Study on the Synthesis and Photothermal Conversion Property of Polyaniline

Li Hong Bao¹, ², *, Xin Liu¹

¹School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China
²Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing 100029, China

*Author for correspondence; E-mail: clyblh@bift.edu.cn

Abstract. A series of polyaniline (PANI) with different HCl/ aniline and DBSA/ aniline molar ratio was synthesized in this paper. The structure of PANI was characterized using IR spectroscopy. The effect of pH, thermal stability and photothermal conversion properties of PANI were investigated. The results showed that the IR spectrum presented typical absorption peaks of PANI-ES. The pH had a big influence on the optical property of PANI. The PANI had high thermal stability in all HCl/aniline molar ratio. The molar ration of DBSA/aniline can influence the photothermal conversion of PANI, whereas the doped PANI showed better photothermal conversion efficiency than that of dedoped PANI.

Keywords: Polyaniline, photothermal conversion, optical property.

1. Introduction

Polyaniline (PANI), the most popular conducting polymer, has gained great attention due to its lower cost, interesting chemical and physical properties, ease of preparation. It has been studied to applied in a wide range of industrial fields, such as rechargeable batteries, gas sensors, polluted water remediation [1], electronic devices, solar cells, and polymer corrosion protection agents.

PANI is a mixed oxidation state polymer consisting of benzoid and oxidized quinoid units [2], the ratio of these two different units change with the synthesis composites and formula, thus endue PANI many unique properties and electronic conduction mechanisms that distinguish it from the other conducting polymers. Emeraldine base (EB), the typical dedoped state of PANI, has a structure consists of equal proportions of amines (–NH–) and imine (=N–) sites, after being protonated by acids HA, resulting in emeraldine salt with the conductivity of a semiconductor level. The electrical properties of PANI have recently been investigated a lot [3-4]. Up to now, only few studies on photo-response of PANI or PANI composite have dealt with. Silvestre B.A. studied the absorption capacity of infrared radiation by PANI nanoparticles dispersion and subsequent conversion to heat, they found under illumination of NIR laser at 780 nm and 100mW power, the temperature of aqueous medium (without PANI nanoparticles) increases only 3 °C after 10 min (600 sec) of laser application, while in presence of PANI nanoparticles the temperature increase 9.5 °C. The temperature change scales up with the concentration of nanoparticles indicating that the nanoparticles absorb strongly the NIR light [5].
functionalized graphene quantum dot shows improved photocurrent by enhancing interconnectivity and carrier transport [6]. polyaniline/ reduced graphene oxide (PANI/RGO) composites under visible light irradiation exhibit amazingly improved activity toward the degradation of cationic and anionic dyes in comparison with pristine PANI or RGO [7]. Thus, it would be very interesting to study the intrinsic photo-thermal conversion of PANI materials in the visible light and near infrared region, which can amplify the application of solar energy. Herein, we synthesized two series of PANI with different HCl/aniline and DBSA/aniline molar ratio and investigated the chemical structure, optical properties and thermal stability of these PANI. We also studied the effect of DBSA/aniline molar ratio on the photo-thermal conversion efficiency of PANI.

2. Experiment

2.1. Chemicals
Aniline (AR, ≥ 99.5%) and ammonium peroxydisulfate (APS, initiator) were purchase from Shanghai Aladdin Bio-Chem Technology Co., LTD. dodecylbenzenesulfonic acid (DBSA surfactant, dopant) was from J&K Scientific Ltd. Aniline was purified by distillation in vacuum before use. Other reagents were used as received without purification.

2.2. Synthesis of polyaniline (PANI)
A typical synthesis of polyaniline was carried out as follows: 1.86g of aniline (0.02mol) was dissolved in 80mL of 1M HCl aqueous solution and stirred for 30min at 0℃. An aqueous solution of 3.48g (0.01mol) DBSA dissolute in 30mL water was added in and stirred for 10min. A prepared solution of 4.56g of ammonium persulfate ((NH₄)₂S₂O₈; 0.02mol) in 20mL of 1M HCl solution, acting as oxidizing agent, was added slowly to the aniline and DBSA solution. The oxidative polymerization proceeded for 3 h at 50℃. The color of polymerization solution changed with polymerization continuing. In the initial stage, aniline/DBSA/ASP solution was transparent. As the polymerization proceeded, the color of the solution changed to yellow, brown and finally to green, which indicates the formation of PANI emeraldine salt (ES). After reaction, the resulting polymer was washed several times with methanol and 1M HCl solution to remove aniline monomers, oligomers, and residual oxidizing agent. The product was then dried in vacuum oven for 24h. Tab. 1 describes the recipes of the respective samples.

