Preparation of high surface area and high conductivity polyaniline nanoparticles using chemical oxidation polymerization technique

S Budi¹*, Yusmaniar¹, A Juliana¹, U Cahyana¹, A Purwanto¹, A Imaduddin² and E Handoko³

¹ Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Negeri Jakarta, Jl. Rawamangun Muka, Jakarta Timur 13220, Indonesia
² Research Center for Metallurgy and Materials, Lembaga Ilmu Pengetahuan Indonesia, Puspiptek, Serpong, Indonesia
³ Department of Physics, Faculty of Mathematics and Sciences, Universitas Negeri Jakarta, Jl. Rawamangun Muka, Jakarta Timur 13220, Indonesia

*Corresponding author: setiabudi@unj.ac.id

Abstract. In this work, polyaniline nanoparticles were synthesized using a chemical oxidation polymerization technique. The ammonium peroxydisulfate (APS)/aniline ratio, APS dropping time, and polymerization temperature were optimized to increase the surface area and conductivity of the polyaniline. The Fourier-transform infrared (FTIR) spectrum confirmed the formation of emeraldine salt polyaniline. X-ray diffraction (XRD) patterns indicated that amorphous and crystalline phases of the polyaniline were formed with crystallinity less than 40%. Scanning electron microscope (SEM) micrographs showed that the finest nanoparticles with uniform size distribution were obtained at the polymerization temperature of 0°C. A surface area analyzer (SAA) showed that the highest Brunauer-Emmett-Teller surface area ($S_{BET}$) of 42.14 m²/g was obtained from an APS/aniline ratio of 0.75 with a dropping time of 0 s at a polymerization temperature of 0°C. A four-point probe measurement conducted at 75–300K indicated relatively high conductivity of the semiconductor characteristic of the polyaniline.

1. Introduction
Polyaniline has been considered as a conjugated polymer that possesses semiconducting properties and shows specific characteristics including corrosion resistance, lightweight, and flexible. This conductive polymer has reversible electrical and optical changing through redox and doping-dedoping or protonation-deprotonation reactions [1,2]. The conducting state of polyaniline can be obtained in the form of protonated emeraldine, which is called emeraldine salt. Simple and cheap processes can synthesize this polyaniline through chemical oxidation polymerization [3] and electro-polymerization [4] methods. Based on its physicochemical characteristics, polyaniline might be potentially used as an electrode in capacitive deionization (CDI) system. CDI is a water processing technology based on charged ion adsorption controlled by the electrical potential difference between two electrodes [5].
This system can be applied to desalination processes, groundwater remediation and hard water softening[6,7]. In this system, the electrode is the most important part used for the adsorption of ions in the water purification process, which are then desorbed back after being saturated, resulting in an electrode that can be used repeatedly. For this condition, the electrode should be stable in an aqueous solution when an electric current is applied, conductive, and have a high surface area [8].

In this study, the conductive form of polyaniline was prepared by doping the half-oxidized structure of the polymer (emeraldine), which was synthesized using a chemical oxidation polymerization technique with protonic acid HCl. This emeraldine form of polyaniline is known to have the highest conductivity and is the most extensively researched since its conductivity can be arranged through doping-dedoping [9]. To obtain polyaniline with a high surface area, the reaction conditions such as the ratio of oxidant/aniline, polymerization temperature, and oxidant dropping time were varied.

2. Methods
Polyaniline was synthesized using a chemical oxidative polymerization method. Pure analysis grade chemicals purchased from Merck i.e., aniline, ammonium peroxydisulfate (APS), and hydrochloric acid (HCl). Double-distilled water was used for the preparation of all solutions used in this work. The aniline solution concentration was 0.2 M, while the APS concentrations were prepared as 0.05 M, 0.15 M, and 0.20 M. The polymerization was performed in solutions with several APS/aniline molar ratios, namely 0.25 (C1), 0.75 (C2), and 1 (C3). In this process, the addition of APS solution was varied according to the following oxidant dropping times: 0 minutes (D1), 60 minutes (D2), and 150 minutes (D3). The initial temperature of the reaction was set up at 0°C (T1) and room temperature (T2).

