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Study The Different Concentrations of Hydrochloric and Sulphuric Acid as Dopants for Polyaniline

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Abstract: Conducting polymers have previously been employed in biosensors because they may be used as immobilisation matrices as well as redox systems. Also have numerous uses in medical, pharmacy, environmental monitoring, food and process control. The conductivity of polyaniline-based compositions may be precisely regulated over a broad range. Polyaniline is ease to synthesis, has high conductivity and good performance in biosensor applications. However, polyaniline is not entirely perfect because of its poor solubility in many solvents and low adhesion to different substrate. In this study, hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) were prepared with different concentration (0.2M, 0.4M, 0.6M, 0.8, 1.0M) for doping process of polyaniline. Fourier-transform Spectroscopy (FTIR), Ultraviolet Spectroscopy (UV-Vis) and Scanning Electron Microscopy (SEM) were used to characterize the properties and morphology of the polyaniline. Four-point probe was used to identify the conductivity of the polyaniline sample. FTIR shows a shift peak at benzenoid rings and quioniod rings. Both acids represent that 1.0 M have high absorbance properties. While SEM shows significant different of agglomeration rate for HCl compared to H_2SO_4. Lastly, the results showed that the conductivity increasing when the concentration of acids increasing. Doping process helps in enhancing the conductivity properties of polyaniline for biosensor application

Keywords: Polyaniline, doping, biosensor, conductivity

1. Introduction

Biosensors are increasingly being used in a variety of healthcare settings. New improvements of biosensor applications were studied by the researchers with different methods and techniques. A range of transduction techniques such as electrochemical, optical and acoustic can be used for biosensors. The characteristics of the biosensors are selectivity, stability, sensitivity, duplicability and linearity [1]. To improve biosensor selectivity, high-affinity reagents like enzymes and synthetic biomolecules can be combined with the transducer. Nanotechnology has a significant influence on current biosensing technology advancements. Certain conducting polymers have exceptional electrical conductivity and transfer electrical charge from redox enzymes to electrodes. Highly conductive polymers are used as electrode materials for supercapacitors as the example are polypyrrole, polyanilline, polyacetylene, polythiophene [2].

Polyaniline is one of the most popular conducting polymers among the others because of its high sensitivity, ease of synthesis, flexibility and good performance in biosensor applications. Theproperties of polyaniline are the key elements of the successful biosensor in sensing various biomolecules. Electrically conductive conjugated polymers have been studied since the early 1960s, including René Buvet and Marcel Jozefowicz on polyaniline [3].

Polyaniline is known as a conducting polymer because of its conductivity towards biosensor applications [4]. The aniline will undergo polymerization process as shown in Fig. 1. Its characteristics and behaviour are almost the same as the other conducting polymers such as polypyrrole, polythiophene and poly (p-phenylene) and many more. However, polyaniline is not entirely perfect with its poor physical and mechanical properties. Its uses are restricted by various of factors like poor solubility in many solvents, low adhesion to a different substrate and, protonic aciddoping's weak chemical reactivity, which can only occur in a very acidic environment (pH ≤ 4) and also low conductivity [7]. A doping approach using functionalized protonic acids such as hydrochloric acid or dodecylbenzene sulfonic acid (DBSA) can be utilized to increase solubility and induce fusibility of the stiff chain of this polymer [8]. Polyaniline powder isa kind of conductive polymer that does not melt well in most solvents [9] as a result, it is not adhesive on a variety of substrates, except for a few organic solvents such as Hydrofluoric acid and Dimethylformamide. At the end of theresearch, the aim is to identify the electric conductivity of the polymer. So the process for preparing the polyaniline is very important to achieve good conductive polyaniline.
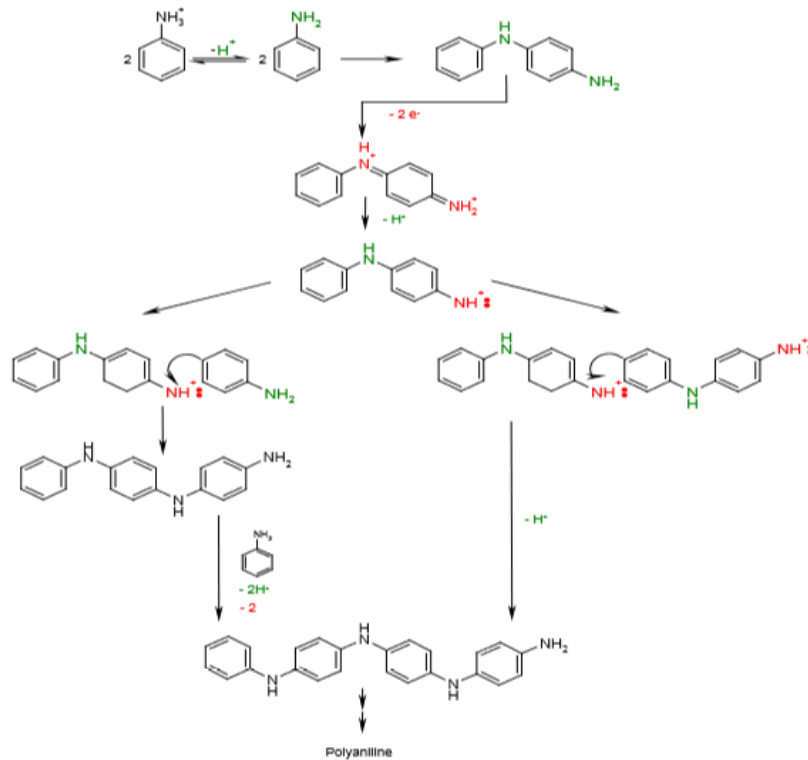

