Influence of annealing effects on polyaniline for good microstructural modification

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H\textsubscript{2}SO\textsubscript{4} doped polyaniline (PANI) has synthesized by chemical oxidation method. The prepared Polyaniline were annealed at 150 ºC, 200 ºC and 250 ºC for 30 min in vacuum. Crystal size, percentage of crystallinity, total percentage of crystallinity properties of untreated and heat treated PANI samples were studied by using X-ray diffraction pattern. The molecular structure of untreated and heat treated samples were examined by using Fourier transform infrared spectrophotometer. UV study shows π−π* transition of untreated and heat treated of polyaniline were found at 328 and 636 nm. The peak at 636 nm reveals the extension of conjugated polymer. Thermal properties of untreated and heat treated PANI sample measured by using thermo gravimetric analysis and differential scanning calorimetric spectroscopy.

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1. Introduction

Conducting polymers have been greatly investigated for their proclaiming applications in gas sensors, batteries, light emitting diodes, solar cells, electrochromic devices (ECDs), field effect transistors, sensors, electronic circuit boards, and fuel cells etc. [1]. Polyaniline has attracted considerable attention due to its low cost, simple synthesis, good optical and electrical properties with exemplary environmental stability. It exhibits p-type semiconductivity at all temperatures. Many studies on polyaniline have shown that its chemical and physical properties strongly depend on the method of the preparation and the composition of the solution [2]. Polyaniline can exist as a salt or base in three isolable oxidation states: (1) leucoemeraldine, the fully reduced state of polyaniline, (2) emeraldine, the half oxidized state, and (3) pernigraniline, the fully oxidized state. The emeraldine salt is electrically conductive while the rest are insulators. They have interesting properties, particularly polyaniline exist in three different oxidized forms, such as reduced (leucoemeraldine-yellow), neutral (emeraldinesalt-green or emeraldine base-blue) and fully oxidized (pernigraniline-black), which shows different conductivities [3]. Usually Polyaniline can be synthesized from an aniline monomer by either chemical polymerization or electrochemical polymerization. Typically, conventional chemical synthesis of polyaniline is based on the oxidative polymerization of aniline using an oxidant in the presence of a strong acid dopant. The heat treatment of PANI at different temperatures causes intrinsic structural change like removal of dopant and intrinsic changes like oxidation, chain scission or cross linking and other chemical reaction and all these thermo-chemical changes do affect its conductivity [4]. The chemical method is a very feasible route for the mass production of PANI, does not need a conducting substrate and is not expensive. The properties of PANI mainly depend on the dopant ion employed. The protonic acid dopants usually used for PANI doping are inorganic acids such as HCl, H\textsubscript{2}SO\textsubscript{4}, HBF\textsubscript{4}, etc., and organic acids like camphor sulphonic acid (CSA), 5-sulphosalicylic acid, dodecybenzene sulphonic acid (DBSA) with large anions. The latter dopants increase the solubility of PANI [5]. Some literatures are also available regarding the effect of heat treatment of H\textsubscript{2}SO\textsubscript{4} doped PANI under air or nitrogen. However, the study on the vacuum heating of H\textsubscript{2}SO\textsubscript{4} doped PANI at different temperatures influencing both extrinsic and intrinsic structural change is relatively rare. In this present paper investigated chemically synthesized H\textsubscript{2}SO\textsubscript{4} doped PANI annealed at 150 ºC, 200 ºC and 250 ºC for 30 min under vacuum oven [4].

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2. Experimental

2.1. Materials

Aniline monomer (99% purity, Merck) was distilled under reduced pressure and stored at low temperature prior to use. Oxidant K2Cr2O7 (98% purity, Merck), Dopant H2SO4 (99% Purity, Merck) and Ammonia solution (99% Purity, Merck) were used as received. De-ionized water was used in all experiments.

2.2. Synthesis of polyaniline

PANI was chemically synthesized by oxidation method at room temperature. Aniline (9.8 ml, 1 M) was dissolved in 100 ml of 1 M H2SO4. 20 ml of K2Cr2O7 (1.4 g) was added to the solution which was magnetically stirred for 24 h. The product was filtered and washed with sulfuric acid (H2SO4) and acetone until the filtrate become colorless, and dried in a 60 °C oven overnight. Approximately 2 g of the above precipitate of emeraldine salt (ES) was added to 50 ml ammonia (NH3) and magnetically stirred overnight. This mixture emeraldine base (EB) became blue-purple in color. The resulting blue suspension product was filtered and washed with de-ionized water. The collected samples dried at 60 °C in vacuum oven for 24 h.

2.3. Annealing effects of polyaniline

For annealing treatment of PANI. Vacuum oven used was fitted with Omni set temperature controller and a rotary high vacuum pump. PANI was heated at 150 °C, 200 °C and 250 °C for 30 min in vacuum oven. The optical, electrical, structural and thermal properties were studied for both untreated and heat treated PANI samples.