The obtained polyaniline powder, which had been dried in a desiccator for one week was characterized by a spectrophotometer Fourier transform infrared (FTIR) to identify the formation of emeraldine polyaniline. X-ray diffraction (XRD) analysis was conducted to identify the phase of the crystallinity of the polyaniline between 20°5 and 60° with a step size 0.02°. The polyaniline powder morphology was analyzed using a Carl Zeiss EVO MA10 scanning electron microscope (SEM). A Micromeritics ASAP 2020 surface area analyzer (SAA) was used to determine the Brunauer-Emmett-Teller surface area (S BET) and the porosity of polyaniline. Degassing was carried out with a mass ≥ 0.3 grams at a temperature of 150°C for six hours before the measurements of the sample. The film form of the resistivity of polyaniline was measured using a four-point probe Keithley 6200 current source and a Keithley 2700 Nanovoltmeter. To ensure the characteristics of the semiconductor materials, the measurement was conducted at a temperature range of 75°to 300 K.

3. Result and discussion
Polyaniline was synthesized in a variety of different polymerization conditions. Figure 1 shows the FTIR spectra of the polyaniline synthesized under different conditions. The three spectra show the absorption peaks of polyaniline including the C=C stretching from the quinoid ring (Q) that was observed in wave numbers of ~1500 cm⁻¹. The C=C stretching of benzenoid rings is the backbone of polyaniline observed at ~1400 cm⁻¹[10]. The stretching of C–N secondary aromatic amine appeared at the height of the spectrum at ~1300 cm⁻¹. The emeraldine salt form of polyaniline was successfully synthesized, as indicated by some of the typical peaks at ~3400 cm⁻¹ showing N–H stretching, and the peak at ~2900 cm⁻¹ indicating the presence of C–H stretching vibrations [11]. A peak of the spectra of emeraldine salt was also obtained at ~1100 cm⁻¹—i.e., the absorption tape Q = NH⁺-B (quinoid = NH⁺-benzenoid)—which is assumed to be the typical peak of polyaniline in conductive conditions [10,12].

XRD analysis shows that the polyaniline formed was composed of amorphous and crystalline phases. Figure 2a shows the diffraction patterns of polyaniline synthesized at 0°C and room temperature with diffraction peaks observed at 20 9,33°, 20,90°, and 25,52°, which indicates the structure of semi-crystalline of polyaniline [10]. The peak at 20 25,52° is typical of polyaniline peak; this peak is considered to come from a parallel arrangement of the polymer chain of polyaniline[13,14]. However, the peak at 20 20,90° shows a polyaniline amorphous peak, and the peak
at 20 9,33° shows a crystalline polyaniline peak [15]. A synthesized polyaniline sample shows the identical position of the diffraction peaks at room temperature (Figure 2b). Based on crystallinity analysis using the High Score Plus (HSP) software, polyaniline prepared at 0°C had slightly greater crystallinity, i.e., 41% compared to that developed at room temperature, which was 37%. The crystallinity difference can be attributed to the increasing regularity of the polyaniline structure and an increased molecular weight along with a decrease in temperature [16–18].

**Figure 1.** The spectra of polyaniline prepared with an APS/aniline ratio of 1

**Figure 2.** XRD patterns of polyaniline prepared from an APS/aniline ratio of 1

Figure 3 shows SEM micrographs of polyaniline prepared at different polymerization temperatures. At a polymerization temperature of 0°C (T1), the micrograph exhibits a uniform size distribution of excellent particles of polyaniline with an average size less than 45 nm (Figure 3a). The nanoparticles were found to form cylindrical-like aggregates. However, a different morphological characteristic was observed in polyaniline prepared at room temperature polymerization (T2), where polyaniline formed as coarse particles with irregular shapes (Figure 3b). This result shows the significant influence of temperature in controlling the process of polyaniline polymerization, and that fine particle generated a high surface area that can be obtained at a low temperature.
Figure 3. Scanning electron microscope (SEM) micrograph of polyaniline prepared with oxidant dropping time 0 s (D1) and different temperatures (T1 [a] and T2 [b]).

Figure 4a shows the curve of nitrogen gas (N$_2$) adsorption-desorption isotherms at 77 K for the polyaniline prepared at 0ºC with different oxidant dropping times. The curves exhibit type-IV isotherms that are a representation of mesoporous characteristics with pores size between 4 and 30 nm. The pore size distribution is determined based on the Barret, Joyner, and Halenda (BJH) methods that shown in the inset of Figure 4. Based on the $S_{BET}$ values presented in Table 1, at a polymerization temperature of 0ºC, the APS/aniline ratio produces very significant changes in the surface area of the polyaniline; the highest surface area of 42 m$^2$/g was obtained at a ratio of 0.75 with an oxidant dropping time of 0 minutes. This value is much higher compared to that obtained under polymerization conditions that have been reported previously [19,20]. However, at room temperature polymerization, the surface area decreases by more than 52% such that it only reaches 20 m$^2$/g. The high BET surface area of polyaniline prepared at 0ºC might be associated with slow polymerization processes at low temperatures that produce fine particle [21–23], which is confirmed by the SEM micrograph (Figure 3a). The $S_{BET}$ is found to decrease at longer oxidant dropping times. In this case, the $S_{BET}$ drops to 16 m$^2$/g at an oxidant dropping time of 150 minutes. This indicates that longer dropping times have improved the process of aniline polymerization, which may extend the polymer chain and increase the particle size, implying a decrease in the $S_{BET}$ value [11,23]. However, at room temperature polymerization, the $S_{BET}$ of the samples does not change much with increases in the oxidant dropping time.

