Variation of Ammonium Persulfate Concentration Determines Particle Morphology and Electrical Conductivity in HCl Doped Polyaniline

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Abstract. Polyaniline (PANI) is one of conducting polymers which is widely used in various applications especially energy field, like solar cells and batteries. PANI emeraldine salt (PANI ES) is the only type of conducting PANI which can be easily synthesized using a direct mixing method in an oxidizing solution. Ammonium persulfate (APS) is one example of a strong oxidizing agent which is often used in PANI synthesis. The APS concentrations used in this study ranged from 0.1 to 1 M. Infrared and Raman spectroscopy shows that the addition of APS concentrations above 0.5 M produces the non-conducting fully oxidized PANI and phenazine species. Scanning electron microscope (SEM) showed morphological changes of PANI ES from nanofiber (diameter 80 - 110 nm) to granules (diameter 20 - 70 nm) as APS concentration increases. Based on Electrochemical impedance spectroscopy (EIS), conductivity of PANI increases as APS concentration increases with maximum conductivity of 0.36 S cm⁻¹ at 0.5 M.

1. Introduction

The development of conducting polymers has attracted great interest in many applications and different fields. Polyaniline (PANI) is one of the most intensively studied conducting polymers during the last decade due to its ease of synthesis, wide-range conductivity, good environmental stability, and interesting redox properties [1,2]. Many research groups reported that PANI has been used in very broad applications like corrosion protection [3], photovoltaic cells [4], and sensors [5]. PANI has three different forms based on its oxidation state: Leucoemeraldine Base (LEB), Emeraldine Base (EB), and Pernigraniline Base (PEB) (Figure 1). Three forms of PANI differ in the ratio of reduced (benzenoid) and oxidized (quinoid) numbers in the repeating unit [6]. Intrinsically, all three forms are insulator. EB has a unique structure where it consists of alternating benzenoid and quinonoid rings. EB can be easily transformed into Emeraldine Salt (ES) through acid doping process [7]. This leads to the formation of bipolaron and polaron enhancing the conductivity up to 5 orders of magnitude with respect to PANI EB.

The polymerization method determines the properties of final products, i.e. chemical composition, oxidation state, and average molecular weight. PANI ES can be synthesized using several methods, e.g. direct mixing [8], electrochemical [9], and interfacial/emulsion processes [10]. Direct mixing is
the simplest method to obtain high yield of PANI ES [11]. In this method, the choice of oxidant is a crucial factor to obtain PANI with desired oxidation state. Previous works reported many different oxidants were used in PANI synthesis. This group of oxidant constitutes sodium or ammonium persulfate [12], ammonium cerium (IV) nitrate mixture [13], potassium chromate [14], and hydrogen peroxide [10]. Ammonium persulfate (APS), firstly introduced by MacDiarmid (1986), is one example of a strong oxidant leading to the formation of PANI emeraldine. APS dissolves easily in water facilitating redox reaction in aqueous medium. Its by-product is also soluble in water and does not interact with PANI simplifying the purification of polymerization product.

![Figure 1. Three isolative species of PANI based on its oxidation state [6].](image)

In this work, we investigate the effect of APS concentration on physicochemical properties of PANI ES. PANI ES synthesis was simply carried out using the direct mixing method with various APS concentration. We expect the optimum APS concentration will produce PANI ES with high conductivity.

2. Experimental Section

2.1. Materials

Aniline and acetone were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) and Ammonium persulfate (APS) were purchased from Merck. All reagents are analytical grade and used without any further purification.

2.2. Synthesis of HCl doped Polyaniline (PANI ES)

PANI was synthesized using a direct mixing method [12]. Two solutions were initially prepared: (1) 3.64 mL of aniline was dissolved in 100 mL of demineralized water and (2) varied amount of APS was dissolved in 100 mL of HCl aqueous solution to obtain different concentration of APS (Table 1). These two solutions were then put at room temperature for 1 hour. Solution (2) was added dropwise to solution (1) under constant stirring for 15 minutes. The mixture was then transferred to a cooling bath (T = -20 °C) and kept for 4 days. Temperature was increased to 8 °C for 18 hours to melt the frozen mixture. The reaction mixture was then filtered, rinsed with HCl and acetone repeatedly, and dried in vacuum oven for 48 hours.
Table 1. APS concentration in HCl doped polyaniline synthesis using direct mixing method

| Sample code | APS Concentration (M) |
|-------------|-----------------------|
| PANI I      | 0.1                   |
| PANI II     | 0.2                   |
| PANI III    | 0.4                   |
| PANI IV     | 0.5                   |
| PANI V      | 0.6                   |
| PANI VI     | 0.8                   |
| PANI VII    | 1.0                   |

