Preparation and Characterization of Polyaniline Emeraldine Base (PANI-EB) Using Langmuir- Blodgett Technique

Siti Amira Othman[1,*], Shahidan Radiman[2]

[1] Department of Physics and Chemistry, Faculty of Applied Sciences and Technology, Universiti Tun Hussein Onn Malaysia, 84600, Pagoh, Johor.
[2] School of Applied Physics, Nuclear Science Program, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor.

*Corresponding author's email: sitiamira@uthm.edu.my

ABSTRACT: Nanostructures of conducting polymers are of great significance due to their unique properties and application in nano-scale electronic and molecular devices. Polyaniline (PANI) is a conducting polymer that is environmentally stable and easy to prepare. This study intends to study the formation of nanostructures especially nanoparticles of polyaniline (PANI) using Langmuir- Blodgett (LB) technique of molecular deposition. Polyaniline monolayer that forms on water interface prepared by LB technique was deposited on Indium Tin Oxide (ITO) glass and followed by a slow drying at room temperature. A decrease in the pH of the sub-phase in the LB trough increases the level of doping (protonation) of polyaniline emeraldine base to emeraldine salt. Variable pressure scanning electron microscope (VPSEM) reveals that nanoparticles are formed when there is an increase in the subphase pH compare to the neutral subphase because of the interaction between PANI and functionalized acid. This result is supported by XRD which shows that pH 5 has strong diffraction peaks due to the existence of well-defined layer structure. U.V.- Visible spectrum shows two peaks at 320 nm and 800 nm due to the transition of π-π* in the benzenoid chain and polaron band. AFM shows that nanoparticles are formed on ITO surface after the deposition of PANI-EB with no significant difference in surface roughness for different pH. In a conclusion, well defined and good molecular arrangement of polyaniline nanoparticles can be achieved by good control of major factors that can influence the deposition process.

Keywords: *PANI; nanoparticle; langmuir-blodgett, subphase, deposition*

1. INTRODUCTION

Recently, the Langmuir- Blodgett technique is extensively employed to obtain ultrathin-organized organic films [1]. Commonly, the LB technique is employed with amphiphilic molecules which have a polar head and non-polar tail. It was just started to study the preparation and properties of thin films, particularly those of the ordered multilayer ultrathin films in recent years, for their potential application as molecular or supramolecular devices. There has been an increased interest in the preparation of conducting polymer LB layers on to desired substrate LB films based on conducting polymers for a variety of applications such as biosensors, ion sensors, integrated optics and molecular electronic devices [2].

2. MATERIALS AND METHODS

0.1M polyaniline emeraldine base (PANI-EB) (Sigma Aldrich; MW 10000) was dissolved using methanol (Merck) as a solvent. The dissolved solution was kept for 1 hour in an ultrasonication bath. Then, filter the resulted solution. A PANI-EB solution was spread over Langmuir- Blodgett trough at the air-water interface and for solvent evaporation, 30 minutes was needed for the process. By using simple filter paper (Wilhelmy plate) that acts as a sensor, surface pressure against area/ molecule isotherm was recorded. The transfer pressure was kept at 12mN/m. The pH for the subphase water was maintained at different levels of 1, 3, 5 and 7 by adding p- toluene sulfonic acid. Langmuir Blodgett trough (Model LB 312DMC) was used to see the formation of the PANI-EB monolayer. VPSEM, AFM and XRD are used for characterization.

3. RESULTS AND DISCUSSION

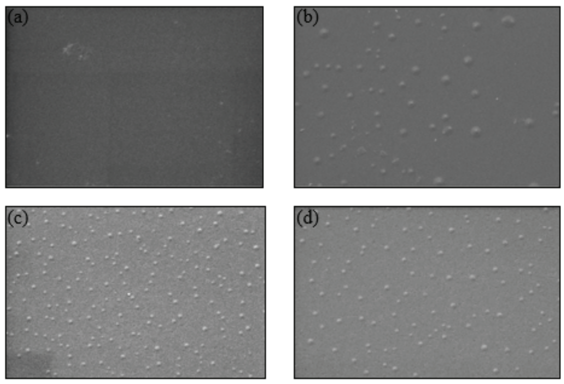

Figure 1 The morphology of PANI-EB deposited on ITO glass with varies pH (a) pH 1 (b) pH 3 (c) pH 5 (d) pH 7

Figure 1 shows the morphology of PANI-EB deposited on ITO glass with various pH (a) pH 1 (b) pH 3 (c) pH 5 and (d) pH 7. Here, pH 7 role as a standard image to another pH when no PTSA was added to PANI-EB. From figure 1, it indicates that nanoparticles are formed when there is an increase in the pH subphase. The pH of the subphase is maintained by adding the p-toluene sulfonic acid (PTSA) that helps in solubility and stability for the formation of PANI-EB monolayer [3]. The difference between each pH is a content of a PTSA that adds into a subphase. pH 1 contains more PTSA besides pH 5. Here, we can see the role of PTSA, PANI-EB is a semi amphiphilic which is it only has a hydrophobic part. So, by adding PTSA it changes the properties PANI-EB by doing the process that we call protonation. So, it indirectly gives PANI-EB novel properties for instance hydrophilic part that helps the PANI-EB to deposited on ITO glass.

