Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2021, т. 19, № 4, сс. 913–922

PACS numbers: 68.37.Ps, 68.55.jd, 73.61.Ph, 78.40.Me, 82.35.Cd, 82.45.Wx

Fabrication and Characterization of Poly(2-Formylpyrrole) Nanoparticles' Thin Films by Anchoration

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The polymer-nanoparticles' thin films are fabricated by anchoring polymer from reaction solution (monomer, alcohol and hydrochloric acid). The thickness of the film increases with time and concentration of monomer and acid, and it decreases at large concentrations of acid. The films have a rough surface and peaks several times greater than the thickness. Thin films are formed on a substrate of gold, ordinary glass and quartz. Film thickness is between 106 nm and 1296 nm. Based on electrochemical impedance spectroscopy, the ohmic resistances of films are of 1090, 235, 176 and 157 (± 12%) Ohm at thicknesses of 780, 487, 102 and 65 nm, respectively, and the double-layer capacitance is of about 149±0.02 μF/cm^2.

Тонкі плівки полімерних наночастинок виготовляються шляхом закріплення полімеру з реакційного розчину (мономер, спирт і соляна кислота). Товщина плівки збільшується з часом і концентрацією мономера та кислоти, і вона зменшується за великих концентрацій кислоти. Плівки мають шерстку поверхню та піки, що в кілька разів перевищують товщину. Тонкі плівки утворюються на підкладинці з золота, звичайного скла та кварцу. Товщина плівки становить від 106 нм до 1296 нм. За даними електрохемічної імпедансної спектроскопії активні електроопори плівок становлять 1090, 235, 176 і 157 (± 12%) Ом за товщини у 780, 487, 102 і 65 нм відповідно, а двошарова ємність становить близько 149±0,02 μF/cm^2.

Key words: polymer thin films, anchoring, 2-formyl pyrrole, polyformyl pyrrole.

Ключові слова: полімерні тонкі плівки, прикріплення, 2-формільний піррол, поліформіл піррол.

(Received 27 January, 2021; in revised form, 31 December, 2021)

1. INTRODUCTION

Conducting polymers such as polypyrrole, polythiophene, polyfuran and its derivatives have received great attention because of their wide applications [1–3]. They used in sensors, biosensors [4, 5], solar cells [6], optical displays [7], light emitting diodes [8], electrochromic devices [9], capacitors [10], rechargeable batteries [11], enzyme immobilization matrices [12], membranes [13], and gas separation membranes [14]. Conducting-polymers' thin films are the most important applications [15]. The fabrication method of thin films varies according to the polymer and the substrate. Thickness, surface morphology, electrical current-conducting properties and polymer may select the thin films applications [16]. Polypyrrole and poly(2-formylpyrrole) thin films have been widely studied due to their applications [17, 18] in catalysts [17], modified electrode [19], photocatalysts [20], solar cells [19], and medical implants [21]. For best applications, the preparation of thin films of the conductive polymer with good properties is needed [22]. However, the development of effective and precise methods for controlling the organization of the polymer in the solid state has been limited because polymers often fail to assemble into organized structures due to their amorphous character and large molecular weight [23].

In this paper, we fabricated poly(2-formylpyrrole) nanoparticles' thin films by anchoring them from reaction solution. Thickness, surface morphology and electrochemical properties of poly(2-formylpyrrole) films were also studied.

2. EXPERIMENTAL

2.1. Materials

Pyrrole-2-carboxaldehyde 98% sigma, hydrochloric acid 35.5% sigma, and golden electrodes (CBC China).

2.2. Measurements

Thin films were characterized by UV spectrometer of PG model T72 between 400 and 800 nm. Electrochemical impedance spectroscopy (EIS) is applied using in $KClO_4$ (1M) solution, 1 mA/cm^2 and 0.58 V in the range of 0.1–10 kHz (AMEL model 2550). Thin film morphologies

were examined with AFM (Nanosurf model eseyscan2).

