, which were also observed in our previous work^[6]. Together with the samples' light absorption and cyclic voltammograms studied afterwards, we infer that newly appeared knolls in the doped sample are likely to be ACA doped PANI particles due to the electro-polymerization of aniline-ACA salt. This phenomenon can be explained by the space steric hindrance effect of the aniline-ACA salt^[16]. At low doping concentration as well as short electro-deposition time, a small quantity of aniline-ACA salt monomer takes part in the polymerization of PANI because of their large space steric hindrance. More densely distributed and larger knolls will appear once the concentration of the aniline-ACA salt is enlarged and enough deposition time is given, so that they become the main composition of PANI films.

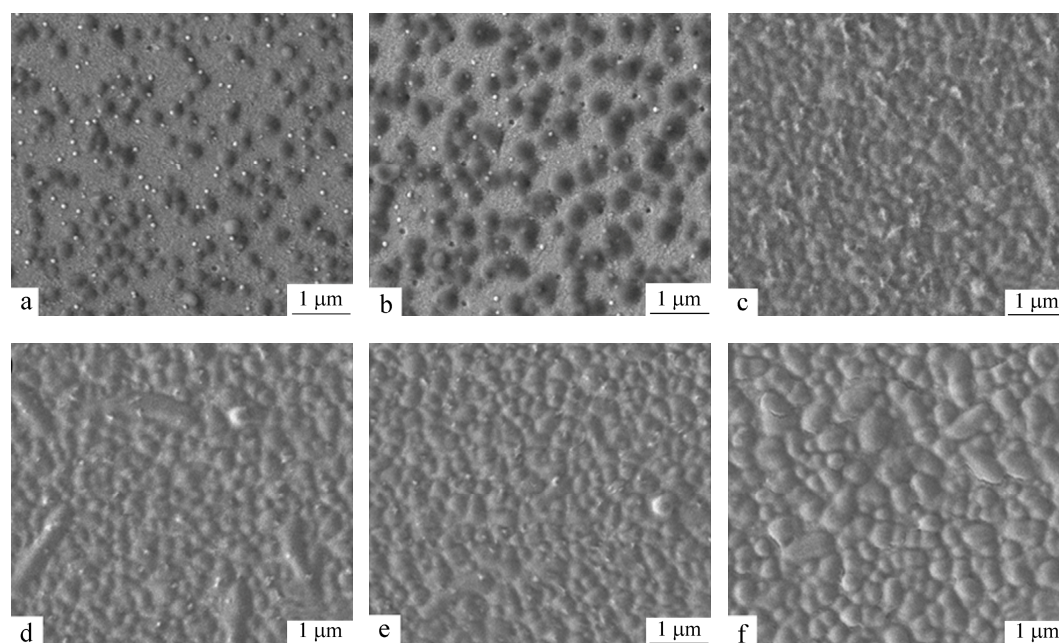


Fig. 3 SEM images of ACA doped PANI films at different reaction time lengths and doping concentrations (ACA:aniline): (a) 40 s, 1:4, (b) 80 s, 1:4, (c) 120 s, 1:4, (d) 180 s, 1:4, (e) 180 s, 1:8 and (f) 180 s, 1:2

The UV-Vis absorption spectra of electro-deposited PANI films with different ACA doping concentrations are shown in Fig. 4. It is shown that the PANI sample without ACA doping has an obvious absorption peak at about 360 nm and a broad absorption tail at 800 nm (Fig. 4a). The ACA doped PANI films with different doping concentrations exhibit one more absorption band at about 550 nm besides the other two at 360 nm and 800 nm. The absorption bands at 360 nm and 800 nm are attributed to $\pi-\pi^*$ transition of the benzenoid ring and the excitation to the polaron band respectively^[17, 18]. The newly appeared absorption band at 550 nm in the ACA doped PANI sample is assigned to the formation of a molecular exciton involving the charge transfer from the two adjacent benzenoid rings to the quinoid ring^[19]. This represents that the polarization and coplanarity of the π system have been affected to some extent, so do the conductivity of the PANI film accordingly. From the former morphology analysis, it must be related to the newly appeared second phase in the film and on its surface. Figure 4 (b) shows the absorption spectra of ACA doped PANI films versus photon energy. The optical band gap

of the ACA doped PANI films can be obtained considering the Tauc relation^[20]:

$$h\nu\alpha = A(h\nu - E_g)^{1/2} \quad (1)$$

where $h\nu$ is photon energy, α is absorbance coefficient, E_g is band gap energy and A is a constant. It can be seen that the optical band gap of ACA doped PANI film is much smaller than that in the undoped samples. From the above analyzing, it can be inferred that ACA molecule should be located near the quinoid ring after polymerization so that electrons' transferring from benzenoid ring to quinoid ring can be enhanced, as is given in Fig. 5 which exhibits the polymerization process and product. Here, just one case of the practical polymerization process is given while actually polymerization process happens more likely among PANI molecules with more adsorbed ACA molecules or monomers. With this doping pattern, the conductivity of electrodeposited films may be influenced. Considering the steric hindrance effect of the doped ACA molecule, the coplanarity of PANI chains is diminished, thus the conductivity of PANI film may be unfavorably affected. However, upon ACA doping, the measured film conductivity was found to be a little increased compared to that without doping (Fig. 6). According to the results from Fig. 3, this variation is thought to be closely related with the composition of electrochemically deposited films. It demonstrates that the gradually increased ACA doped PANI particles positively influence the film conductivity by virtue of an extended conjugation toward the side-direction which can enhance electron transfer among conductive/nonconductive regions^[21].

