Microstructure Investigation of Polyaniline (PANI) Conductive Polymer Synthesized through Chemical Polymerization

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Abstract. The synthesis of Polyaniline (PANI) conductive polymer was successful through chemical polymerization method. Based on characterization results, it has an excellent surface structure which has a potential to use for electrochemical devices such as supercapacitor because of its surface structure. EDX and mapping results were confirmed that all desired constituent was present in this material. The FTIR and Raman spectroscopy results show that this material has strong chemical bonding between the entire constituent in the material. This material is highly recommended for further investigation for some applications especially electrochemical energy storage devices.

1. Introduction
Polyaniline (PANI) is one of the popular conducting polymers which can be used for some applications such as energy storage devices (semiconductor and batteries), organic field transistors, and anticorrosive coatings and so on [1,2]. It is attractive due to its high conductivity, environmental stability, fast redox activity and high specific capacitance [3,4]. For semiconductor application, PANI is usually mixed with nanomaterial to become nanocomposite material to give high performance for semiconductor. Nanomaterial is usually prepared through some methods such as sol-gel method [5,6], auto combustion [7] and thermal method [8]. There are some methods that have been developed to prepare PANI, such as chemical oxidation (chemical polymerization), standard polymerization, a course of chemical oxidation and electrochemical oxidation [9]. In this research, PANI was prepared through chemical polymerization because it’s simple and environmentally friendly method.

The limitation of PANI is the poor electrochemical stability as a result of significant volume change due to shrinkage of polymeric chains during redox cycling limits its application to a great extent [10]. In order to overcome the limitation, several studies have been making doping this material with other materials to become nanocomposite material. Nanocomposite like PANI and holey graphene nanoribbons have been developed and it is yielding an excellent electrochemical properties [11]. In other cases PANI has been
mixed with carbon nanotubes (CNT) for supercapacitor electrode that shows competitive specific capacitance [12]. PANI material with nanostructures will give better electrochemical properties because of its distinctive characteristics of conducting pathways and surface interaction. Several types of PANI such as PANI nanowires, nanorods, nanotubes, nanoparticles and nanofibers have been studied [13,14,15].

The objectives of this paper are to evaluate the microstructure, chemical bonding and possibility of the material to be used in electrochemical devices such as semiconductor. The synthesis and characterization of PANI were done through chemical polymerization and the characterization was using FESEM with EDX and mapping, FTIR for chemical bonding evaluation and Raman spectroscopy.

2. Methodology

2.1 Material preparation

The preparation of the material was done by using raw materials such as aniline (C₆H₅NH₂), 1 M hydrochloric acid (HCL) and ammonium persulphate ((NH₄)₂S₂O₈. The aniline and hydrochloric acid were mixed in 500 ml beaker glass and put in ice bath for 1 hour to make the temperature down until 0°C. The mixed of ammonium persulphate with distilled water was also placed in the ice bath using 500 ml beaker glass to make the temperature of mixture drop at 0°C. After the temperature reached 0°C, the persulphate solution was dropped wise into aniline solution. After the solution changing its color wait around 1 hour to make sure the interaction between aniline and ammonium persulphate is work, then the solution is ready to filtered and rinsed with distilled water. The wet powder of PANI will obtained after the filtration, after that it is ready to heat up in the oven at temperature 60°C for 5 hours to make it dry. Figure 1 described the flow chart of the material preparation.
2.2 Characterization
The characterization of the material was done by using FESEM to investigate its surface structure, energy dispersive x-ray (EDX) analysis and mapping of the material. Another characterization was examined using Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy which investigates the chemical bonds of the material.

3. Results and Discussion

3.1 Field Emission Scanning Electron Microscope (FESEM)
Figure 2a and 2b shows a typical FESEM image of the PANI nanospheres in solution 0.1 M aniline with heat treatment 80°C. It shows the PANI microspheres were successfully prepared. High magnification of FESEM shows that, the surface area of PANI has spaces between the material. This structure would enhance the penetration of electrolyte ion during the electrochemical properties measurement.

Figure 2. FESEM Images of PANI for (a) 50 kx, (b) 20 kx
3.2 Energy Dispersive X-Ray (EDX) Analysis

Figure 3a and 3b show the spectrum position of PANI for the EDX examination. According to the EDX results in Table 1, percentage of atomic carbon has the highest percentage which is 88.09 % and followed by O, S, and Cl respectively. The high carbon quantity will give an advantage for electrochemical properties characterization. The typical carbon material will be useful to give higher performance on double layer capacitor (EDLC).

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C K     | 84.9     | 88.09    |
| O K     | 14.42    | 11.34    |
| S K     | 1.20     | 0.47     |
| Cl K    | 0.29     | 0.10     |
| **Total** | **100.00** |          |

Table 1. Atomic percentage of PANI

Figure 3. (a) Electron image of PANI, (b) EDX Spectrum

3.3 Mapping of PANI

Mapping is used to confirm the presence of constituent inside of the material. Based on mapping result, it shows that inside of this conductive polymer has C, S and Cl as the major constituent. The corresponding color maps show the homogeneous distribution of S and Cl throughout the material and inhomogeneous of carbon atom in the material.
3.4 Fourier transform infrared spectroscopy (FTIR)

Figure 5 shows the typical FTIR spectrum of PANI nanospheres. The bands at 2024 and 1621 cm$^{-1}$ can be assigned to aromatic C-H stretching modes. The characteristic absorbance at about 1511 and 1348 cm$^{-1}$ indicate the signature of the PANI backbone due to the stretching modes of the protonated quinoid ring and the benzenoid ring. The band at 1191 can be assigned to the C-N stretching mode in a secondary aromatic amine. Band at 831 cm$^{-1}$ correspond to an aromatic C-H in-plane bending mode. Therefore, the results of FTIR spectrum demonstrated the PANI were prepared and existed in the conducting emeraldine form.

![Figure 5. FTIR spectrum of PANI](attachment:image.png)
3.5 Raman Spectroscopy Analysis
The Raman spectrum of PANI is shown in Figure 6. The bands at 1405, 1494 and 1595 cm\(^{-1}\) corresponds to the C-N stretching mode of delocalized polaronic charge carriers. These 3 bands have strong intensity which means the concentration of C-N stretching mode was high. The peak at 2818.35 can be assigned as C-C deformation bands of semiquinone ring. Characteristic of N-H bending deformation is shown at peak 2022.6. In addition, the bands at 415.62, 573.5 and 840.87 may be attributed to existence of the semiquinone structure and C-N stretching mode.

![Figure 6. Raman spectrum of PANI nanospheres](image)

4. Conclusion
The PANI conductive polymer was successfully synthesized through chemical polymerization. FESEM results shows really fine surface structure and majority of elements inside the material are C, S, O and Cl. Based on FTIR and Raman spectroscopy results, it shows that the bonding of the constituent in the material is well formed. Through surface structure of this material, it seems this material has the potential to be used for electrochemical energy storage devices.

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