Fabrication and Study Thin Films from PFPy by Anchoration

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Fabrication and Study Thin Films from PFPy by Anchoration

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Abstract: A novel polymer thin films was fabricated by anchoring polymer from reaction solution (monomer, Alcohol and hydrochloric acid). The thickness of the film increases with concentration of monomer and acid, and it decreases at large concentrations of acid. The surface roughness of films were increased with thickness. Mean diameter of polymer particles in thin films were about 280.4,180.7and 135.3 nm For returned film, mean diameter of polymer particles were about 81.5 nm and it was less roughness. In EIS, the ohmic resistance of film 180±23 at thickness=110 nm and 13710±2170 Ohm at thickness = 907 nm.

Keywords: polymer thin films, anchoration , 2-formyl Pyrrole, poly formyl pyrrole (PFPy), thin films.

1 Introduction

Conductive polymers which have heterocyclic structures (polypyrrole, polythiophene, etc.) have received great attention [1]. They used in sensors [2][3], biosensors[3], capacitors[4], solar cells [5], optical displays [6], light emitting diodes [7], as rechargeable batteries [8], enzyme immobilization matrices [9], membranes [10], gas separation membranes [11] and electro chromic devices [12]. The most applications use conducting polymers as thin films [13]. The polymer, thickness, surface morphology and conductive may select the applications [14]. Polypyrrole thin films have been widely studied due to their applications in catalysts and photo-catalysts [15], solar cells [16], medical implants [17] and modified electrode [18]. For best applications, the preparation of thin films of the conjugated polymer with good properties is needed [19]. However, The possibility of developing an effective method for controlling the formation of polymers in the solid state was limited due to their properties including amorphous structure and large molecular weight [20]. In this paper, we fabricated poly (PFPy) thin films by anchoring it from reaction solution. Thickness, surface morphology and electrochemical properties of the films were studied.

2 Experimental Sections

2.1 Materials

Pyrrole-2-carboxaldehyde 98% sigma, Hydrochloric acid 35.5% Sigma, hydrazine solution 35% Sigma, and golden and platinum electrodes CBC China.

2.2 Measurements

Thin films were characterized by UV spectrometer was PG model T72 on between 400 and 800 nm. Electrochemical impedance spectroscopy (EIS) is applied using in KClO4 (1M) solution, 1mA/cm2 and 0.58V in the range of 0.1Hz - 10kHz (AMEL model 2550). Thin film morphologies were examined with AFM (Nanosurf model eseyscan2).

2.3 Fabrication of Thin Films

The film was fabricated by anchoration in the reaction solution (2-formyl Pyrrole (10mmol,0.97g) was dissolved in the alcohol (25ml) then hydrochloric acid 35.5% (10ml) was added). The substrate was immersed in the reaction solution after adding the acid, and left in the solution for some time and removed from the solution. The substrate with film was washed with deionized water, then with alcohol and left to dry without touching the film surface. The thickness of the film was determinated by weight method. One of films was returned by dipped in hydrazine solution (5%) for half an hour thin in distilled water. And dry it at room temperature and keep for study.

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3 Results and Discussion

3.1 Thin Films Fabrication

Fig. 1 shows the film images which formed on glass as substrate. The films seem darker with increasing the concentration of acid and monomer concentration. this means that with higher acid or monomer concentration the polymer precipitated faster and the films would be more thick and dark. but high concentration of acid gives low thickness because it helps dissolve the polymer and damage the film. The films were fabricated on a substrate of platinum, gold, glass, porcelain and quartz. No effect of substrate type was observed on the thickness of the film.
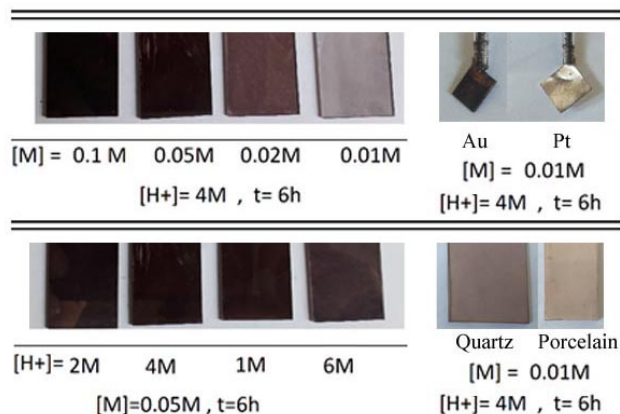
Fig. 1: film images on platinum, gold, glass, porcelain and quartz. as substrates.