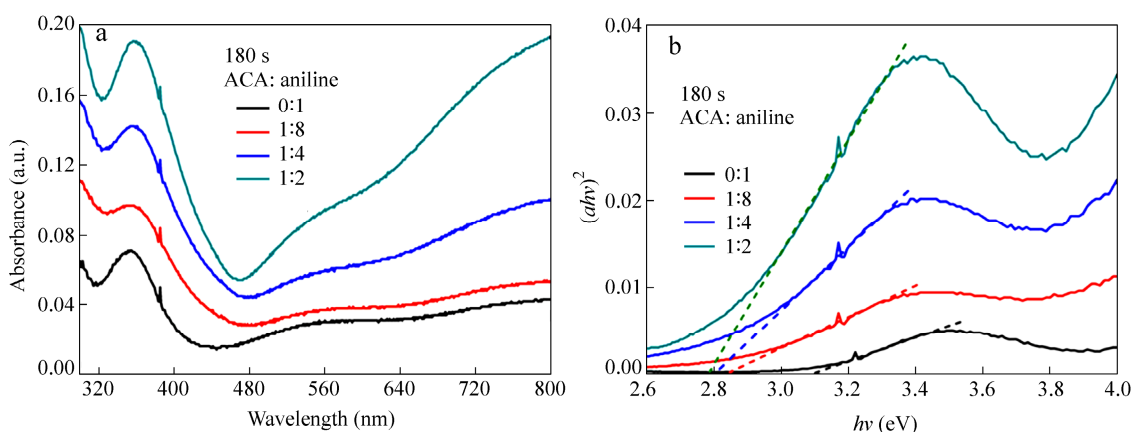


Fig. 4 UV-Vis absorption spectra of PANI films with different doping ratios: (a) absorbance versus wavelength and (b) absorbance versus photon energy

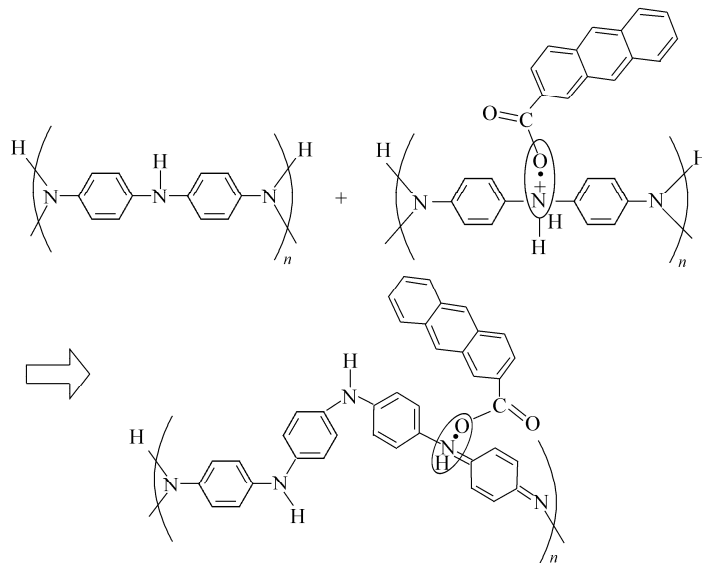


Fig. 5 The polymerization process of ACA doped PANI

Cyclic voltammogram (CV) is commonly used as a preliminary characterization technique^[22, 23] to determine the redox properties of a polymer film. In this work, the PANI films were electrochemically deposited on the conductive ITO glass, allowing us to study the electro-activity of PANI films with and without ACA doping (Fig. 7).

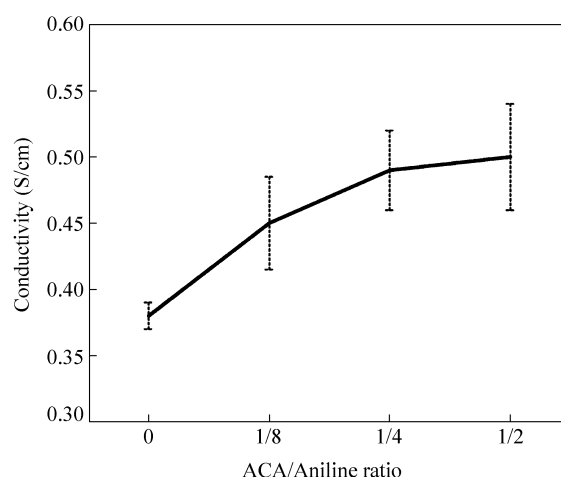


Fig. 6 ACA/aniline ratio dependence of film conductivity (The data under each doping concentration were averaged among six samples.)

