

Effect of Ammonium Peroxydisulphate (APS) Addition on Polyaniline Nanofiber Microstructure in Interfacial Polymerization Method

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ABSTRACT

Synthesis of polyaniline nanofiber has been carried out using interfacial polymerization method. Polyaniline nanofiber was a material of interest for biosensors because this material was capable and effective as a mediator for electron transfer in redox and enzymatic reactions. The surface morphology of polyaniline nanofiber was much wider than conventional polyaniline, resulting in the process of molecular diffusion into the polyaniline nanofiber structure being faster and the penetration of molecules deeper, thus having the potential to increase the sensitivity and responsiveness of a sensor.

The interfacial polymerization method used includes a water phase (dopant, initiator and aquadestilate) and an organic phase (toluene as an organic solvent and aniline monomer). Based on the experiments that have been carried out, a relationship was obtained between the molar ratio of aniline and ammonium peroxy disulphate (APS). An indication of the adding effect of initiator can be seen through the morphology and functional groups of the polyaniline produced.

The experimental results showed that the diameter of the polyaniline nanofibers formed was observed to be larger when APS was added as an initiator. The diameter of polyaniline with the percentage of addition APS to aniline of 25%, 33% and 50% is

(72.7 ± 0.8) nm, (68.9 ± 0.9) nm and (67.7 ± 1.3) nm, respectively. FTIR results indicate that polyaniline is in a semi-oxidation state and is in the form of emeraldine salt. The main characteristics of polyaniline nanofiber are characterized by the presence of N-H stretching modes (3356-3460 cm⁻¹), C = N (1548-1571 cm⁻¹) and C = C (1482-1489 cm⁻¹) for quinoid and benzenoid rings as well as stretching modes C-N (1207-1363 cm⁻¹) for the benzenoid ring. The degree of polyaniline oxidation increases with increasing quinoid/benzenoid ring ratio.

Keywords: polyaniline nanofiber, ammonium peroxy disulphate, interfacial polymerization

INTRODUCTION

Polyaniline nanofiber is polyaniline which consists of aniline monomers in the form of discrete threads with an average diameter of between 30 nm to 100 nm [1]. Polyaniline nanofiber has a specific surface area with a greater molecular penetration depth, resulting in process molecular diffusion into the polyaniline nanofiber structure taking place more quickly. This unique fiber size influences electrical and optical properties of polyaniline nanofiber. This property plays a very important role in detection sensitivity in sensor applications [2].

The development of polyaniline nanostructures, especially nanofibers, has become a major focus in recent years.

Polyaniline nanofiber displays its own advantages in fiber size. The size of the fibers in nanofiber produces a wider surface area compared to other materials. Polyaniline morphology is influenced by the size of the fibers formed. This unique fiber size influences the electrical and optical properties of polyaniline nanofiber. As a consequence, this property plays a major role in detection sensitivity [3] in sensor applications [2]. Various methods have been developed for the synthesis of polyaniline nanofibers [4], including interfacial polymerization methods [5-8], electrospinning methods [9,10], chemical oxidative polymerization reactions [11-13], bulk polymerization [14], and rapid mixing polymerization [15-17].

One of the methods used to obtain polyaniline nanofiber is the interfacial polymerization method. Interfacial polymerization is a polymerization stage that occurs at the interface between a water solution containing the first monomer and an organic solvent containing the second monomer [18]. In this synthesis, a reaction occurs between the acid solution, oxide and the organic aniline layer together. This is what creates a reactive interface when polymerization occurs. During the polymerization process, polyaniline nanofibers will diffuse into the water layer leaving a reactive interface to prevent excess fiber growth and allow homogeneous nucleation to occur. Conditions in interfacial synthesis can be adjusted depending on the type of acid and oxidant used.