3.2 UV-Vis Spectra

UV-Vis spectra were recorded for dry films on glass in the visible field only. **Fig. 2**-A shows the absorption spectra of the films studied at different thicknesses. The films have a maximum absorption peak at 490nm. Fig. 2-B shows absorption at 490nm wavelength vs film thickness. By Beer-lambert law, the absorption coefficient linear of the films was ($\mathcal{E}'$ =0.0031 nm-1).
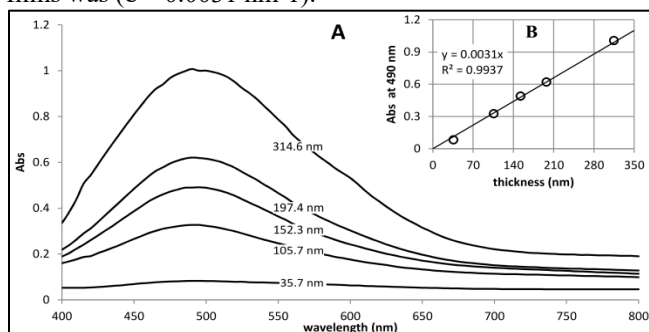

Fig. 2: A) absorption spectra of the films, B) absorption vs film thickness

3.3 Surface Morphology

Atomic force microscopy (AFM) is an excellent tool to study morphology and texture of diverse surfaces [21] and employed as a powerful technique to study the morphology of thin films surfaces and determinate mean diameter of polymer particles [22]. Atomic force microscopy (AFM) scans area of polymer films with several thicknesses. **Fig. 3** shows 3D image, Topography, and Mean diameter of polymer film on glass as substrate. Surfaces of films seem as balls that merge together to form rough surface and had a lot of mountains. The surface becomes less rough for more thickness and the mountains become fewer and higher. In Fig 3, mean diameter of polymer particles in thin films were about 280.4,180.7, 135.3 and 81.5 nm. The film 4 was studied after returned by dipped in hydrazine solution (5%) for half an hour thin in distilled water. And dry it at room temperature
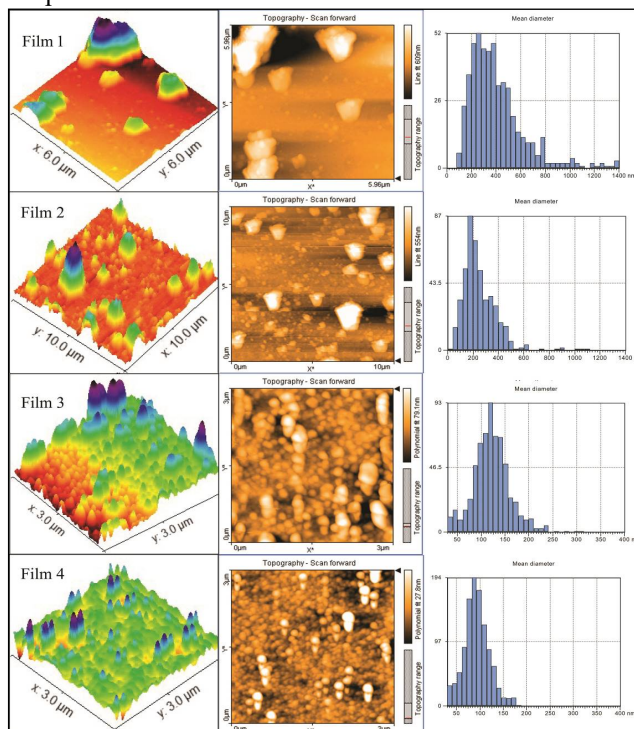
Fig. 3: AFM images (3D , topography and elevation distribution) of the polymer films on glass as substrate.
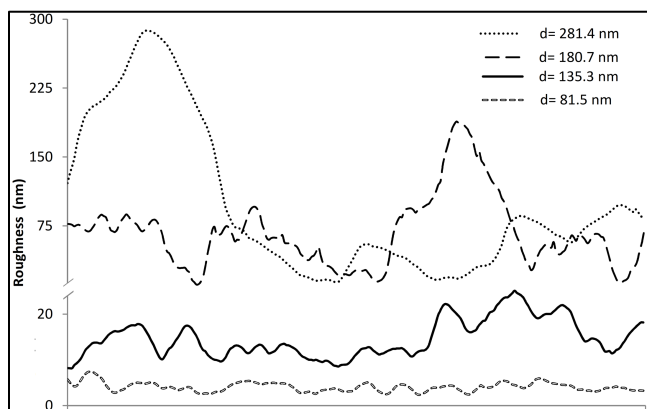
3.4 Roughness of Thin Films

Atomic force microscopy (AFM) is employed as a powerful technique to statistical study and analysis the morphology and roughness of polymer thin films surfaces with parameters such as roughness (R_a) root mean square (RMS) and kurtosis (Ku) [22]. **Fig 4** shows Roughness of polymer film. Statistical analysis of AFM data shows the surface parameter (**Table 1**) when polymer formed and precipitated the active pointes in surface of substrate absorb polymer chains. They accumulate on surface and grow to join together, and form a rough layer which seems as joined balls.

