Research Paper

HCL Dopant Effect on Absorbance Pattern Polyaniline Nanofibers as an Active Material in Gas Sensors

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ABSTRACT

Observations of influence dopants on absorbance polyaniline nanofiber as an active material for gas sensors have been made. The polyaniline nanofiber used is result of interfacial polymerization an organic phase (toluene-aniline) with a water phase (aguadest-HCl-ammonium peroxydisulfate). The synthesis was carried out with molar variations of the HCl dopant from 0.6 to 3 M. From the UV-Vis results it can be seen that the absorbance increases as the dopant concentration increases. The higher the absorbance, it is hoped that the sample will also have high sensitivity to gas. Variations in the morphology of the resulting film are also influenced by the presence of dopants. The greater the molar concentration, the smaller and more regular the fiber size will be.

Keywords: polyaniline, nanofiber, absorbance, morphology

INTRODUCTION

Various materials and methods have been used and developed to obtain good sensor characteristics. Especially for gas sensors, many varied materials are used, including organic conductive polymers such as polyaniline (PANI) [1,2] and polypyrrole (PPy) [3, 4]. Metal oxide based ceramic materials have disadvantages in terms of sensitivity, selectivity and stability compared to conductive polymer materials. In addition, conductive polymer materials can operate at room temperature, while ceramic materials will operate well at higher temperatures [5].

Sensitive parameters in the sensor indicate changes in the work function, optical absorption coefficient or conductivity of the polymer. Most of the sensors mentioned above are based on measuring electrical properties such as changes in resistance, voltage, and current passing through the sensing layer. However, the weakness of detection methods based on electrical properties is their dependence on the environment such as humidity, temperature and oxidation. Apart from that, the long recovery time is also one of the weaknesses in applying electrical property measurement methods.

PANI is a conductive polymer that can be used as an ammonia gas sensor material. PANI will re-protonate the amine group in the emeraldine salt which converts it into emeraldine base, this affects the conductivity of the material. Upon exposure to ammonia gas, rapid diffusion of gas molecules occurs in the Pani layer and dedoping of Pani with H^+. The neutrality of the electrical properties present in the polymer is achieved by charge transfer between the ammonia molecules and the specific active site (H^+ doped imine-nitrogen placed in the Pani), the result being a decrease in the charge carrier density [6, 7]. Therefore, this research will observe the effect of dopant variations on the absorbance pattern of polyaniline nanofiber

as an active material for gas sensors.

LITERATURE REVIEW

Polyaniline (PANI) is one of the most studied conductive polymer materials recently because it has unique physical and chemical properties so that it has potential applications in the fields of electronics and optics (photonics). Unlike other conjugated materials, polyaniline has chemical doping/dedoping properties through simple and reversible acid and base reactions that make it possible to control its solubility, electrical conductivity and optical activity[8]. So far, polyaniline materials have been used in various applications such as gas or chemical vapor sensors [8], electrochromic devices [9], photovoltaic cells [10], polymer LEDs [11], secondary batteries [12] and FETs [13].

Compared to other conductive polymer materials, polyaniline has attracted more attention because of its excellent environmental stability, easier synthesis and ability to react with chemical species at room temperature. When polyaniline materials react with protonation and deprotonation agents, their conductivity changes as do their optical properties. Its conductivity depends on the ability to transport charge carriers along the polymer backbone and jump between polymer chains [14].

Polyaniline was composed of pairs of oxidative aniline monomers, which link nitrogen atoms and benzene chains. Polyaniline has a conjugated double bond structure, a benzoid ring, between the quinoid imine and benzenoid amine structures. The main structure of polyaniline consists of benzenoid rings with an imine backbone and quinoid rings with an amine backbone (double bonded NH). The benzenoid rings react with oxidative agents and the quinoid rings react with reducing agents. When exposed to oxidative gases, hydration or acidic media, the benzenoid rings change into quinoids, this property is reversible. If exposed to oxidative gases, such as NO_2, polyaniline becomes doped and increases its conductivity. On the other hand, if exposed to reductive gas (such as NH3), polyaniline becomes undoped and becomes more resistive (insulator)[15].