Fig. 1 - Mechanism of polyaniline formation [5,6]

In this scope of the study, the research is focused on the effect of acid doping concentration on polyaniline. The various concentration of hydrochloric acid and sulphuric acid were prepared to perform doping process for polyaniline. Doping might be used to increase the conductivity ofpolyaniline. In chemistry, it is known as protonation process where adding proton (H^+) to atom, molecule or ion. This reaction will forming a conjugate acid. A filtering process by using filter paper is important to separate the solvents and precipitate since the polyaniline need to be characterized. Fourier-transform Spectroscopy (FTIR), Ultraviolet-visible Spectroscopy (UV-Vis) and Scanning Electron Microscopy (SEM) are used toinvestigate the structural of doped samples. The conductivity of the polyaniline samples was identified using four-point probe. The final data will be collected and discussed.

2. Materials

The main raw material was conductive PANI with its conductivity 7.5 S/cm and molecular weight of 55,000 g/mol brand Emory. The different concentration of acids (0.2M, 0.4M, 0.6M, 0.8M, 1.0M) were prepared by diluting the acids from 37% of HCL and 97% of H_2SO_4 brand Merck, Germany Then, 1 mg of conductive polyaniline was dissolved in different concentration of HCl and H_2SO_4 as shown in Fig. 2. Ten samples of polyaniline solutions were produced.
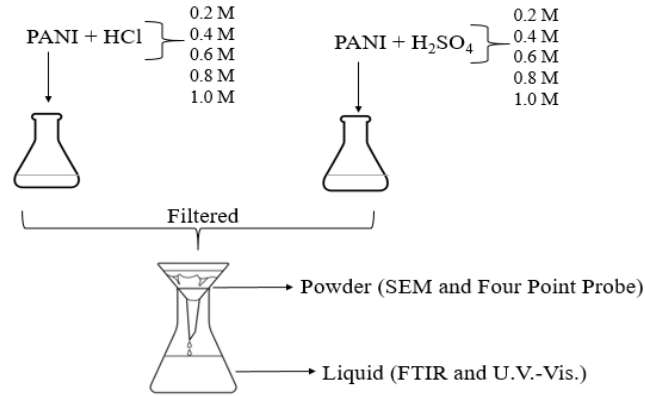
Fig. 2 - Experimental setup

3. Methodology

To prepare each dilute solution, one needs to know the volume of the concentrated liquid that was required. Dilution is the process of diluting a solution by adding more solvent to lower its concentration. The amount of solute remains constant, but the total amount of solution is increased, lowering the ultimate concentration as shown in Table 1 and 2.

