EFFECT OF OXIDANT AND DOPANT LOADINGS ON DIRECT ULTRASONIC IRRADIATED POLYANILINE WITH NANOSTRUCTURE

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A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Science

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24 MAY 2020

ACKNOWLEDGEMENT

Through the study of my project, many lovely people give me great encouragement and assistance. My parents and sibling supported me a lot and without their infinite love I could not imagine to finish my study. I would like to express my sincere gratitude to Prof. Madya Dr Agus bin Arsad. As my main supervisor, he gave me great suggestions and guidance, his critics made me improve a lot and the humorous in his personality added happiness during my study. I am also thankful to my co-supervisor Prof Dr Azman B. Hassan, who gave me a lot of handful suggestions about my thesis and encouragement. My gratitude is also given to the coordinator Dr Norfhairna, who helped me a lot on the official matters, like class registration, thesis submission, to name a few.

The technicians of characterization of my samples are all very helpful and gave me good result with their professional knowledge.

My senior Phd student Ali who has helped me a lot on the procedure of doing the experiment and characterization. My fellow friends, Hani and Helmi are also lovely to help me overcome the difficulties of my study and living as a foreign student.

ABSTRACT

Polyaniline (PANI) has been applied in many fields nowadays. In this study, direct ultrasonic irradiation, which means immersing the ultrasonic horn directly into the reaction solution, was used to polymerize polyaniline at frequency of 20 kHz, power of 600W. The overall objective of this study was to synthesize PANI with nanostructure and high conductivity under direct ultrasonic irradiation. The effects of oxidant, viz., ammonium persulfate (APS) and dopant, viz., hydrochloric acid (HCl) concentration on the structure integrity, morphology, and electrical conductivity properties of the prepared polyaniline were examined. As the molar ratio of APS to aniline varied from 0.1 to 1.25, the conductivity of PANI samples reached a maximum of 0.24 S/cm at the ratio of 1. Characteristic peaks at 1558, 1477, 1296, and 1226 cm^{-1} corresponded to quinonoid ring stretching, benzenoid ring (B) stretching, C-N stretching of secondary aromatic amine, and C-N stretching in B-NH-B-NH-B unit showed in the Fourier transform infrared (FTIR) spectra, respectively. In the ultra violet-visible (UV-vis) spectra, the intensity ratio of absorbance bands at 570-670 nm and 330-400, denoted as p-π^* excitation of quinonoid segment and π-π^* excitation of benzenoid part respectively, attained a zenith at APS/aniline molar ratio of 1. The area percentage of three sharp, equal intensity, equal distant peaks at 7.02, 7.14, 7.27 assigned to ammonium protons reached a maximum at APS/aniline molar ratio of 1 in the nuclear magnetic resonance (NMR) spectroscopy. As the molar ratio of APS/aniline increased, four peaks at 2θ=8.7°, 14.8°, 19.9° and 25.2° appeared in the X-ray diffraction (XRD) spectroscopy, and the crystallinity achieved a maximum at the molar ratio of 1. Field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) images showed vein-like structure, nanorods, nanofiber, bridge like structure and plate when APS/aniline molar ratio increased. Subsequently, the concentration of HCl was changed from 0.01 M to 2 M under the same preparation method with the optimized molar ratio of APS/aniline of 1. The conductivity of PANI samples increased with the increase of HCl concentration and reached a maximum of 0.5 S/cm at HCl concentration of 2 M. Characteristic peaks at 1554, 1480, 1287, and 1246 cm^{-1} corresponded to quinonoid ring stretching, benzenoid ring (B) stretching, C-N stretching of secondary aromatic amine, and C-N stretching in B-NH-B-NH-B unit showed in the FTIR spectra, respectively. In the UV-vis spectra, the intensity ratio of absorbance bands at 590-620 nm and 330-360, denoted as p-π^* excitation of quinonoid segment and π-π^* excitation of benzenoid part respectively, attained a zenith at HCl concentration of 2 M. The area percentage of three sharp, equal intensity, equal distant peaks at 7, 7.13, 7.26 assigned to ammonium protons reached a maximum at HCl concentration of 2 M in the NMR spectroscopy. As the HCl concentration increased, four peaks at 2θ=8.6°, 14.9°, 19.9° and 25.2° appeared in the XRD spectroscopy, and the crystallinity achieved a maximum at the concentration of 2 M. FESEM images showed nanorods, nanostick, and petal-like structures when HCl concentration increased.