Depending on the degree of oxidation, polyaniline can be synthesized in several isolative forms such as fully reduced leucomeraldine base (LB), semi-oxidized emeraldine base (EB) and fully oxidized pernigraniline base (PB). The chemical structures of the three oxidation states (states) of polyaniline are shown in Figure 1.
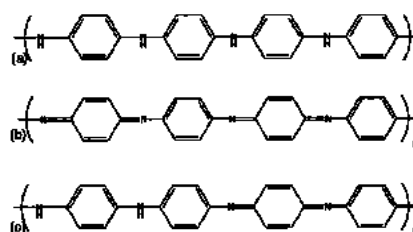

Figure 1. Differences in oxidation states of Pani. (a) leucomeraldine base, (b) pernigraniline base (c) Emeraldine base [16]

Of these three forms, EB is the most stable and the most extensively studied of this family, because its conductivity can be adjusted through doping from 10 -10 S /cm to 100 S/cm while the LB and PB forms cannot be made conductive. The emeraldine base (EB) form consists of reduced [-(C6H4)-N(H)-(C6H4)-N(H)-] and oxidized [-(C6H4)- N = (C6H4) = N-] units. with the same amount. The conductive form of emeraldine salt (ES) is achieved by doping EB with protonic acid di where protons are added to –N= sites while the number of electrons in the chain remains constant. The conductive form of polyaniline (emeraldine salt) protonates the imine nitrogen in the polymer backbone and induces charge carriers. When heavily doped with a strong acid, the electrical conductivity of polyaniline increases strongly compared to the undoped form (emeraldine base).

A key parameter for a number of potential applications of polyaniline, for example, in electronics, energy storage, and chemical sensors, is its electrical conductivity[12]. The conductivity of conductive polymer materials can be increased severalfold by

doping them with oxidative/reductive agents or donor/acceptor radicals.

Doping is a process in which a polymer in the form of an insulator or semiconductor is exposed to a charge transfer agent (dopant) in the gas or solution phase or through appropriate electrochemical oxidation or reduction. This process will increase the polymer's ability to conduct electricity due to increasing the concentration of charge carriers in the polymer. Pure polyaniline in the undoped state is a weak semiconductor with a conductivity of around 10^{-8} S/m. However, when doped, the conductivity can increase considerably depending on the level of doping applied. Doping with certain acids can increase conductivity because doping forms a polaron/bipolaron structure which will increase the polyaniline charge due to increased relocalization.

One application of sensors made from polyaniline is as an ammonia gas sensor. Polyaniline material responds to ammonia gas through changes in electrical properties (conductivity) and changes in optical properties (absorptivity and refractive index, as well as color) when it reacts with ammonia gas. When ammonia gas enters the polyaniline cavities, it causes the color of the polyaniline film to change from green (emeraldine salt) to bluish (emeraldine base). As the color changes, the refractive index value also changes. This change in color and refractive index occurs due to protonation or deprotonation of polyaniline, the degree of protonation depends on the concentration of ammonia absorbed[17].

Changes in resistance in polyaniline films occur through reduction and oxidation (redox) reactions. For example, the reduction reaction with ammonia will increase its resistance due to deprotonation or dedoping, namely the release of proton ions (H^+) followed by the binding of ammonium ions (NH_4^+) to the polyaniline structure. The greater the ammonia concentration, the greater the absorbance value of polyaniline. The ammonia absorbed by the polyaniline layer will affect the resulting absorbance value with respect to concentration variations. In general, polyaniline coatings can respond to ammonia gas at high concentrations. The optical properties (absorptivity) of polyaniline depend on the doping or protonation conditions. In the doped or protonated condition, polyaniline has the form of emeraldine salt and is in the conductor phase, while in the undoped or deprotonated condition the polyaniline is in the form of emeraldine base and is in the insulator phase.

One of the advantages of conductive polymer materials is that they are easy to synthesize at low cost. In general, polyaniline is made through the oxidation of aniline monomers either through electrochemical oxidation or ordinary chemical oxidation with peroxydisulfate oxidants such as $(NH_4)_2S_2O_8$ in an acidic atmosphere[18]. The conventional electrochemical method was the earliest method used to grow a polyaniline layer on a conductor substrate through an oxidation reaction using an external electrical source[19]. A relatively simple method is chemical oxidation (*in-situ*), this method does not require external energy like electrochemistry and only uses an oxidant material as an initiator for the polymerization process[20]. Another method is chemical evaporation, namely by evaporating the aniline monomer solution and the dopant to the substrate on which polyaniline will be deposited[21]. A more complicated and more expensive method is a vacuum system where polyaniline powder is evaporated on a substrate in a chamber with a pressure of 10 Pa [22] including using the plasma discharge polymerization method. The above methods usually produce polyaniline samples (film or powder) in bulk form.