2.3. Thin Films' Fabrication

The film was fabricated by anchoration in the reaction solution (2-formyl pyrrole (10 mmole, 0.97 g) was dissolved in the methanol (50 ml); then, hydrochloric acid 35.5% (20 ml) 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.

Effect of immersed time, acid concentration, and monomer concentration was studied. The thickness of film was determined by weight method.

3. RESULTS AND DISCUSSION

3.1. Characterization of PFPy Thin Films

Figure 1 shows the film images formed at different times, acid, and monomer on glass as substrate. The films seem darker with increas-

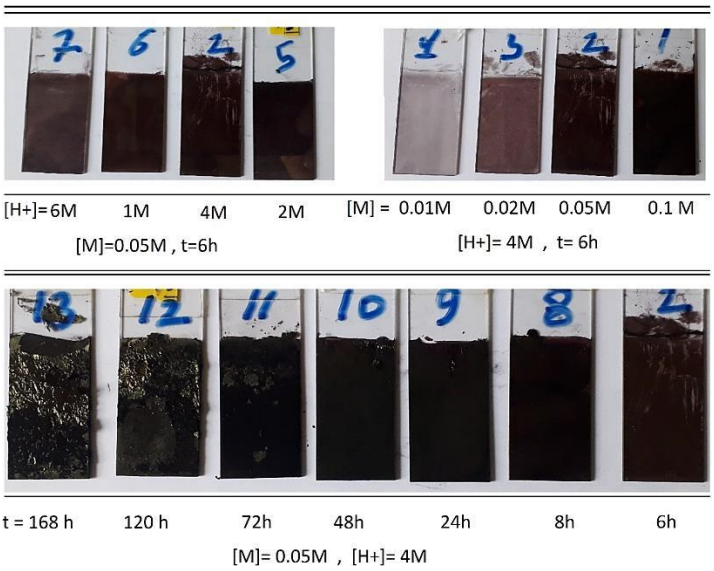

Fig. 1. Film images formed during different times and at many concentrations of acid and monomer on glass.

ing the concentration of acid and monomer concentration and time. After 120 hours, they become more thickness and were easily separated from the substrate to make flakes. This means that, with higher acid or monomer concentration, the polymer precipitated faster, and the films would be more thick and dark.

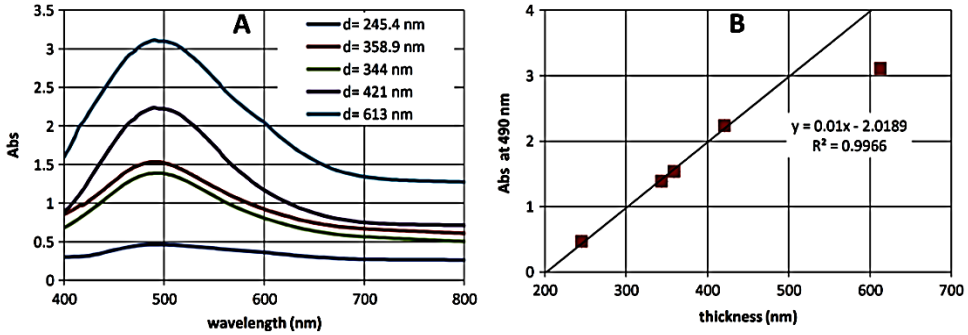

Fig. 2. *a*—absorption spectra of the films; *b*—absorption *vs* film thickness.