Table 1 - Preparation of different concentration HCl solution

Sample prepared of 50 ml HCl	Starting solution of 12 M HCl	Distilled water
0.2M	0.85 ml	49.15 ml
0.4M	1.70 ml	48.30 ml
0.6M	2.54 ml	47.46 ml
0.8M	3.40 ml	46.60 ml
1.0M	4.24 ml	45.76 ml

Table 2 - Preparation of different concentration H_2SO_4 solution

Sample prepared of 50 ml H_2SO_4	Starting solution of 18M H_2SO_4	Distilled water
0.2M	0.56 ml	49.44 ml
0.4M	1.12 ml	48.88 ml
0.6M	1.68 ml	48.32 ml
0.8M	2.23 ml	47.77 ml
1.0M	2.80 ml	47.20 ml

3.1 Doped Polyaniline with Different Concentration of Acids

The polyaniline was doping with different concentration (0.2M, 0.4M, 0.6M, 0.8M, 1.0M) of HCl and H_2SO_4. Firstly, 1.0mg of polyaniline was mixed with the 0.2M of HCl then the solution was stirred using a magnetic stirrer for 5 minutes at room temperature. After that, the solution was filtered by filter paper to separate the solvent and precipitate followed by a drying process for 24 hours. The dried precipitate then was collected and weighed. The same process was repeated with other acid concentration until the ten polyaniline samples were obtained.

Polyaniline state in two conditions after filtering and drying process which is liquid and powder. The polyaniline in liquid state was characterize using FTIR and UV-Vis while the powder polyaniline was characterize using SEM and four-point probe. UV-Vis was used to analyze light absorbance across the ultraviolet and visible ranges of the electromagnetic spectrum, while FTIR was applied to detect infrared light absorption at various wavelengths.

4. Result and Discussions

The FTIR spectroscopy of doped PANI dopants with different concentration of HCl and H_2SO_4 were

investigated. This was accomplished by comparing the bands position and intensities observed in IR spectra with wave numbers for determining functional groups present in polyaniline. The characteristics of FTIR can distinguish between benzenoid rings and quioniod rings in the range 1350-1960 cm^{-1}.

4.1 Doped PANI-HCl

Fig. 3 shows FTIR spectra of doped PANI-HCl with different concentration (0.2 M, 0.4 M, 0.6 M, 0.8 M, 1.0 M) in the range 400-4000 cm^{-1} that prepared at room temperature. PANI-HCl with 0.2 M concentration shows the peaks around 3338.69 cm^{-1}, 1634.73 cm^{-1}, and 419.03 cm^{-1}. The concentration of 0.4 M shows the peaks around 3338.80 cm^{-1}, 1634.64 cm^{-1}, and 418.86 cm^{-1}. The concentration of 0.6 M shows the peaks around 3338.20 cm^{-1} and 1634.52 cm^{-1}. The peaks of 0.8M shows around 3339.32 cm^{-1}, 1634.56 cm^{-1}, and 404.13 cm^{-1} while 1.0 M had shown at 33340.14 cm^{-1} and 1634.27 cm^{-1}. The peaks around 415 cm^{-1}, 1634 cm^{-1}, and 3338 cm^{-1} of all spectra correspond to PANI-HCl.
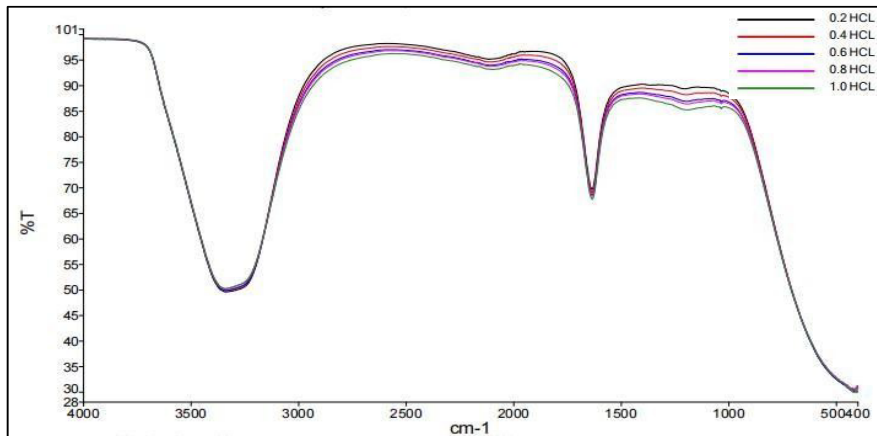