The interfacial polymerization method has been widely used to obtain polyaniline nanofibers. In its development, Banerjee (2009) carried out interfacial polymerization for further studies on photoluminescence on polyaniline nanofibers doped with hydrochloric acid (HCl). The photoluminescence spectrum shows a band peak in the violet region ($\lambda=405$ nm) and indicates that the decrease in fiber diameter is proportional to increase in HCl concentration [19]. Abdollahi (2012) observed the uniformity of polyaniline

nanofiber synthesis through interfacial polymerization. This mechanism uses chloroform (20 ml) 4 mili mole aniline as the organic phase and 1 M HCl (20 ml) 4 mmol APS as the aqueous phase [7]. Observations on the effectiveness of synthesis to control growth of polyaniline nanofiber were carried out by Li et al (2013). As the organic phase, aniline (0.46 ml) was used, organic solvent (toluene / chloroform) (1 ml) and the aqueous phase was used 1 M acid dopant and APS (1.14 gr) [20]. Observation of the performance of polyaniline nanofiber-graphene oxide hybrids with oil-water interfacial polymerization was also carried out using Aniline (3 gr) dissolved in 100 ml chloroform as the organic phase and APS (1.8 gr) 1 M HCl solution (100 ml) as the aqueous phase. [4].

In this research, polyaniline was synthesized using the interfacial polymerization method. Aniline monomer is added with an oxidant as an initiator. The choice of initiator fell on ammonium peroxy disulphate (APS)- $(\text{NH}_4)_2\text{S}_2\text{O}_8$ because it has strong oxidizing characteristics. Ammonium persulfate (APS) is a colorless (white) salt that is highly soluble in water, much more soluble than the related potassium salt. APS is a strong oxidizing agent used as a catalyst in polymer chemistry, as an etchant, and as a cleaning and bleaching agent. In this research, it will be observed whether the oxide will affect the polymerization process or not. The effect of this oxidant will be seen from the results of morphology and functional groups of the sample.

MATERIALS & METHODS

The main material used for polymerization in this experiment was aniline monomer $\text{C}_6\text{H}_5\text{NH}_2$. As an oxidant or initiator, ammonium peroxy disulphate (APS)- $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is used. Aniline and APS were obtained from Merck. Meanwhile, as a dopant, Hydrochloric acid - HCl which comes from Smart Lab is used. The organic phase was used toluene - $\text{C}_6\text{H}_5\text{CH}_3$ (Smart

Lab.) and the water phase was used aquadestilate

In the polyaniline nanofiber synthesis process, interfacial polymerization is carried out by adding aniline to toluene so that the volume of the organic phase reaches 50 ml. Likewise with APS, HCl and aquadestilate solvent are mixed in a certain ratio so that the volume of the water phase reaches 50 ml. At this stage, HCl was used only with a concentration of 3 M, while the addition of APS to aniline varied from 25%, 33% and 50%.

RESULT & DISCUSSION

In interfacial polymerization process, interaction between initiator and monomer is limited to the dimensional space between interface of the organic phase and water phase [21]. Therefore, only initiator molecules at interface are possible to produce nucleation. This interfacial polymerization uses HCl dopants and ammonium peroxy disulphate (APS)- $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as initiators. In this research, APS was added as an initiator to the aniline monomer with a percentage of 25%, 33%

and 50% in the 3 M HCl dopant. This shows an increase in use of APS as an initiator.

In the experiments that have been carried out, reducing molarity of APS results in the color of precipitate becoming darker green. Meanwhile, at the same molar ratio of aniline to APS, precipitate is slightly brownish green. The color change to dark green indicates that polyaniline produced is conductive. Low APS concentrations result in insufficient "active nucleation centers", but this function is replaced by granular particles in second nucleation. When nucleation center is excessively active due to too much oxidant, the reactive radical and advanced oligomeric cations collide with each other to fulfill Brownian motion. The amount of APS used in reaction will affect the branches and length of resulting fiber structure [14].

Figures 1 to 3 present the SEM photo results along with the fiber width distribution obtained from variations in the addition of APS to 25%, 33% and 50% aniline with 3 M HCl dopant.

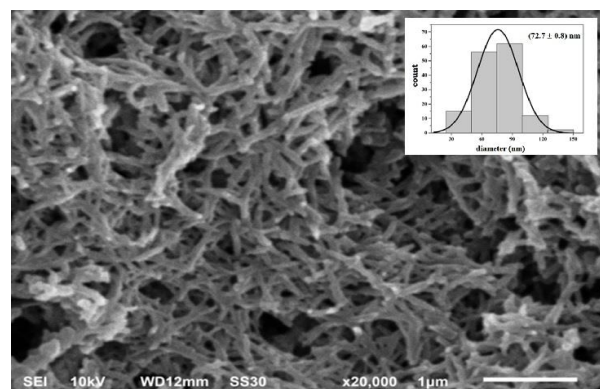


Figure 1 SEM results of polyaniline nanofiber with 3 M HCl dopant concentration with the addition of 25% APS to aniline