3. Characterization

X-ray diffraction patterns of polyaniline sample performed using advance diffractometer with monochromatic Cu Kα radiation (λ = 1.54 Å) is used to identify crystalline nature of the samples. The crystallite size was determined from Scherrer relation

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( K \) is the shape factor for the average crystallite (0.9), \( \lambda \) is the wavelength of the X-ray which is 1.54 Å for Cu target, \( \beta \) is the full width at half maxima of the crystalline peak in radians, \( q \) is the angle between incident and reflected rays.

The FT-IR spectra of the PANI samples were recorded at room temperature using FT-IR Spectrometer Make: PerkinElmer; model: Spectrum RX 1; range: 400–4000 cm\(^{-1}\); resolution: 4. The sample was prepared in the pellet form by mixing the PANI powder with KBr by the ratio 1:10 and pressing it in the PerkinElmer hydraulic device using 15 t pressure. UV–vis spectra of the synthesized PANI were determined using a UV–vis spectrometer, model: Lambda 35; range: 400–1100 nm; resolution: 4; mode of operation: 1. transmission (T%) and absorbance (A%). Reflectance (R%). Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) were performed using PerkinElmer STA 6000 thermal analyzer. Heat from 50.00 °C to 400.00 °C at 20.00 °C/min.

4. Result and discussion

4.1. XRD spectrum of untreated and heat treated PANI samples

The X-ray diffraction patterns of PANI untreated and heat treated at 150 °C, 200 °C, 250 °C and 350 °C are shown in Fig. 1(a–e), respectively. There is a continuous decrease in the crystallinity and crystallite size with the increase in heat treatment temperature. This change may be due to heat effect or loss of other materials. The percentage of crystallinity of the samples was estimated from the ratio of crystalline peak area to total peak area. Crystallite size and percentage of crystallinity of untreated and heat treated PANI Samples are shown in (Table 1). The total crystalline size was found to be 212 nm, 129 nm, 98 nm and 60 nm. [5].

4.2. FTIR spectrum of untreated and heat treated PANI samples

Fig. 2(a–e) shows FTIR Spectra of PANI doped H2SO4 untreated and heat treated at (150 °C, 200 °C, 250 °C and 350 °C). The N–H symmetric stretching of PANI appears at 3429.39 cm\(^{-1}\), 3394.61 cm\(^{-1}\), 3405.78 cm\(^{-1}\), 3424.57 cm\(^{-1}\) and 3405.69 cm\(^{-1}\). The aromatic C–H asymmetric vibration was observed at 826.93 cm\(^{-1}\), 824.33 cm\(^{-1}\), 826.69 cm\(^{-1}\) and 817.50 cm\(^{-1}\). C–C stretching appears around 1589.90 cm\(^{-1}\), 1589.76 cm\(^{-1}\), 1589.15 cm\(^{-1}\), 1590.87 cm\(^{-1}\), 1591.47 cm\(^{-1}\) is due to oxidation state of polyaniline. The peaks at 1308.86 cm\(^{-1}\), 1303 cm\(^{-1}\), 1308 cm\(^{-1}\) and 1306 cm\(^{-1}\) are due to C–N stretching vibration. The peaks at 1115.18 cm\(^{-1}\), 1112.12 cm\(^{-1}\), 1138.24 cm\(^{-1}\), 1113.21 cm\(^{-1}\) and 1122.74 cm\(^{-1}\) are due to C–H in plane bending [6–8]. FTIR study reveals that the intensity of each spectrum is decreasing their stretching values. The intensity decreases while increasing

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>FWHM</th>
<th>λ (nm)</th>
<th>PC (%)</th>
<th>TPC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>16.6993</td>
<td>0.0836</td>
<td>99</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.0028</td>
<td>0.1004</td>
<td>80</td>
<td>80</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>20.2387</td>
<td>0.2342</td>
<td>36</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Heat treated at 150 °C</td>
<td>17.4064</td>
<td>0.1004</td>
<td>80</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>46.3868</td>
<td>0.2676</td>
<td>32</td>
<td>32</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>61.1672</td>
<td>0.5353</td>
<td>17</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Heat treated at 200 °C</td>
<td>17.4402</td>
<td>0.1338</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>51.8756</td>
<td>0.4015</td>
<td>22</td>
<td>22</td>
<td>98</td>
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<tr>
<td></td>
<td>55.3506</td>
<td>0.3533</td>
<td>16</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Heat treated at 250 °C</td>
<td>17.3795</td>
<td>0.2676</td>
<td>30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>66.1163</td>
<td>0.4896</td>
<td>19</td>
<td>19</td>
<td>60</td>
</tr>
</tbody>
</table>