Table 1: Percentages of solutions for sample preparation.

	Ra	RMS	Rz	kurtosis

|	(nm)	(nm)	(nm)	
Film 1	85.5	140.5	302.6	2.97
Film 2	67.15	110.6	226.4	3.84
Film 3	14.7	20.11	46.5	1.56
Film 4	4.03	6.15	16.22	3.949

The Roughness of film surface becomes less with its thickness. When the films returned by dipped in hydrazine solution, the outer surface of polymer crumbles up and the surface becomes less rough and its particles appear.

Fig. 4: Roughness of polymer thin films

## 3.5 Studying the Electric Resistance of Films

In order, to study the electrical conductivity of films, the electrical resistance between two electrodes of gold that were immersed in the reaction mixture was measured with thickness. **Fig. 5** shows the electrical resistance vs film thickness. At first, the films are thin and their resistance is low then it increase to maximum value. After that, film becomes less resistance because Surfaces of films become roughness. When the thickness of the polymer becomes so big, the resistance increased significantly. This is due to the multi-layers in film, which causes additional resistance between the layers.
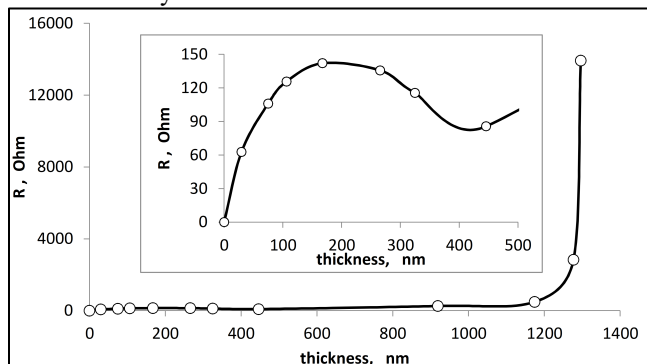
Fig.5: films thickness dependence of the electrical resistance of thin film.

3.6 Electrochemical Impedance Spectroscopy

Fig. 6 shows the electrochemical impedance spectrum for two films precipitated on the gold as substrate / potassium chlorate solution at potential (0.58V) and the intensity of the current (0.001A) and frequency 10 kHz – 0.1Hz. Both curves consist of two parts. The first is semicircular at high frequencies and the other is linear at low frequencies, with low thickness film, semicircular part is less clear
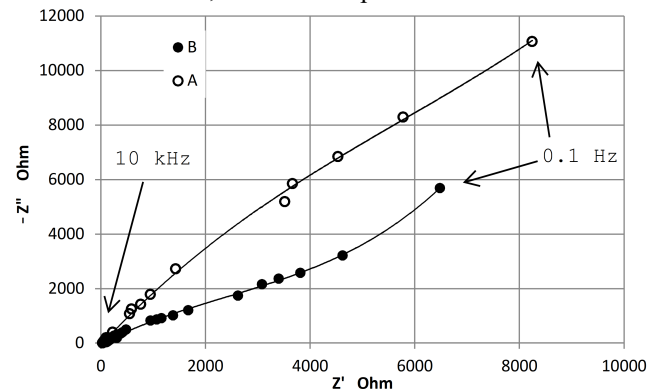
Fig. 6: Nyquist plot for films at gold A) thickness =110 nm and B) thickness = 907 nm

In order to analysis the EIS results, we fitted the impedance data to equivalent electrical circuits (**Fig. 7**), which consist of a first resistance (solution resistance R1), (30±2 Ohm). Warburg Impedance (noted W) or capacitance is therefore ascribed to the diffusive capacitance (A:40.3±1.2 and B:91.1±4.6 (mOhm)-2). Warburg Impedance is in parallel with the faradic component, which is composed resistance (R2) serially associated with a capacitance (Q). Resistance (R2) is the sum of the charge transfer and the ohmic resistance of film (A:180±23 and B:13710±2170 Ohm), while Q is the double-layer capacitance (A:0.151±0.01 and B:0.153±0.01 µF/cm2).
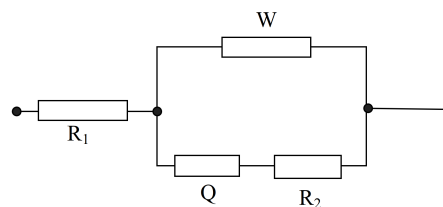
Fig.7: Equivalent electrical circuits for the films.

4 Conclusions

A novel polymer thin films was fabricated by a simple and easy method by anchoring polymer in reaction solution. A polymer thin film can be formed on a substrate (platinum, gold, glass, porcelain and quartz.) by immersing the substrate in the mixture reaction. The thickness of the film increases with concentration of monomer but decreases at large concentrations of acid.