Fig. 3 - FTIR spectra of doped PANI-HCl

4.2 Doped PANI-H$_2$SO$_4$

Fig. 4 shows the FTIR spectra of doped PANI-H$_2$SO$_4$ with different concentration (0.2 M, 0.4 M, 0.6 M, 0.8 M, 1.0 M) in the range of 400-4000 cm^{-1}. PANI- H$_2$SO$_4$ with 0.2 M concentration shows the peaks at 3338.37 cm^{-1}, 1634.77 cm^{-1}, and 403.02 cm^{-1}. The 0.4 M concentration shows the peaks at 3339.13cm^{-1}, 1634.89cm^{-1}, 1194.72cm^{-1}, 1051.20cm^{-1}, and 407.49cm^{-1}. The concentration of 0.6 M shows the peaks at 3338.53cm^{-1}, 1634.55cm^{-1}, 1194.78cm^{-1}, and 1050.84 cm^{-1}. The concentration of 0.8 M shows the peaks at 3338.88 cm^{-1}, 1634.69 cm^{-1}, 1192.33 cm^{-1}, and 1050.48 cm^{-1} while concentration of 1.0 M shows the peaks at 3339.07 cm^{-1}, 1634.35 cm^{-1}, 1189.88 cm^{-1}, and 1049.84 cm^{-1}. The spectra at peaks around 1050cm^{-1}, 1190cm^{-1}, 1634cm^{-1}, and 3338cm^{-1} correspond to PANI-H$_2$SO$_4$.
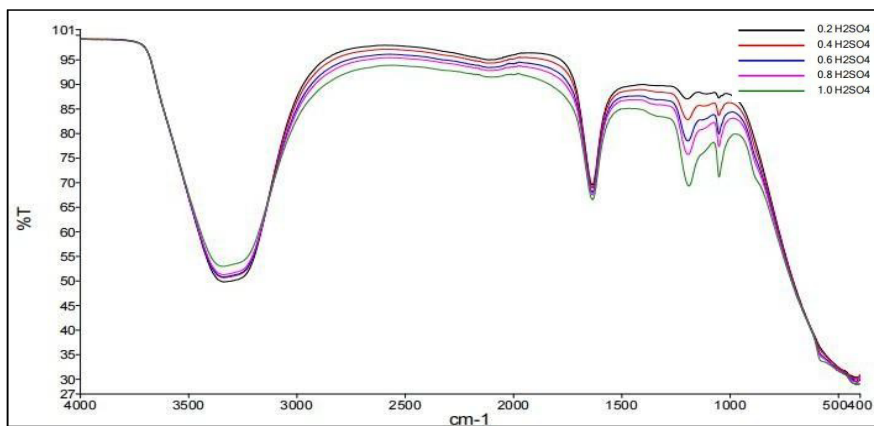