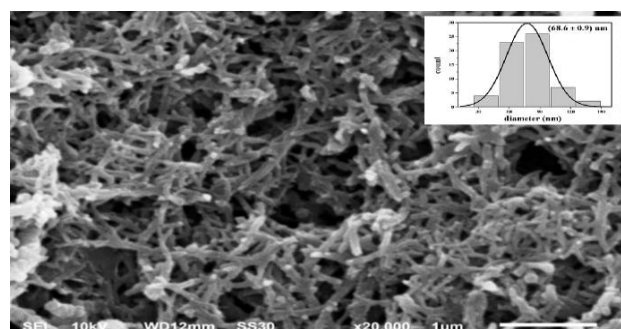


Figure 2 SEM results of polyaniline nanofiber with 3 M HCl dopant concentration with the addition of 33% APS to aniline

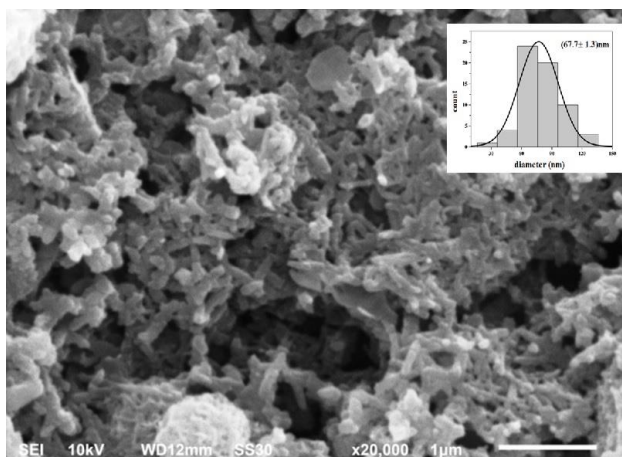


Figure 3 SEM results of polyaniline nanofiber with 3 M HCl dopant concentration with the addition of 50% APS to aniline

Consecutively, SEM images of polyaniline nanofiber dopant 3 M HCl with addition of aniline to APS 25%, 33% and 50% have been presented. Figure 1 shows a scanning electron microscope (SEM) depiction of polyaniline nanofiber dopant 3 M HCl with addition of 25% APS, resulting in a fiber with a diameter of (72.7 ± 0.8) nm. Figure 2 depicts the SEM image for polyaniline nanofiber dopant 3 M HCl with addition of 33% APS, resulting in fibers with a diameter of (68.9 ± 0.9) nm. And in Figure 3, you can see the SEM image of polyaniline nanofiber dopant 3 M HCl with addition of 50% APS, resulting in a fiber with a diameter of (67.7 ± 1.3) nm. From these three results, it appears that there is a decrease in fiber size when the amount of APS added to aniline increases by 25%, 33% and 50% respectively. When the APS concentration is low, the active nucleation center is insufficient, this results in the nanofibrils being surrounded by aniline monomers so that secondary nucleation is formed which develops into granular particles. The increase in granular particles will increase the diameter of the fibers formed [20]. When the APS concentration increases, it will automatically reduce the formation of secondary nucleation. Reduced secondary nucleation results in less granular particles growing.

Fourier Transformation Infra Red (FTIR) is a spectroscopic technique used to view the chain structure characteristics of polyaniline

including functional groups of polyaniline sample being observed. This FTIR reliably interprets the reactions of multifunctional monomers including rearrangement and isomerization [22]. By using this FTIR spectrum, the oxidation state and protonation level of the conductive polymer, in this case polyaniline nanofiber, can also be observed [14]. The spectroscopic pattern of polyaniline nanofiber shows the infrared spectrum of absorption peaks. The characteristic peaks of polyaniline correspond to the functional groups of polyaniline obtained from interfacial polymerization synthesis with HCl as a dopant. Figure 4 shows the infrared spectrum of polyaniline nanofiber obtained via interfacial polymerization.