Figure 4. N$_2$ adsorption-desorption isotherms of polyaniline prepared with different oxidant dropping times at 0ºC (a) and room temperature (b). The insets depict BJH pore size distribution.
Four-point probe measurements determine the electrical conductivity characteristic of polyaniline. Figure 5 shows resistance value curves measured in the temperature range between 75 and 300 K. The curves confirm that the synthesized polyaniline has the characteristics of a semiconducting material. The conductivity value for each sample is calculated based on the measured resistance values according to the following, obtained by equations:

$$\rho = A \frac{R}{l} \quad (1)$$
$$\sigma = \frac{1}{\rho} \quad (2)$$

where \( \rho \) is resistivity, \( R \) is resistance, \( l \) is length, \( A \) is the cross-sectional area, and \( \sigma \) is conductivity.

![Figure 5](image1.png)

**Figure 5.** Resistivity (log scale) vs. temperature plot measured using four-point probe method.

![Figure 6](image2.png)

**Figure 6.** Conductivity (log scale) vs. temperature, calculated from resistivity measurement results.
Figure 5 shows the curve of resistivity versus temperature of all samples. All of the samples showed an increased curve along with a decrease in temperature, indicating that all samples had overall semiconductor properties. However, in the sample C2-D1-T2, there is a decrease of the gradient starting at 200K, this gradient then recovers below 150K. The C2-D1-T1 sample also shows a slight decrease in gradient below 170 K, and then the gradient rises again below 140 K. This indicates the change of semiconductor properties that begins to transform into a conductor but become semiconductor properties again at low temperatures. The transform from semiconductor properties to become conductor looks greatest in the sample C2-D1-T2. It is also supported by the resistivity value of C2-D1-T2 at room temperature which is the lowest value among all samples. Figure 6 shows the curve of conductivity versus temperature of all samples, calculated based on the resistivity measurement results shown in Figure 5. Figure 6 also shows a sample of C2-D1-T2 which has the highest conductivity value at room temperature and shows an increase in the gradient at 200 K and then decrease below 150K.

Based on the calculated data shown in Table 1, polyaniline conductivity is greatly influenced by the preparation conditions. The highest conductivity value of 1.79 x 10⁻¹ S/cm was obtained from the polyaniline samples synthesized at a polymerization temperature of 0°C with a molar ratio of 1. This can be attributed to the increase of molecular weight and crystallinity of polyaniline formed at low-temperature polymerization [17,18]. This result confirmed by XRD data, where polyaniline prepared at 0°C has higher crystallinity than one obtained at room temperature.

| Samples code | $S_{BET}$(m²/g) | Conductivity (S/cm) |
|--------------|----------------|--------------------|
| C1-D1-T1     | 19.82          | 7.60 x 10⁻²        |
| C2-D1-T1     | 42.14          | 9.40 x 10⁻²        |
| C3-D1-T1     | 23.58          | 1.79 x 10⁻¹        |
| C2-D1-T2     | 20.07          | 1.57 x 10⁻¹        |
| C2-D2-T2     | 24.82          | 7.00 x 10⁻²        |
| C2-D3-T2     | 23.63          | 2.45 x 10⁻²        |
| C2-D2-T1     | 20.88          | 6.22 x 10⁻²        |
| C2-D3-T1     | 15.95          | 3.13 x 10⁻²        |

4. Conclusion
Polyaniline nanoparticles as a semiconducting material were prepared using a chemical oxidative polymerization method. The surface area and conductivity of polyaniline were successfully enhanced by adjusting the ratio of APS/aniline, the oxidant dropping time, and the temperature of polymerization. The optimum APS/aniline ratio is 0.75. The addition of the oxidant directly (0 minutes) was found to be more appropriate than gradual addition, i.e., dropping times of 60 and 150 minutes can decrease the BET surface area and the conductivity of the polyaniline. Low temperature (0°C) polymerization can produce fine particle size and uniform size distribution, which implies a high surface area of the polyaniline.

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