Fig. 4 - FTIR spectra of doped PANI-H$_2$SO$_4$

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4.3 UV-Vis Spectrum

The UV-Vis was recorded as a plot of absorbance (a.u) against wavelength (nm). The raw data re-plot was performed by using spreadsheet software. Fig. 5(a) shows the UV-Vis spectrum of PANI-HCl. The concentration of 1.0 M HCl shows the maximum absorption at 322 nm followed by 0.8 M, 0.6 M, 0.4 M, and 0.2 M. Figure 5(b) shows the UV-Vis spectrum of PANI- H_2SO_4. From the figure below, the max absorption is represented by 1.0 M at 325 nm while the lowest peak represented by 0.2 M.
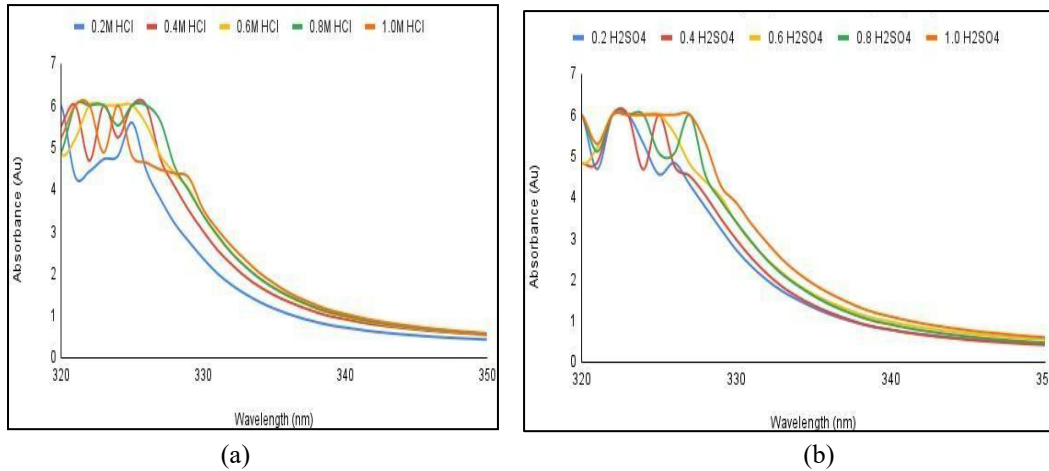

(a)   (b)

Fig. 5 - UV-Vis spectrum of (a) PANI-HCl; (b) PANI-H$_2$SO$_4$

4.4 Morphology of Polyaniline

Fig. 6 show the morphology of the doped polyaniline of pure PANI-ES before doping process, 1 M of PANI-HCl and 1 M of PANI- H_2SO_4. The morphology of pure polyaniline had shown granular shaped. Moreover, polyaniline is one of the class polymer that difficult to soluble in water. 1 M PANI-HCl had shown the same surface as pure polyaniline with it granular shaped particles. PANI-HCl had structure of aggregates from particles. The surface morphology of 1 M PANI-H_2SO_4 had shown less granular shaped from the particles because of the properties of H_2SO_4 that was high of acidity which can help to make the polyaniline more soluble than HCl even in small changes [10]. H_2SO_4 is a hydrophilic material and helps in forming different structural and chain length of PANI. Chain length affect the conductivity properties of PANI. The PANI conductivity was decreased when the chain length decrease and becomes more compact [11, 12].
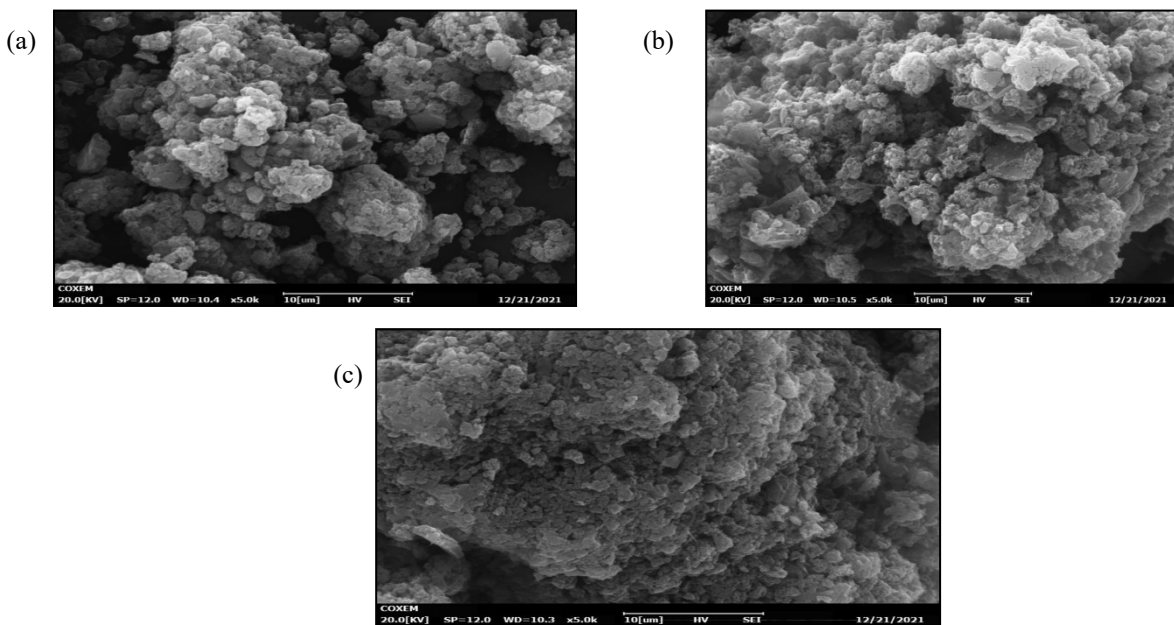