The FTIR spectrum of polyaniline nanofiber formed indicates that polyaniline was formed in a semi-oxidation state. The peaks mentioned in FTIR indicate polyaniline in doped form [23]. The main characteristics of polyaniline nanofiber are characterized by the presence of N-H stretching mode, C = N and C = C stretching modes for the quinoid and benzenoid rings [23,24], as well as C-N stretching mode for the benzenoid ring [4,25]. From this it can be seen that polyaniline produced is in the form of emeraldine salt [24]. The presence of these two bonds (quinoid ring and benzenoid ring) clearly indicates that polymer consists of amine and imine units. The oxidation degree of polyaniline increases with increasing quinoid/benzenoid ring ratio, so the number

of quinoid rings in molecular structure of conductive polymer also increases. The bonds that appear based on C indicate that polyaniline produced is in formation of polyaniline nanofiber [26]. The phenomenon of shifting infrared spectrum

shows the interaction between $\pi - \pi$ and hydrogen bonds in the resulting polyaniline backbone [4]. The distribution of polyaniline nanofiber peak stretching modes from FTIR can be seen in table 1 below.

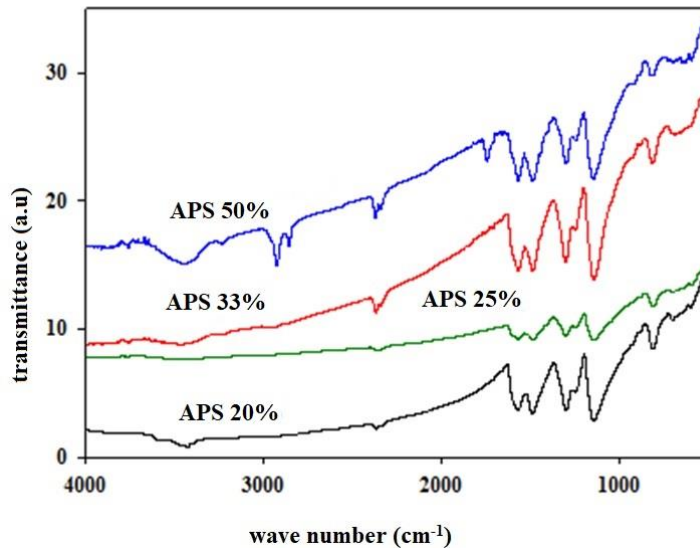


Figure 4 FTIR spectrum of HCl dopant polyaniline nanofiber with the addition of 20%, 25%, 33% and 50% APS.

Tabel 1 The FTIR peak stretching mode indicates the presence of polyaniline nanofiber

Stretch Mode	Wave Number (cm ⁻¹)	Sample
N - H	3460	APS 50%
	3408	APS 33%
	3356	APS 25%
	3430	APS 20%
C = N	1571	APS 50%
	1578	APS 33%
	1548	APS 25%
	1563	APS 20%
C = C	1482	APS 50%
	1489	APS 33%
	1489	APS 25%
	1482	APS 20%
C - N	1363 – 1207	APS 50%
	1363 – 1207	APS 33%
	1370 – 1215	APS 25%
	1363 – 1207	APS 20%

CONCLUSION

Polyaniline nanofiber has been successfully prepared through interfacial polymerization with varying molar dopants. This interfacial polymerization produces polyaniline nanofiber with variations in the ratio of aniline to APS at optimum molar dopant (3

M HCl). Diameter of polyaniline with percentage addition of APS to aniline of 25%, 33% and 50% is (72.7 ± 0.8) nm, (68.9 ± 0.9) nm and (67.7 ± 1.3) nm, respectively. When the APS concentration is low active nucleation centers are insufficient and nanofibrils are surrounded

by aniline monomers resulting in secondary nucleation forming which develops into granular particles. The more the APS concentration increases, less secondary nucleation will occur. As a result, the granular particles formed are reduced. The reduction in granular particles will cause the protonated monomer to move freely and be reactive, this will result in increased conductivity.

From the FTIR spectrum, it appears that polyaniline is formed in a semi-oxidation state. The main characteristics of polyaniline nanofiber are characterized by presence of N-H stretching modes ($3356-3460\text{ cm}^{-1}$), C = N ($1548-1571\text{ cm}^{-1}$) and C = C ($1482-1489\text{ cm}^{-1}$) for quinoid and benzenoid rings as well as stretching modes C-N ($1207-1363\text{ cm}^{-1}$) for benzenoid ring. The polyaniline produced is in the form of emeraldine salt. The oxidation degree of polyaniline increases with increasing quinoid/benzenoid ring ratio, so the number of quinoid rings in molecular structure of conductive polymer also increases.

Declaration by Authors

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