2.3. Characterizations

The chemical structure of PANI was characterized by a Bruker Alpha FTIR-ATR spectrometer and a Bruker Senterra Raman spectrometer with laser line excitation at 785 nm. LCR meter Agilent E4980A was used to determine the electric conductivity of the samples. Electron micrographs of samples were obtained using a SEM JEOL-JSM-6510LV.

3. Results and Discussion

3.1. Synthesis of HCl doped Polyaniline (PANI ES)

Direct mixing synthesis produces green powder samples with slightly different tone depends on APS concentration (Figure 2). At low APS concentration (PANI I and II), slightly bluish powder samples were obtained. Bluish green color corresponds to the presence of less oxidized species of PANI. As APS concentration increases (PANI III to VI), the color becomes intense green which is typical color of PANI ES. When APS concentration reaches 1 M, the color of PANI VII turns black which corresponds to the non-conducting fully oxidized PANI species, the Pernigraniline salt/PANI PS [15].

![Figure 2](http://example.com/f2.png)

Figure 2. HCl doped PANI samples with different green tones synthesized at different ammonium persulfate concentration: (a) PANI I (b) PANI II (c) PANI III (d) PANI IV (e) PANI V (f) PANI VI and (g) PANI VII.

3.2. Chemical structure investigation

To confirm our previous findings, Infrared and Raman spectroscopy analysis were carried out. In general, Infrared spectra of all samples provide similar features (Figure 3a). The main characteristic bands of PANI are associated with C–C and C= C stretching from quinonoid rings (1609 and 1574 cm\(^{-1}\) respectively), C=C from benzenoid rings (1485 cm\(^{-1}\)), C–N (1310 cm\(^{-1}\)), C~N\(^{+}\) in polaronic structure
(1249 cm\(^{-1}\)), N=Q=N (1177 cm\(^{-1}\)), Q=NH–B and B–NH–B (1152 cm\(^{-1}\)) [16]. The last band at 804 cm\(^{-1}\) is associated with the out of plane bending vibration mode of C–H [16]. We observed changes in Infrared spectra with the increase of APS concentration. As APS concentration increases, bands at 1609 and 1177 cm\(^{-1}\) are also increasing in intensity. This corresponds to the formation of higher oxidation that indicated by the increase of quinonoid ring numbers. Another change is observed at high APS concentration (PANI VI and VII) with the presence of the band at 1689 cm\(^{-1}\). This is consistent with the presence of non-conducting phenazine species that commonly considered as defect in PANI [17].

Figure 3b shows Raman spectra of PANI samples presenting some characteristic features of PANI ES. Both bands at 419 and 515 cm\(^{-1}\) correspond to the in-plane amine deformation. Band at 575 cm\(^{-1}\) associates to the ring (6b) deformation. Bands at 720 and 807 cm\(^{-1}\) correspond to the imine (C–N= C bending) and amine (C–N–C bending) deformations, respectively. The intense single band at 1177 cm\(^{-1}\) is the characteristic of C–H bending in the emeraldine (9a) species. The presence of polaron species is confirmed by the occurrence of band at 1332 cm\(^{-1}\) which correlates to the C–N\(^+\) stretching. The band at 1374 cm\(^{-1}\) is attributed to the C–N stretching vibration that appeared in the quinonoid ring neighborhood. Band at 1510 cm\(^{-1}\) is assigned to the N–H deformation vibrations associated with the semiquinoid structure. The band at 1590 cm\(^{-1}\) corresponds to the C=C stretching in Q [18]. Band intensity at 1332 cm\(^{-1}\) increases with APS concentration indicating more polaron species in PANI. This change is followed by the increase of band intensity at 575 cm\(^{-1}\) that associates with the formation of non-conducting phenazine species.