Recently, the development of nanomaterials has also extended to conductive polymer materials such as polyaniline. The development of nanostructured polymer materials (nanoparticles, nanowire, nanotubes, nanofiber) has progressed rapidly in the last two or three years. So far

polyaniline materials have been able to be synthesized in nanostructured form, in including *nanofibers* (nanofiber)[8, 12-14, 23-25], nanowires[26], nanotubes[12], nanocomposites and nanoparticles. The development of nanostructured polyaniline materials is intended to improve the performance of the material in its applications in various fields, one of the most promising being chemical sensors. So far polyaniline nanostructures, especially nanofibers, have been widely developed as chemical sensors, especially gas or chemical vapor sensors[23-25] and biosensors[27]. Nanostructured polyaniline materials are also applied in nonvolatile memory [28], FET [13], rechargeable batteries [12]. In chemical sensor applications, especially gas sensors, nanostructured polyaniline materials (nanoparticles, nanowire, nanotubes, nanofiber) have advantages over bulk polyaniline. In particular, polyaniline nanofibers are very effective as chemical sensors because the nanofiber structure (nanofiber) has a much larger exposed surface area so that the diffusion process of vapor or gas molecules into the polyaniline nanofiber structure will take place faster and more effectively, resulting in penetration depth gas or vapor molecules into nanofibers are much larger than those in the bulk structure [14, 24, 25]. Thus, it will be possible to significantly increase the sensitivity and responsiveness of the sensor. Various methods have been developed to synthesize nanostructured polyaniline. Specifically for the synthesis of polyaniline nanofibers, they can be made using methods such as electrospinning [13], the "seeding" method[29], interfacial polymerization[24], and rapid-mixed reaction[30]. The electrospinning method is relatively more expensive and more complicated, because it requires a high potential source and other equipment. The " seeding " method, interfacial polymerization, and fast reaction are relatively very simple chemical methods, only requiring simple equipment such as beakers, syringes, filter paper, and so on.

MATERIALS & METHODS

The polyaniline nanofiber obtained was formed from the results of interfacial polymerization between the water phase (dopant, initiator and water) and the organic phase (organic solvent and aniline monomer). 0.32 M Aniline 99.5% ($C_6H_5NH_2$) added to Toluene (C_7H_8) thus obtaining 50ml of organic phase (aniline-toluene). 4 mmol APS ($(NH_4)_2S_2O_8$) was added to a 37% HCl solution with varying molar concentrations ranging from 0.5 M to 3 M to obtain 50 ml of the water phase. The two solutions with different phases were mixed (Fig. 2) and left overnight to take the complete polymerization results in the form of polyaniline nanofiber. The polymerization precipitate obtained was then filtered and washed to obtain polyaniline nanofiber. During the filtration process, the bulk polyaniline formed is placed on a glass substrate, to be characterized using UV-Vis and SEM.
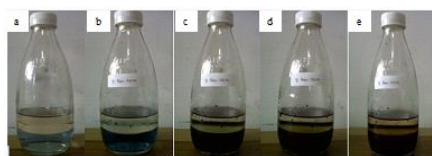

Figure 2. Interfacial polymerization of polyaniline with five molar variations of HCl dopant, (a). 0.6 M, (b). 1.2 M , (c). 1.8 M, (d). 2.4 M and (e). 3 M

RESULT & DISCUSSION

In this research, polyaniline nanofiber was synthesized using the interfacial polymerization method with varying HCl dopant concentrations ranging from 0.6 M to 3 M, in a two-phase solution system, namely the organic phase and the aqueous phase (*table* 1). Aniline monomer solution is mixed with Toluene solution as organic phase and APS solution with HCl dopant and *distilled water* as the water phase (*aqueous*). The two phases were mixed in one clear glass bottle without stirring and left overnight. The next day, filtration and washing were carried out to obtain the polyaniline suspension. This polyaniline suspension was then coated on a glass substrate to observe its absorbance via the

UV-vis method and its microstructure via   SEM.