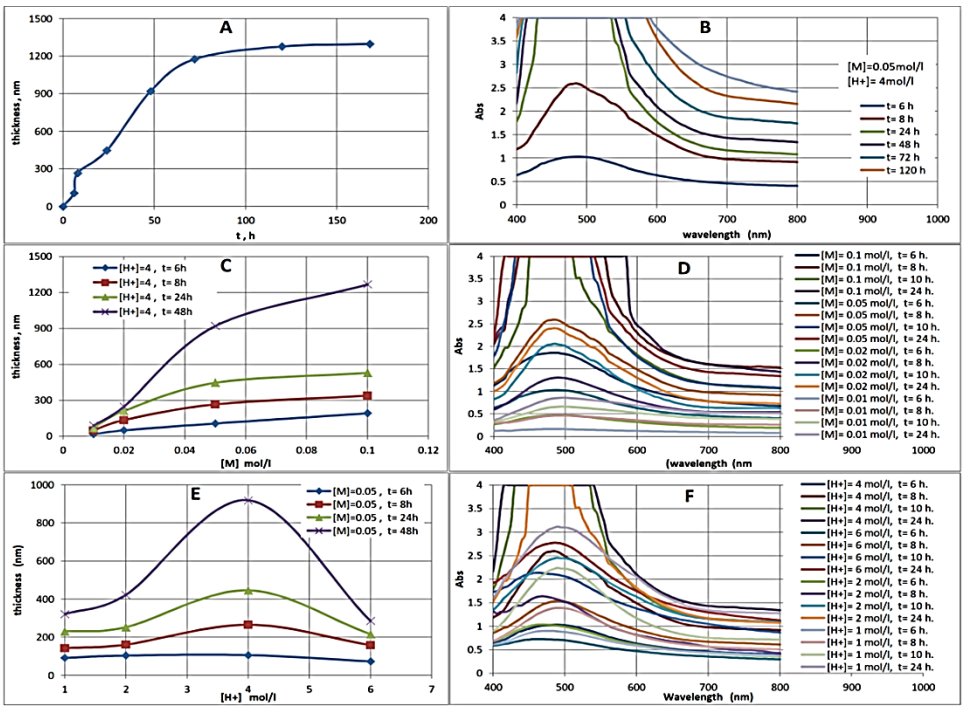

Fig. 3. UV-Vis spectrum (*b*, *d* and *f*) of the films. (*a*, *b* and *c*) thickness *vs* monomer, acid concentration and time.

3.2.1. UV-Vis Spectra

UV-Vis spectra were recorded for dry films on glass in the visible field only. Figure 2, *a* shows the absorption spectra of the films studied at different thicknesses. The films have a maximum absorption peak at 490 nm. Figure 2, *b* shows absorption at 490 nm wavelength *vs* film thickness. By the Beer–Lambert law, the absorption coefficient of the films was linear ($\varepsilon' = 0.01$ nm^{-1}).

3.2.2. Effects of Monomer, Acid Concentration and Time on the Anchoring Films

The effects of monomer, acid concentration and time on the fabrication of films were studied. Figure 3 shows UV-Vis spectrum of the films and thickness *vs* monomer, acid concentration and time. Film thickness becomes greater when acid, monomer or time increase, 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 gold, ordinary glass and quartz. No effect of substrate type was observed on the thickness of film.

3.2.3. Surface Morphology

Figure 4 shows the AFM images of the polymer films on glass as substrate. Surfaces of films seem as balls that merge together to

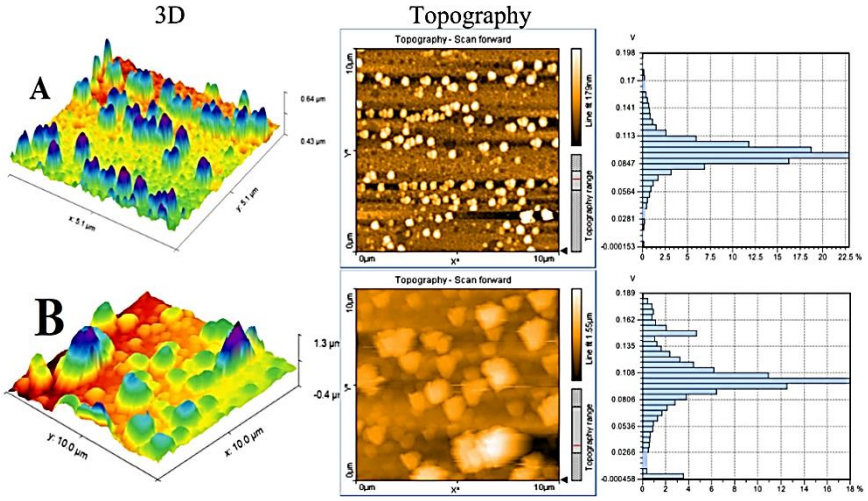

Fig. 4. AFM images (3*D*, topography and elevation distribution) of the polymer films on glass as substrate: *a*) thickness = 106 nm; *b*) thickness = 918 nm.