The roughness of film surface was increased with thickness. Electrical resistance of films decreases with the surface roughness and increases with thickness.

Acknowledgement

References

[1] Kim J., Sohn D., Sung Y. and Kim E.R, Synthetic metals., **132**, 309-313, 2003, Doi: 10.1149/ma2014-02/28/1563.

[2] Hernandez S. C., InterScience, **19(19-20)**, 2125-2130, 2007.

[3] Zhang, Y.-P., Lee, S.-H., Reddy, K. R., Gopalan, A. I., & Lee, K.-P. Journal of Applied Polymer Science., **104(4)**, 2743–2750, 2007. doi:10.1002/app.25938

[4] Rudge, A., Davey, J., Raistrick, I., Gottesfeld, S., & Ferraris, J. P. Journal of Power Sources., **47(1-2)**, 89–107,1994. Doi:10.1016/0378-7753(94)80053-7

[5] Zhang, J. C., Zheng, X., Chen, M., Yang, X. Y., & Cao, W. L. Express Polymer Letters., **5(5)**, 401–408, 2001. doi:10.3144/expresspolymlett.2011.39

[6] AMINA MIRSAKIYEVA Mirsakiyeva A. PhD thesis : School of Engineering Sciences,KTH Royal Institute of Technology,Stockholm, Sweden, 2017.

[7] Kasa T. and Gebrewold F., Advances in Physics Theories and Applications, ISSN 2225-0638 (Online)., **62**, 28-37, 2017.

[8] Duan, L., Lu, J., Liu, W., Huang, P., Wang, W., & Liu, Z, Colloids and Surfaces A: Physicochemical and Engineering Aspects., **414**, 98–103, 2012. doi:10.1016/j.colsurfa.2012.08.033

[9] Bayramoğlu, G., Karakışla, M., Altıntaş, B., Metin, A. U., Saçak, M., & Arıca, M. Y., Process Biochemistry., **44(8)**, 880–885, 2009. doi:10.1016/j.procbio.2009.04.011

[10] Gherras H., Yahiaoui A., Hachemaoui A., Belfeda A., Dehbi A. and Mourad A.I, Journal of Semiconductors., **39(9)**, 1-7, 2018.

[11] Ding, X., Tan, F., Zhao, H., Hua, M., Wang, M., Xin, Q., & Zhang, Y., Journal of Membrane Science., **570-571**, 53–60. 2019, doi:10.1016/j.memsci.2018.10.033

[12] Shim, G. H., & Foulger, S. H., Photonics and Nanostructures - Fundamentals and Applications., **10(4)**, 440–446. 2012. doi:10.1016/j.photonics.2011.12.001

[13] Kang, T.G., Park, J.K., Kim, B.H., Lee, J. J., Choi, H. Lee, H.J., & Yook J.G., Measurement., **23(3)**, 272-277, 2019. doi:10.1016/j.measurement.2019.01.032.

[14] . Fernández, B., Pereiro, R., & Sanz-Medel, A., Analytica Chimica Acta., **679(1-2)**, 7–16, 2010. doi:10.1016/j.aca.2010.08.031

[15] Alsultan, M., Choi, J., Jalili, R., Wagner, P., & Swiegers, G. F, Molecular Catalysis., **490**, 110955, 2020. doi:10.1016/j.mcat.2020.110955

[16] Huang, J., Liu, X., Lu, Y., Zhou, Y., Xu, J., Li, J., … Song, W., Solar Energy Materials and Solar Cells., **184**, 73–81, 2018. doi:10.1016/j.solmat.2018.04.002

[17] Klein, E., Huber, K., Paul, O., & Ruther, P., Thin Solid Films, 137715. 2019. doi:10.1016/j.tsf.2019.137715

[18] Fu, Y., Lin, Y., Chen, T., & Wang, L, Journal of ElectroanalyticalChemistry.,**687**,25–29,2012. doi:10.1016/j.jelechem.2012.09.040

[19] Talham, D. R.,Chemical Reviews., **104(11)**, 5479–5502, 2004. doi:10.1021/cr030665u

[20] Ravindranath, R., Ajikumar, P. K., Advincula, R. C., Knoll, W., & Valiyaveettil, S., Langmuir., **22(21)**, 9002–9008, 2006. doi:10.1021/la060539w

[21] B.Rajesh Kumar, T. Subba Rao., Digest Journal of Nanomaterials and Biostructures., **7(4)**,1881-1889,2012.

[22] Arjomandi, J., Raoufi, D., & Ghamari, F., The Journal of Physical Chemistry C., **120(32)**, 18055–18065, 2016. doi:10.1021/acs.jpcc.6b04913.

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