3.3. **Particle Morphology**

SEM images of all synthesized PANI ES are presented in Figure 4. Particle morphology of PANI ES evolve from nanofiber to granules with APS concentration. Average diameter of nanofiber PANI ES varied from 80 to 110 nm (Figure 4h). The nanofiber average diameter increases from PANI I to IV before abruptly decreases at PANI V. Further increase of APS concentration, PANI VII particles tend to form granules. The granules is an agglomerate structure, consist of small particles with diameter 20 – 70 nm. This mechanism is in a good agreement with proposed mechanism in previously reported
works how the PANI particles formed and evolved [19-21]. In the reaction mixture, two major species are present, namely the anilinium and radical anilinium cations. The presence of radical anilinium cations has been discovered by Ding et al using the radical trapping method [22]. These two species will react to initiate the polymerization forming active cationic radicals, then followed by propagation steps consuming the anilinium cations [11]. At low APS concentration, the anilinium cations is the major species in the reaction mixture. This will produce longer chains of PANI ES due to the limitation of radical anilinium cations. Those PANI chains will interact each other through intermolecular interactions (Hydrogen bonding) to form nanorod particles.

The diameter of nanorods increases with APS concentration because the cationic radicals concentration increases. The cationic radical concentration determine the reaction kinetics. The reaction rate increases with cationic radical concentration, while the cationic radical still act as the limiting reagent. The low APS concentration is a kinetic controlled reaction condition. In this condition, the monomers are present in abundant. The diameter of nanorods will be determined solely by the synthesis duration. All reactions were carried out with the same reaction time, therefore faster reaction produces larger particles. At high APS concentration, the radical anilinium cations is the major species in the reaction mixture. The competition of propagation and termination process will be severed due to high radical/reactive species concentration. As consequence, shorter PANI ES chains are produced. Those chains interact each other forming small particles that agglomerates resulting granules.

![Figure 4. SEM images of PANI synthesized with different ammonium persulfate concentration: (a) PANI I (b) PANI II (c) PANI III (d) PANI IV (e) PANI V (f) PANI VI and (g) PANI VII. Average nanofiber diameter as a function of APS concentration (h).](image)

3.4. Conductivity measurement

Figure 5a presents the frequency response of electrical conductivity for samples synthesized with different APS concentration. The steepness in conductivity decrease profile tends to increase with APS concentration and reached the maximum at PANI IV. This kind of conductivity profile is typical for materials with metallic conduction. Thus, PANI ES samples synthesized at low APS concentration provide metallic conduction. This behavior is less pronounced at higher APS concentration. PANI VI and VII have a semiconductor conduction type. Semiconductor conduction shows an increase of conductivity in their frequency response profile. The conductivity value at 20 Hz tends to decrease as APS concentration increases with the maximum value of 0.36 S cm⁻¹ at PANI IV (Figure 5b). This due
to the larger nanofiber diameter with APS concentration as observed in SEM images (Figure 4). We also determined the number of charge carrier \((n)\) in each sample by using Drude model approach using the following equation [23]:

\[
n(\omega_0) = \frac{2m_e}{\pi\alpha^2} \int_0^{\omega_0} \sigma(\omega) \, d\omega
\]

(1)

![Figure 5](image)

**Figure 5.** Conductivity profile (a) and value (b) at 20 Hz of PANI ES.

It is obtained that \(n\) value is in order 10\(^7\) – 10\(^8\) and have a similar tendency with conductivity value. We can correlate this phenomenon to our previous findings that PANI ES synthesized at high APS concentration contains phenazine structure and have granular structures. The presence of phenazine structure can either stabilize or trap the charge carriers reducing the electrical conductivity [24]. Nanorod morphology is also well known to facilitate better electron flow than granules in PANI ES due to the lower limit of percolation of rod-like particles with respect to spherical particles [25].

4. **Conclusions**

PANI IV, which has ammonium persulfate (APS) concentration of 0.5 M, demonstrates the optimum condition for HCl doped PANI synthesis using direct mixing method. PANI ES has nanorod morphology, while granules were obtained at PANI VII. Infrared and Raman spectroscopy revealed that APS concentration usage below or above 0.5 M will lead to the formation of lower or higher oxidation state of PANI ES respectively. PANI ES has metallic conduction at low APS concentration, while semiconductor conduction produced at high APS concentration. The conductivity value
decreases with APS concentration. The presence of phenazine species is also responsible decreasing electrical conductivity besides particle morphology and PANI oxidation state.

5. References
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