form rough surface and had a lot of mountains. The surface becomes less rough for more thickness and the mountains become fewer and higher. As noted in Fig. 4, *a*, its thickness is 106 nm, and the maximum height of its mountains is of 197 nm, while, in Fig. 4, *b*, the thickness is 918 nm, and the maximum height of its mountains is of 1550 nm.

From above, making films can be described as follows: 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 (as in AFM; Fig. 4). Some pointes grow faster and make moun-

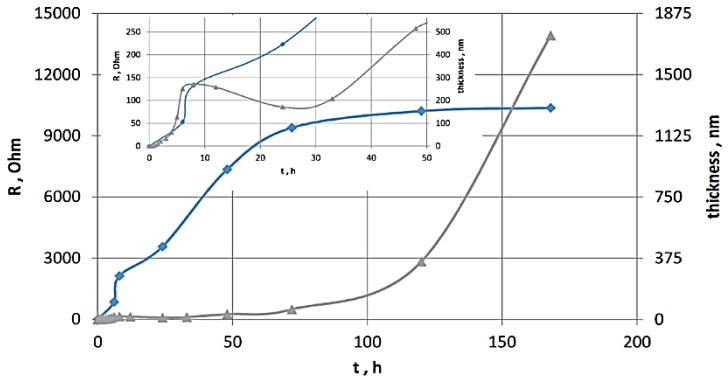

Fig. 5. Time dependence of the electrical resistance and films' thickness of thin films.

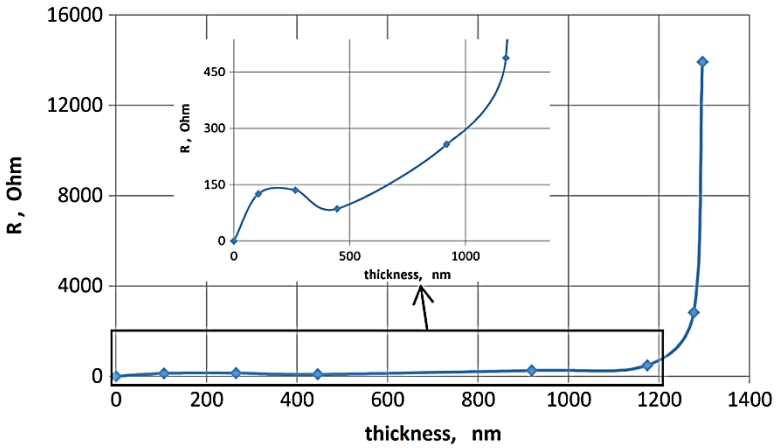

Fig. 6. Films' thickness-dependence of the electrical resistance of thin films.

tains. As well, when polymer chains form faster (by high concentration of monomer or acid), film will be rapidly formed too.

3.3. Studying the Electric Resistance of Films

In order to study the electrical conductivity of films, the electrical resistance between two electrodes of gold, which were immersed in the reaction mixture, was measured *versus* time.

Figure 5 shows the electrical resistance and films' thickness *vs* time, and Fig. 6 shows the electrical resistance *vs* film thickness. At first, the films are thin, and their resistance is low; then, it increases to maximum value. After that, film becomes less resistant because surfaces of films become roughness. When the thickness of the polymer becomes so large, the resistance is increased significantly. This is due to the multilayers in film, which cause additional resistance between the layers.

3.4. Electrochemical Impedance Spectroscopy

Figure 7 shows the electrochemical impedance spectrum (EIS) for four films precipitated on the gold. All curves have semi-circular at high frequencies and linear at low frequencies. With low thickness film, semi-circular part is less clear.