Generally, redox behavior with three pairs of peaks can be seen in both the doped and undoped films, corresponding to conversion among different oxidation states. Under the same deposition time of 180 s (Fig. 7), the onset of the oxidation peak is slightly shifted to the higher potential when the ACA doping ratio (Rd) is increased, from about 0.15 V of the undoped PANI film to 0.16 V, 0.2 V and to 0.22 V when Rd = 1:8, 1:4 and 1:2 respectively. Considering the variation of the films configuration in Fig. 3, it can be concluded that the oxidation reaction of the PANI film occurs more hardly due to the presence of component that contains more ACA dopant. This is due to two effects. On the one hand, the carboxylic group in the ACA side chain withdraws electrons from the aromatic rings, making the bone chains more difficult to oxidize. On the other hand, the steric effect of the ACA side chain decreases the coplanarity of the PANI molecules which makes the overlapping of molecules more difficult.

With the C-V results analyzed above, the energy level distribution can be obtained by calculating the following^[24]:

$$\text{HOMO} = -e(\Phi_{\text{on}} + 4.66) \quad (2)$$

$$\text{LUMO} = \text{HOMO} + E_g \quad (3)$$

where HOMO represents the highest occupied molecular orbit, e is energy of electron, Φ_{on} is the onset oxidation potential which has already been obtained in the C-V characterization, LUMO is the lowest unoccupied molecular orbit and E_g is the value of energy band gap of PANI film that is given in the optical measurement. The calculated results of different PANI films are shown in Fig. 8.

The decreasing of LUMO and HOMO levels is caused by introducing and increasing ACA doping into PANI films, so is the value of energy band gap, E_g (Fig. 8). In all the ACA-PANI samples, the LUMO locate at a high energy level larger than -2.4 eV while the HOMO locates at a low energy level between -4.8 eV and -5.0 eV. It is noticed that the LUMO values of ACA-PANI films are much larger than those in the commonly used organic semiconductors or inorganic p-type semiconductors (such as P3HT with a LUMO value of about 3.0–3.2 eV). At the same time, the HOMO values are just distributed near the work function of the common ITO anode. Thus, electronically, the synthesized PANI films can play the role of anode buffer layer in some optic-

electric devices such as solar cells or light emitting diodes, prohibiting leak current while transferring holes to anode. Therefore, our work provides an easy processing, low-cost and flexible conducting substrate for some optic-electric devices aiming at commercialization.

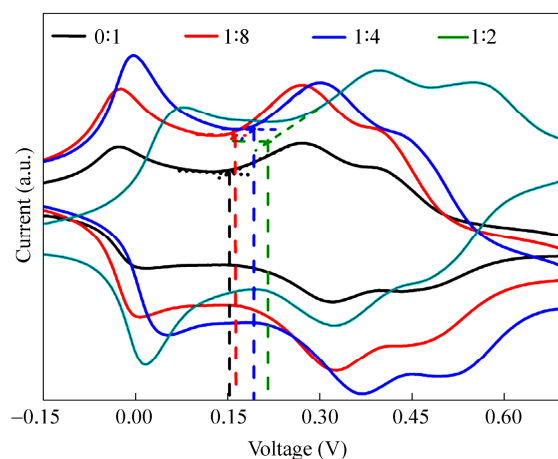


Fig. 7 Cyclic voltammograms of PANI samples with different doping ratios

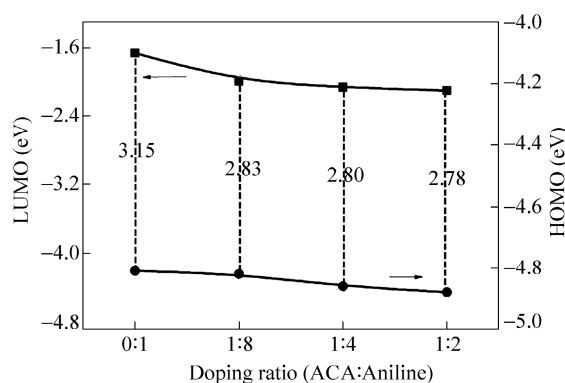


Fig. 8 Energy level distribution of PANI films with different doping ratios
The numbers between LUMO and HOMO curves represent values of energy band gap (E_g) of corresponding PANI films.

CONCLUSIONS

We have electrochemically synthesized PANI thin films doped with a small conjugated molecule. The film morphology turns out to be closely dependent on the doping concentration as well as deposition time. Correspondingly, the films absorption and electrochemical properties have been changed. A calculated energy levels distribution of different PANI films electronically indicates their potential as anode buffer layers of some optic-electric devices such as solar cells.

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