ABSTRAK

Hari ini, polyaniline (PANI) telah banyak digunakan dalam pelbagai bidang. Kajian ini dilakukan dengan merendam sepenuhnya batang ultrasonik untuk memancarkan ultrasonik secara langsung ke dalam larutan tindak balas proses polimerisasi PANI dengan kekuatan 20 kHz dan kuasa 600 W. Objektif utama kajian ini adalah untuk menghasilkan PANI yang berstruktur nano serta nilai kekonduksian yang tinggi. Kajian terhadap kesan pengoksidaan ammonium persulfat (APS) dan dopan asid hidroklorik (HCl) pekat dijalankan terhadap sifat-sifat integriti struktur, morfologi, dan sifat kekonduksian elektrik PANI. Nisbah molar APS kepada aniline diubah dari 0.1 ke 1.25 dan hasil kekonduksian PANI mencapai nilai maksimum pada 0.24 S/cm dengan nisbah 1. Kajian Spektrum Inframerah Transformasi Fourier (FTIR) pula menunjukkan pencirian puncak-puncak pada 1558, 1477, 1296, dan 1226 cm^{-1} dikaitkan dengan peregangan cincin quinonoid, peregangan cincin (B) benzenoid, peregangan C-N aromatik sekunder amina, dan peregangan C-N di unit B-NH-B-NH-B, masing-masing. Dalam Spektrum Ultra Violet-Visible (UV-vis), nisbah penyerapan intensiti ditunjukkan pada jalur 570-670 nm dan 330-400, ditandakan sebagai eksitasi p-π* segmen quinonoid dan eksitasi π-π* bahagian benzenoid, masing-masing didapati pada nisbah APS/aniline adalah 1. Berdasarkan keputusan spektroskopi Resonans Magnetik Nuklear (NMR), peratusan luas tiga puncak, intensiti yang sama, jarak intensiti yang sama pada 7.02, 7.14 dan 7.27, masing masing dikaitkan kepada proton amonium mencapai nilai maksimum pada nisbah APS/aniline 1. Apabila nisbah molar APS/aniline ditingkatkan, empat puncak diperolehi pada $2\theta = 8.7°$, 14.8°, 19.9° dan 25.2° dalam spektroskopi difraksi Sinar X (XRD), dan nilai kristalitinya mencapai maksimum pada nisbah molar adalah 1. Mikroskop Pengimbasan Elektron Pelepasan Medan (FESEM) dan Mikroskop Elektron Bertransmisi Resapan Tinggi (HRTEM) menunjukkan struktur seperti vena, rod nano, serat nano, struktur seperti jambatan dan plat dilihat apabila nisbah APS/aniline molar berkurangan. Selanjutnya, kepekatan HCl diubah dari 0.01 M hingga 2 M dengan kaedah penyediaan yang sama dengan menetapkan nisbah molar optimum APS/aniline adalah 1. Kekonduksian PANI meningkat dengan peningkatan kepekatan HCl dan mencapai nilai maksimum pada 0.5 S/cm apabila kepekatan adalah 2 M. Pencirian puncak-puncak adalah pada 1554, 1480, 1287 dan 1246 cm^{-1} ditunjukkan pada spektrum FTIR adalah cincin quinonoid, cincin benzenoid (B), peregangan C-N aromatik sekunder amina, dan peregangan C-N di unit B-NH-B-NH-B. Spektrum UV pula mendapati band penyerapan nisbah intensiti pada 590-620 nm dan 330-360, masing-masing dinamakan sebagai eksitasi p-π* segmen quinonoid dan eksitasi π-π* bahagian benzenoid masing-masing, mencapai kemuncak di kepekatan HCl sebanyak 2 M. Daripada spectroskopi NMR, peratusan luas tiga puncak, intensiti yang sama, jarak puncak yang sama pada 7, 7.13 dan 7.26 yang dikaitkan dengan proton amonium telah mencapai nilai maksimum apabila kepekatan HCl 2 M. Dari hasil keputusan spektroskopi XRD, apabila kepekatan HCl meningkat, empat puncak diperolehi adalah pada $2\theta = 8.6°$, 14.9°, 19.9° dan 25.2°, dan nilai kristaliniti mencapai maksimum pada kepekatan 2 M. Gambar-gambar FESEM menunjukkan rod-rod nano, stick nano, dan struktur seperti kelopak bunga dilihat jelas apabila kepekatan HCl meningkat.