In order to analysis the EIS results, we fitted the impedance data to equivalent electrical circuits (Fig. 8), which consist of a first re-

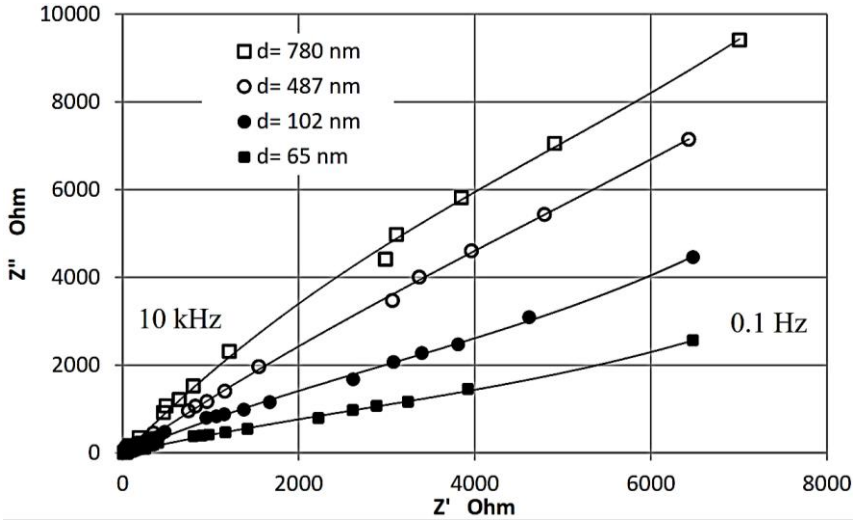

Fig. 7. Nyquist plot for films at gold.

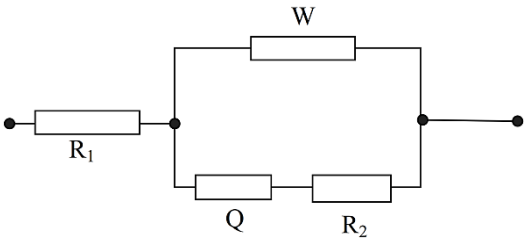

Fig. 8. Equivalent electrical circuits for the films.

TABLE 1. Volumes of electrical circuits.

Thickness, nm	R_1, Ohm	W, mOhm^{-2}	R_2, Ohm	Q, μF/cm^2
780	31±2	740±15.3	1090±56	0.149±0.03
487	30±1	387±8.4	235±42	0.156±0.03
102	29±2	42±3.5	180±27	0.148±0.02
65	32±3	27±1.6	162±18	0.143±0.02

sistance (solution resistance R_1), Warburg impedance (noted W), or capacitance is therefore ascribed to the diffusive capacitance. Warburg impedance is in parallel with the faradic component, which is composed of resistance R_2 serially associated with a capacitance Q. Resistance R_2 is the sum of the charge transfer and the ohmic resistance of film, while Q is the double-layer capacitance (see Table).

4. CONCLUSIONS

Polymer nanoparticles' thin films were fabricated by a simple and easy method by anchoring poly(2-formylpyrrole) in reaction solution. Polymer thin films can be formed on a substrate (glass and gold) by immersing the substrate in the mixture reaction. The thickness of the film increases with time and concentration of monomer and acid, and it decreases at large concentrations of acid. The films had a rough surface and peaks several times greater than the thickness. Electrical resistance of films decreases with the surface roughness and increases with thickness. The best thin films with less resistance can be made by a mixture reaction consisted of monomer concentration 0.01 M, acid 4 M, and for the time of 24 h.

5. HIGHLIGHTS

Novel polymer thin films were fabricated by a simple and easy method by anchoring polymer in reaction solution.

Control of film thickness by procedural factors in the experiment (time and concentration of the reaction materials) is provided.

The used polymer is new and previously unused, easy to prepare and has good properties.

COMPLIANCE WITH ETHICAL STANDARDS

This study was funded by Al-Furat University and Damascus University.

Authors declare that they have no conflict of interest.

ACKNOWLEDGEMENTS

We extend our thanks and gratitude to Prof. Ebrahim Al-Karibi and Prof. Hasan Kalawi for support of this work.

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