| | | | | | |
|--------|--------|------|--------|---------|
| a | 2θ is the peak angle in degree. | b | \( D \) is the crystallite size. | c | PC is the percentage crystallinity of the corresponding peaks. | d | TPC is the total percentage of crystallinity of each sample. |
Table 2
FTIR region of untreated and heat treated PANI samples.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Sample name</th>
<th>Types of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N–H stretching</td>
</tr>
<tr>
<td>1</td>
<td>Untreated</td>
<td>3429.39</td>
</tr>
<tr>
<td>2</td>
<td>Heat treated at 150 °C</td>
<td>3394.61</td>
</tr>
<tr>
<td>3</td>
<td>Heat treated at 200 °C</td>
<td>3405.78</td>
</tr>
<tr>
<td>4</td>
<td>Heat treated at 250 °C</td>
<td>3424.57</td>
</tr>
<tr>
<td>5</td>
<td>Heat treated at 300 °C</td>
<td>3405.69</td>
</tr>
</tbody>
</table>

Fig. 2. FTIR spectrum of untreated and heat treated PANI samples.

Annealing treatment of each sample. The types of vibration and corresponding wave number (cm⁻¹) as shown in Table 2.

4.3. UV–vis spectrum of untreated and heat treated PANI samples

Fig. 3 shows UV–vis spectra of polyaniline base form in DMSO solution. Using DMSO as solvent, it was found that there exist two absorption bands, one located at 328 nm, and the other at 636 nm. It is known that ~328 nm absorption band was assigned to π–π* transition and ~636 nm absorption band to quinoidring transition in the chain of polyaniline. When polyaniline salt instead of base form was dissolved in DMSO solvent, the two peaks imply the interaction between polyaniline and DMSO. Since DMSO is a highly polar solvent, the solute–solvent interaction would be strong enough so the C=O group in the DMSO molecule would like to form a hydrogen bond with the NH segment of the polymer chain [9–13]. This in turn would bring de-protonation of the polymer chain which would result in conversion of the salt phase into the insulating emeraldine base. The strong band at ~600 nm is extension of conjugation in the polymer chain. The higher wavelength of transition enhances the intrinsic conductivity of samples. The observed shift of peaks from ~300 nm to ~650 nm. This is the characteristic of the fully oxidized form of Polyaniline. There is an increase in the band gap with the increase in heat treatment temperature as shown in Table 3 [13–18].

Table 3
UV–vis spectral data and band gap of untreated and heat treated PANI samples.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Sample name</th>
<th>Wavelength (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Band: 1</td>
<td>Band: 2</td>
</tr>
<tr>
<td>1</td>
<td>Untreated</td>
<td>331.83</td>
<td>636.44</td>
</tr>
<tr>
<td>2</td>
<td>Heat treated at 150 °C</td>
<td>328.00</td>
<td>633.13</td>
</tr>
<tr>
<td>3</td>
<td>Heat treated at 200 °C</td>
<td>327.98</td>
<td>632.14</td>
</tr>
<tr>
<td>4</td>
<td>Heat treated at 250 °C</td>
<td>324.17</td>
<td>625.00</td>
</tr>
<tr>
<td>5</td>
<td>Heat treated at 300 °C</td>
<td>318.10</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 3. UV-spectrum of untreated and heat treated PANI samples.

Fig. 4. (a) TGA spectrum of untreated PANI. (b) TGA spectrum of heat treated at 250 °C PANI.
5. Thermo gravimetric analysis (TGA) and differential scanning calorimetric of untreated and heat treated PANI samples

The TGA plot of untreated and heat treated PANI is given in Fig. 4(a and b). There are six steps of weight loss occurred during heating cycle under nitrogen atmosphere. The first step of weight loss below may be due to unbound water [19], the second step of weight loss occurring in between may be due to the unbound H₂SO₄, the third step of weight loss within may be due to bound water acting as secondary dopant [20]. Differential scanning calorimetric spectrum of untreated and heat treated PANI as shown in Fig. 5(a and b) and comparison of TGA and DSC spectrum as shown in Fig. 6(a and b).

The fourth step of weight loss over the temperature range is for bound H₂SO₄ acting as primary dopant, the fifth step of weight loss within is for thermal decomposition of PANI into some chemical forms and the final step of weight loss at around may be due to the final carbonization of intermediate chemicals. The relative weight percentage of bound and unbound water and H₂SO₄ loss with respect to PANI. Percentage of unbound water and unbound H₂SO₄ loss with respect to PANI decreases as the heat treatment temperature is increased [21].

6. Conclusion

Untreated and heat treated H₂SO₄ doped PANI at elevated temperature leads to destruction of crystal structure. The heat treatment always decreases the crystallinity and crystallite size of PANI. FTIR study reveals that the intensity of each spectrum is decreasing their stretching values as the heat treatment temperature is increased. UV study there is an increase in the band gap with the increase in heat treatment temperature. Polymer chain scission, cross-linking, quinoid to benzenoid ring conversion and vice versa along with doping and dedoping process depending upon the heat treatment temperature. Percentage of unbound water and unbound H₂SO₄ loss with respect to PANI decreases as the heat treatment temperature is increased.

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References