Fig. 6 - Morphology of (a) PANI; (b) PANI-HCL; (c) PANI-H$_2$SO$_4$

4.5 Conductivity of Polyaniline

The conductivity of polyaniline with the different concentration of acids were identified using four-point probe. The values of conductivity increase as the concentration of acids increase [13] (Fig. 7 and 8). Based on the Table 3, the conductivity of the 0.6 M HCl decrease and then continue increase by 0.8 M and 1.0 M. This is because of the destruction of the polyaniline sample when the acid given was too high resulting the sudden decrease of conductivity [14]. Table 4 had shown increasing conductivity from 0.2 M to 1.0 M of PANI-H_2SO_4. In study done by [15], the conductivity of PANI will increased if conductive paint were used together with PANI because its ability to support the current transmission.

Table 3 - Conductivity of PANI-HCl

Molarity (M)	Conductivity, 10^{-2} (S/cm)
0.2	3.94
0.4	5.74
0.6	4.59
0.8	6.47
1.0	10.00
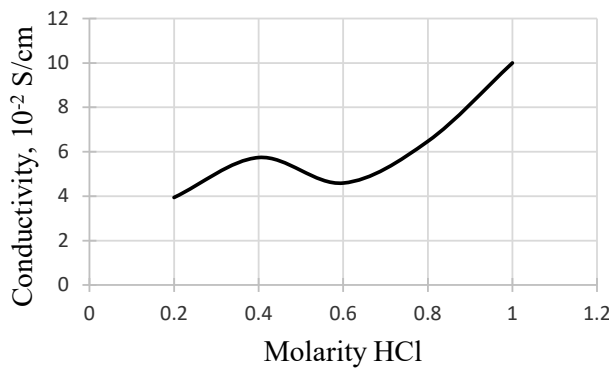
Fig. 7 - Graph of conductivity against HCl molarity

Table 4 - Conductivity of PANI-H_2SO_4

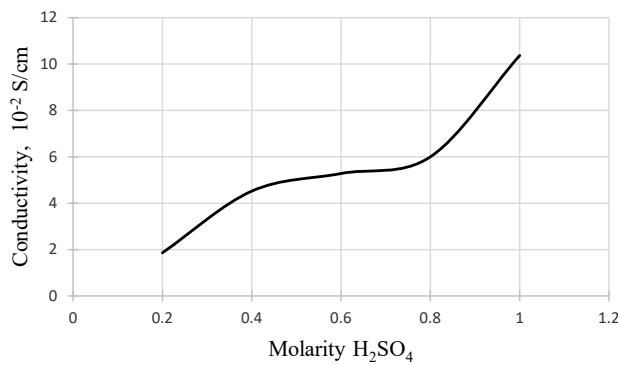| Molarity (M)	Conductivity, 10^{-2} (S/cm)
0.2	1.86
0.4	4.52
0.6	5.28
0.8	6.00
1.0	10.37

Fig. 8 - Graph of conductivity against H_2SO_4 molarity

5. Conclusion

HCl and H_2SO_4 is the protonic acid that has been used in the doping process of polyaniline. The different concentrations of hydrochloric acid and sulphuric acid which act as a dopant can help to increase the conductivity of polyaniline. From the study, we investigated the morphology, absorption of U.V. light and infrared spectrum of doped PANI-HCl and PANI-H_2SO_4 with various concentration. The conductivity of the polyaniline can be improved with increase the concentration of the acids. These properties are suitable in biosensor applications.

Acknowledgement

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