2.3. Dedoping of polyaniline
Dedoped PANI was prepared by treatment with ammonia solution. Polyamine was first dispersed in ammonia solution at room temperature under ultrasonication for 10min. The resulting product was washed with methanol and then dried in vacuum oven for 24h at room temperature.

2.4. Characterization
The UV-Vis spectra of the PANI samples dispersed in N-methyl-2-pyrrolidone were measured on an iS10 UV/Vis spectrophotometer (Scinco, USA). The FT-IR spectra were obtained using a Nicolet iS10 Fourier transform infrared spectrophotometer (Scinco, USA) at a resolution of 4cm⁻¹ using the attenuated total reflectance technique.

Thermogravimetric experiments were performed on a TGA-105(Shanghai Jiubin Instrument Co., Ltd) analyzer. PANI powder samples ranging from 5 to 7 mg and heated from 25 to 600 ℃ under N₂ atmosphere at a heating rate of 10 ℃/min.

Photothermal conversion experiments were performed under simulated sunlight PLS-SXE300C (filter) (Beijing Bofeilai Technology CO., LTD.). The temperature changes over time were recorded using an intelligent auto thermometer with a platinum electrode.
Tab. 1 Composite of PANI

| Sample | Aniline (mol) | DBSA (mol) | HCl (mol) | APS (mol) |
|--------|---------------|------------|-----------|-----------|
| PANI1  | 0.02          | 0.01       | 0.02      | 0.02      |
| PANI2  | 0.02          | 0.01       | 0.06      | 0.02      |
| PANI3  | 0.02          | 0.01       | 0.1       | 0.02      |
| PANI4  | 0.02          | 0.01       | 0.14      | 0.02      |
| PANI5  | 0.02          | 0.02       | 0.1       | 0.02      |
| PANI6  | 0.02          | 0.03       | 0.1       | 0.02      |

3. Results and discussion

3.1. FT-IR

![FT-IR spectrum of PANI](image)

FT-IR spectra of PANI sample was shown in Fig. 1. The bands of 1460 and 1554 cm\(^{-1}\) are assigned to C=C stretching of benzenoid and quinoid rings, respectively [8]. These bands appeared at lower wave number compared to that of dedoped PANI observed near 1500 and 1600 cm\(^{-1}\). The peak at 1294 cm\(^{-1}\) is assigned to C-N stretching of secondary amine of PANI backbone. The peak at 1235 cm\(^{-1}\) is the typical characteristic peak of conducting PANI-ES form [9]. The peak at 1108 cm\(^{-1}\) is assigned to a plane bending vibration of C-H that formed during protonating process. The peaks ranging from 2800 cm\(^{-1}\) to 3300 cm\(^{-1}\), are very small and slightly can be seem, are assigned to aliphatic C-H stretching mode correspondence to the long alkyl tail of DBSA. Therefore, this FT-IR spectra clearly illustrated the well-doped PANI-ES.

3.2. Yield and solubility

Tab. 2 Yield and solubility of PANI with different composition

| Sample | PANI1 | PANI2 | PANI3 | PANI4 | PANI5 | PANI6 |
|--------|-------|-------|-------|-------|-------|-------|
| Yield  | 160.6 | 153.1 | 151.04| 147.8 | 103.16| 169.15|
| Solubility | 24.60 | 27.35 | 29.47 | 40.76 | 22.23 | 37.22 |