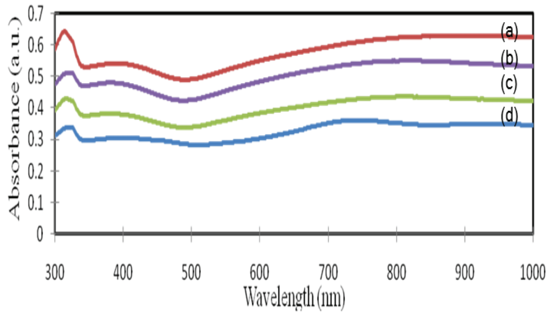

Figure 2 Variation of the UV-visible spectrum of PANI-EB in different subphase at (a) pH 1 (b) pH 3 (c) pH 7 (d) pH 5

The UV-visible spectra of PANI-EB deposit on ITO glass with different pH subphases are shown in figure 2. PANI-EB is an organic polymer that can absorb electromagnetic radiation because of the existence of its electron valency that can be excited to a higher level. It indicates that all pH give the same peak at a certain wavelength and PANI-EB in pH 1 has a higher rate of absorption than another pH because of the excessive addition of PTSA.

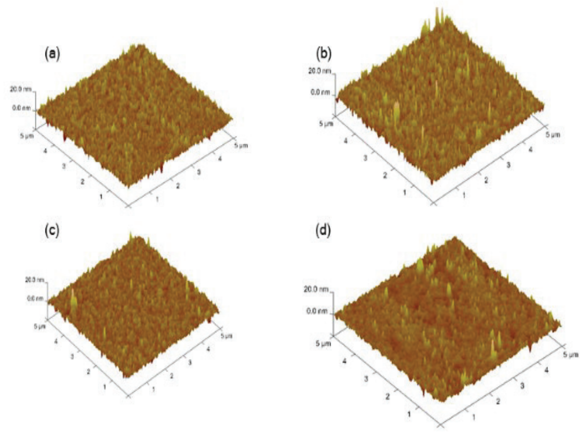

Figure 3 AFM images of PANI deposited on ITO glass for various pH (a) pH 1 (b) pH 3 (c) pH 5 (d) pH 7

Figure 3 shows the AFM images of PANI deposited on ITO glass for different pH. Here we want to determine the quality or structure surface and roughness average, R_a of the PANI-EB deposited on ITO glass. The difference between each pH is the volume of PTSA that add into the subphase. The value for roughness average, R_a for each pH are 1.58 nm (pH 1), 1.50 nm (pH 3), 1.25 nm (pH 5) dan 1.01 nm (pH 7). In terms of roughness surface, pH 1> pH 3> pH 5 > pH 7.

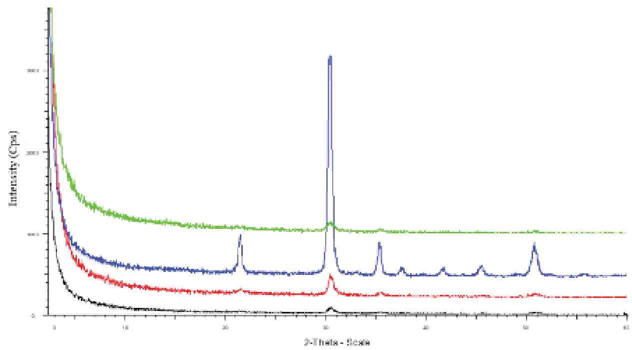

Figure 4 XRD spectra of PANI-EB for various pH (a) pH 1 (b) pH 3 (c) pH 5 (d) pH 7

Figure 4 shows the XRD spectra of PANI-EB for various pH (a) pH 1 (b) pH 3 (c) pH 5 (d) pH 7. There is one peak that exists for each pH at $2\theta = 20.5^0$ that indicates the peak of PANI-EB. pH 5 shows a strong peak. This may be caused by a homogeneous and stable PANI-EB film are formed and also the interaction between PANI-EB and PTSA.

4. CONCLUSION

We concluded that the stability of Langmuir monolayer PANI-EB and formation of PANI-EB nanoparticles can be achieved by using the acidic subphase in a Langmuir-Blodgett trough. VPSEM, AFM, U.V.-Visible and XRD prove there are differences in morphology and existence of peaks that show the interaction between PANI-EB and PTSA.

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REFERENCES

[1] Paloheimo, J., Stubb, H., Yli-Lathi, P., Dyreklev, P. & Inganas, O. *Electronic and optical properties with Langmuir- Blodgett transistors*. J. Thin solid Films 210-211: pp 283, 1992.

[2] Ram, M.K. & Malhotra, B.D. *Preparation and Characterization of Langmuir- blodgett films of polyemeraldine base*. J. Polymer 37: pp 4809-4813, 1996.

[3] Sabapathy, M., Anudeep, J., Saptarshi, M., Saibal, G. & Kajari, K. *Formation of nanorods and nanoparticles of polyaniline using Langmuir-Blodgett technique: Performance study for ammonia sensor*. Journal of Sensors & Actuators B 133: 182- 194, 2008.