Table. 1 Interfacial Polymerization of 0.32 M Aniline with 4 mmol APS

Aniline (ml)	Toluene (ml)	APS (gr)	HCl (ml)	Aquades (ml)	Molar HCl
1.5	48.5	0.9	2.5	47.5	0.6
1.5	48.5	0.9	5.0	45.0	1.2
1.5	48.5	0.9	7.5	42.5	1.8
1.5	48.5	0.9	9.9	40.1	2.4
1.5	48.5	0.9	12.4	37.6	3.0

Figure 3 shows the absorbance pattern of polyaniline nanofiber synthesized using the interfacial polymerization method and with variations in the HCl dopant from 0.6 to 3 M. It can be seen that there is an increase in absorbance along with the addition of molar dopant in the wavelength range of 300 to 500 nm. The high absorbance of polyaniline indicates the high absorbance of ammonia gas that will be absorbed. The higher the absorbance of the material, the higher the sensitivity to gas. This is also supported by SEM data (figure 4). The increase in dopant apparently affects the morphology of the obtained nanofibers. The more dopant increases, the neater and more patterned the fiber structure.
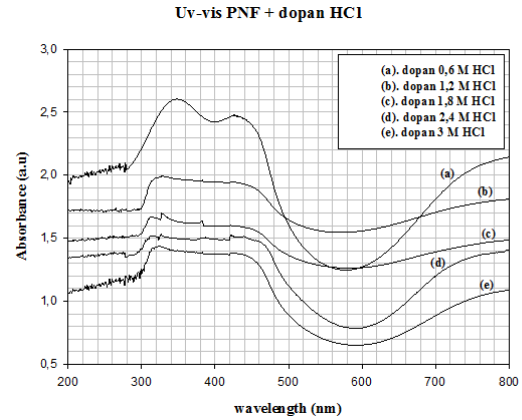

Figure 3. Absorbance pattern of the results of interfacial polymerization of polyaniline with five molar variations of HCl dopant, (a). 0.6 M, (b). 1.2 M , (c). 1.8 M, (d). 2.4 M and (e). 3 M
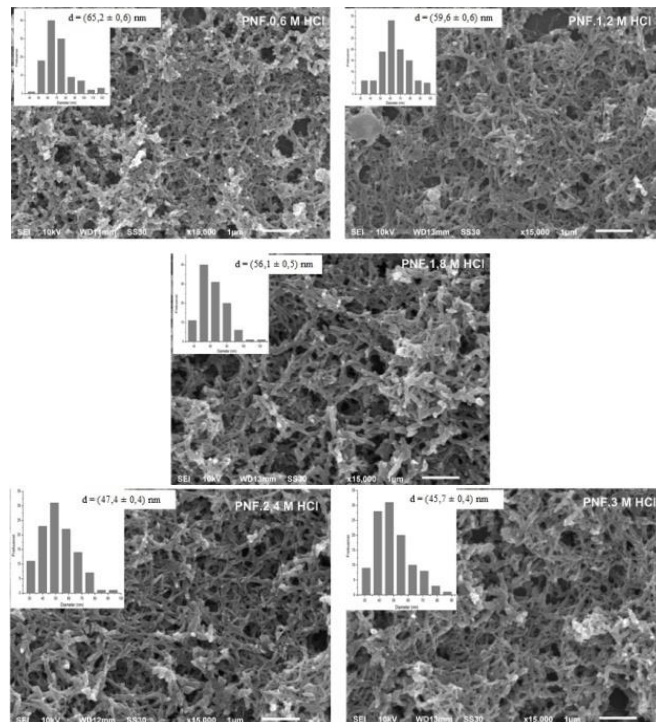

Figura 4. SEM pattern of the results of interfacial polymerization of polyaniline with five molar variations of HCl dopant, (a). 0.6 M, (b). 1.2 M , (c). 1.8 M, (d). 2.4 M and (e). 3 M

CONCLUSION

The absorbance of polyaniline nanofiber was observed using UV-Vis. The tested samples were prepared by interfacial polymerization synthesis of aniline with HCl as a dopant. Dopant variations were made from 0.6 M to 3 M. Dopant molarity affected the sample absorbance value. There is an increase in absorbance as the dopant concentration increases. The higher the absorbance, it is hoped that the sample will also have high sensitivity to gas. Variations in the morphology of the resulting film are also influenced by the presence of dopants. The greater the molar concentration, the smaller and more regular the fiber size will be.

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