Tab. 2 showed the yield and solubility of PANI synthesized with different components ratio. The results demonstrated that with the increase of HCl/aniline molar ratio, the yield decreased, and the solubility increased. Which may be due to protonation degree increased with the increase of HCl usage. The yields were higher than 100% for all PANI products was attributed to the existence of sulfonate anion [10]. Tab.2 also showed that the effect of DBSA on the solubility of PANI was more obvious than HCl. This verified the surfactant action of DBSA, which resulted in the better solubility of PANI [11].
3.3. Effect of pH
Commercially NMP product is alkaline, when PANI dissolve in it, the organic sulfonate acid will interact with NMP and result in the dedoping of PANI in a certain degree and form some emeraldine base. Adjusting the PANI3 solution with buffer solution, we can get PANI3 solution with different pH. The UV-vis spectrum of these solution was recorded and shown in Fig. 2. As shown in Fig. 2, when the pH was higher than 5.36, a strong absorption peak appeared in 620nm, which corresponded to a local charge transfer between quinoid ring and the adjacent imine-phenyl-amine unites [12]. At the condition of lower pH, two obvious absorption peaks occur in 430nm and 800nm respectively. Which are due to π-polaron band and polaron-π* band transition of emeraldine salt. What’s more, with the pH decrease, the absorption peak increase remarkably, this demonstrated that the amount of PANI emeraldine salt increase gradually.

Fig. 2 UV-Vis spectrum of PANI3 solution with different pH

3.4. TGA

Fig 3 shows the results of TGA measurement for PANI with different aniline/HCl molar ratio. It is clear that the thermal stability of all samples is quite high. The weight loss below 100°C was due to small amount of water contained in the products. The degradation between150 and 200°C was probably attributed to the loss of doped DBSA[13]. Whereas, the main weight loss located at about 300 °C is caused by the degradation of PANI main chain. There is no significant difference in the spectra among these samples, which indicated that the amount of HCl has little effect on the thermal stability of PANI polymer.

Fig. 3 TGA curves of PANI
3.5. **Photothermal conversion property**

![Photothermal conversion of PANI with different Aniline/DBSA molar ratio](image)

Photothermal conversion experiments were carried out on the PANI and dedoping PANI solution. Their conversion curves are shown in Fig. 4. Tab. 3 lists the temperature changes along the illumination time and the highest temperature the solutions can reach. The results indicated that the temperature of the PANI increased faster than that of dedoping PANI as the illumination of the Xenon lamp. This phenomenon can be ascribed to the PANI, which showed green color and had a significant absorption in the infrared radiation region (see Fig. 2b) and can generate heat directly. In contrast, the dedoping PANI, presented blue color, only has a weak absorption in the visible light region and needed to convert the light to thermal energy through a nonradiative decay process. The results suggested that doped PANI could be considered as an effective photothermal agent and pave the way for future solar thermal conversion materials.

| Sample  | a500s/℃ | b1000s/℃ | c1500s/℃ | T\textsubscript{max}/℃ |
|---------|---------|-----------|-----------|----------------------|
| PANI5   | 65.125  | 74.00     | 75.37     | 75.87                |
| PANI3   | 60.75   | 70.25     | 70.25     | 71.37                |
| PANI6   | 55.12   | 63.50     | 65.37     | 65.87                |
| Dedoping PANI3 | 49.25 | 51.75 | 52.5 | 53.87 |

Note: a, b, c are temperatures of PANI solution at 500s, 1000s, 1500s respectively.

4. **Conclusion**

A series of PANI was synthesized under the present of DBSA. The IR spectrum showed that a typical stretching peak at 1235cm\(^{-1}\) for conducting PANI-ES appeared. The yield and solubility study demonstrated that with the increase of HCl/aniline molar ratio, the yield decreased, and the solubility increased. pH has a big influence in the optical property of PANI and when the pH ranges from 3.71~6.66, the PANI showed absorption peaks in a different wavelength, that means it had different color and attributed to the various exciting process. The thermal stability for all PANI samples of different HCl/aniline molar ration were all quite high and the biggest degradation occurred at 300℃. The photothermal conversion results for PANI and dedoping PANI showed a significant difference. The PANI-ES had a higher efficiency and can reach a higher temperature under illumination at the same time. So, this kind of substance present potential application to future solar thermal conversion materials.

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