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LIST OF SYMBOLS

°C - Degree Celsius

g/mol - Gram per mol

g/ml - Gram per milliliter

kHz - Kilo herz

mHz - Mega herz

nm - Nanometer

µm - Millimeter

rpm - Revolution per minute

$S \cdot cm^{-1}$ - Siemens per centimeter

wt.% - Weight Percentage

LIST OF ABBREVIATIONS

PANI - Polyaniline

EB - Emeraldine Base

ES - Emeraldine Salt

DBSA - Dodecyl Benzene Sulfonic Acid

CSA - Camphor Sulfonic Acid

PTSA - P-toluene Sulfonic Acid

NMP - N-methyl-2-pyrrolidone

DMSO - Dimethyl Sulfoxide

DMF - Dimethyl Formamide

THF - Tetrahydrofuran

CTAB - Cetyltrimethylammonium Bromide

APS - Ammonium Persulfate

ANI - Aniline

EDOT - 3,4-ethylenedioxythiophene

PEDOT - Poly (3,4-ethylenedioxythiophene)

PSS - Poly (styrene sulfonate)

DEG - Diethylene Glycol

FTIR	-	Fourier Transform Infra-Red
NMR	-	Nuclear Magnetic Resonance
FIB-SEM	-	Focus ion Beam Scanning Electron Microscopy
EDX	-	Energy Dispersive X-ray Spectroscopy
HRTEM	-	High Resolution Transmission Electron Microscopy
UV-Vis	-	Ultra Violet-visible
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polyaniline (PANI), an intrinsically conducting polymer, has attracted much attention of scientists and engineers from all over the globe, ascribed to its extinctive electrical properties and facile preparation, as well as its excellent environment stability. An electrical conductivity as high as 400 S/cm could be obtained for PANI in doped state (Le et al., 2017). Although there are some drawbacks for PANI, viz., inability to be processed by conventional methods and poor mechanical properties, it can still be used in many areas due to its excellent electrical and electrochemical properties, such as supercapacitors (Zhou et al., 2018), gas detection (Tanguy et al., 2018), and solar cells (Lee et al., 2017).

PANI could be synthesized mainly by chemical oxidation polymerization (Kumar and Yadav, 2016) and electrochemical polymerization (Bhandari and Khastgir, 2016). Among chemical oxidation synthesis, apart from traditional solution polymerization (Lin et al., 2017), several novel techniques have been employed to prepare PANI, such as, interfacial preparation (Zhang et al., 2019), and ultrasonic irradiation (Mohsin et al., 2019a). For conventional chemical polymerization method proceeded under mechanical stirring, it always takes a long time to get a polymer with comparatively high conductivity (Tang et al., 2013). Furthermore, a disappointing aggregate structure was usually obtained rather than nanosized particles (Casado et al., 2014). Compared with chemical oxidation, which is simple and could be employed in large-scale producing, electrochemical method confers PANI films with higher purity, nevertheless, the area of the product is confined in small size (Ezzati et al., 2018).

Reaction parameters are found to be a key role on the properties of PANI. Fang et al. (2018) found that lower ratio of oxidant ammonium persulfate (APS) to aniline resulted in smoother surface and longer length of the nanofibers compared with those of the higher APS/aniline molar ratio. APS could attribute to a higher conductivity compared with potassium dichromate and iron (III) chloride (Fe_3Cl) when it was employed to oxidize aniline (Blaha et al., 2017). Noby et al. (2019) reported different morphologies of PANI by varying concentration of hydrochloric acid (HCl), such as nanoflowers, nanotubes and nanofibers, when aniline was polymerized in a high-pressure autoclave. In their work, PANI doped with HCl exhibited higher conductivity than that doped with sulfuric acid. The conductivity of PANI increased with the increasing of HCl concentration, and the maximum value (3.7S/cm) was reported with 5M HCl**.**

Ultrasonic irradiation, has become immensely popular in promoting various reactions. In this method, reaction proceeds in microreactors, which are known as cavitation bubbles. There are direct and indirect ways to conduct ultrasonic irradiation, viz., ultrasonic probe and ultrasonic bath. Compared with ultrasonic bath, there is no reduction of the intensity of ultrasonic power when the probe is directly immersed into the reaction system (Capelo-Martinez, 2008).

Exciting advantages have been exhibited by ultrasound method when it is applied to polymerization of PANI or PANI based composites. With the assistance of ultrasonic bath, PANI nanoparticles (Fukui et al., 2015), and PANI nanosticks with diameter of ca. 40 nm and aspect ratio higher than 3 (Ai and Jiang, 2011) were attained. While nanosized particles cannot be obtained facilely by conventional chemical methods, a template or typical process are generally needed in order to get nanostructures (Baker et al., 2017). PANI and PANI/starch blends prepared by ultrasonication demonstrated higher conductivity compared with that resulted from magnetic stirring, according to Mohsin et al. (2016). Compared with chemical oxidation method, this technique needs only short reaction period. Wang et al. (2014) obtained 1 dimensional nanostructures of PANI within 1 hour. Furthermore, it took only 30 minutes for Mohsin et al. (2019a) to polymerize PANI with a conductivity as high as 1.78 S/cm through direct ultrasonic irradiation polymerization. Whereas, Kumar and Yadav (2016) synthesized PANI by traditional chemical oxidation method after 4 hours of magnetic stirring , and the same duration was applied in the work of Lin et al. (2017), as well, which was 3 times longer than that of Mohsin et al. (2019a).

1.2 Problem Statement

Although some researchers have prepared PANI using ultrasonic irradiation, most of them fixed the oxidant and dopant concentrations. Furthermore, they had no concern of electrical conductivity test, and most of them applied indirect method, viz., ultrasonic bath (Ai and Jiang, 2011; Wang et al., 2014). In comparison with direct pathway, ultrasonic bath method does possess its drawbacks. The ultrasonic power could not be transferred effectively to the reaction system in ultrasonic bath, which results in a low intensity than expected (Capelo-Martinez, 2008).

Jing et al. (2007) varied the molar ratio of APS/aniline and attained the highest conductivity at the ratio of 1 in ultrasonic bath. The nature and concentration of dopant acid were changed by Lu et al. (2006), in whose work nanotubes and nanofibers were formed at lower and higher acid concentration, respectively. However, the conductivities of the samples, which are of significant importance for conducting polymers, were not investigated by them. Furthermore, both of these papers applied ultrasonic bath method, in which the intensity will be reduced by the containers of the reaction solution. Fortunately, Mohsin et al. (2019) polymerized PANI nanoparticles by direct ultrasonic method, but they only investigated the influence of reaction time on the properties of PANI and kept other parameters constant. In their work, the concentration of HCl was kept as 1M, and the ratio of APS/aniline was fixed as 1:1.

To date, no research has been done on the effect of HCl concentration and ratio of APS to aniline on the morphology and electrical conductivity of PANI synthesized by direct ultrasonic irradiation polymerization. Therefore, the effect of oxidant and dopant concentration in direct ultrasonic irradiated PANI is noteworthy to be determined thoroughly to obtain product with desired properties.

1.3 Objective of the Study

The overall objective of this study was to synthesize PANI with nanostructure and high conductivity under direct ultrasonic irradiation, and the specific objectives were as follows:

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