

Studying of Plasma-Polymerized Pyrrole at Variable Gas Flow Rates Via Plasma Jet

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Abstract

This manuscript presents a study of the production of plasma polymerized pyrrole (C_4H_5N) nanoparticles prepared by atmospheric pressure non equilibrium plasma jet through the parametric studies, particularly gas flow rate (0.5, 1 and 1.5 L/min). The plasma jet that was used operates with alternating voltage 8 kv and frequency 29 kHz. The plasma flow characteristics were investigated based on optical emission spectroscopy (OES). UV-Vis spectroscopy was used to distinguish the oxidization state for polypyrrole. The major absorption appears around 464.1, 449.7 and 435.3 nm at the different argon gas flow rate. The chemical composition and structural properties of the contained samples, which were synthesized at 0.5 L/min argon gas flow rate, were analyzed by Fourier transformation infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM point to a uniform distribution of polypyrrole (PPY) nanoparticles matrix. XRD technique showed a semicrystalline pattern for PPY thin film. The excellent quality plasma polymer synthesized by atmospheric pressure plasma jet method may serve as conducting materials.

Key words

Atmospheric pressure plasma jet, polypyrrole, conducting polymers, Raman spectroscopy, plasma polymerization.

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دراسة البايروول المبلمر بالبلازما بمعدلات تدفق غاز متغيرة باستخدام بلازما النفط

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الخلاصة

في هذا البحث تم إنتاج جسيمات البايروول (C_4H_5N) المبلمرة بواسطة بلازما النفط غير المتزنة التي تعمل بالضغط الجوي ودراسة تأثير تغير معدل جريان غاز الأركون (0.5، 1، 1.5 الدقيقة/لتر). بلازما النفط تعمل بجهد متناوب 8 كيلوفولت وتردد 29 كيلوهرتز. تم فحص معلمات البلازما بناءً على التحليل الطيفي للانبعاثات الضوئية المسجلة باستخدام Optical emission spectroscopy (OES). تم توصيف الخصائص البصرية لل polypyrrole باستخدام UV-Vis spectroscopy. تظهر قمم الامتصاص الرئيسية عند 464.1 و 449.7 و 435.3 نانومتر لثلاث قيم لمعدل جريان غاز الأركون. تحليل التركيب الكيميائي و الخصائص الهيكلية للعينات المحتواة التي تم تصنيعها عند 0.5 لتر/دقيقة كمعدل تدفق غاز الأركون تم عن طريق استخدام المجهر الإلكتروني الماسح (SEM)، ومطياف رامان وتشكيل الأشعة السينية (XRD). أظهرت صور المجهر الإلكتروني الماسح إن الجسيمات النانوية مرتبة بشكل منتظم على شكل مصفوفة. كما أظهر فحص حيود الأشعة السينية إن للجسيمات تركيب شبه بلوري. إن الجسيمات النانوية أغشية إل (PPY) المحضر بطريقة بلازما النفط عند الضغط الجوي والتي كانت عالية الجودة يمكن استخدامها كمادة موصلة.

Introduction

Polypyrrole (PPY) could be considered as one of the most interesting conducting polymers. It has high environmental stability, than many other conducting polymers, excellent mechanical properties and easy production [1, 2]. These properties are suitable for applications mainly in electronic devices, chemical sensors, gas sensors, biosensors, wires, antielectron static coatings, and solid electrolytic capacitor and electrochromic windows [1, 3]. The physical and spectral characteristics of polypyrrole mainly depend on the method of sample preparation. There are many ways to prepare polypyrrole such as electrochemical polymerization or an oxidatively chemical of pyrrole but it can be easily prepared by plasma polymerization of pyrrole [3-5]. The atmospheric pressure plasma polymerization has different advantages, such as it works at room temperature waterless process and little-cost habitual continuance. This method is appropriate for using many types of substrates without being damaged by heat on these slides [6-8]. The characteristics of prepared polypyrrole thin films by plasma jet system could be superior with high deposition rate thanks to most favorable discharge gas flow rate [9-11].

The aim of this research is to prepare nano-films of polypyrrole using atmospheric plasma jet technique and study optical and structural properties of these films. Physical-chemical description has considered UV- visible, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and raman scattering. The link between conditions of production and the obtained characteristics have enhanced the production of polypyrrole films convenience for given applications.

Experimental work

In this work, polypyrrolenano-thin films were deposited on glass substrates using the plasma jet technique. Argon (Ar) gas of high purity was used to generate the plasma. The liquid pyrrole monomer was vaporized by a container (bubbler) that provides the gas at different flow rates (0.5, 1 and 1.5) L/min. The distance between the slide and the plasma tip is 2.5 cm. The liquid pyrrole monomer was guided by the Ar gas vaiteflon pipe to the plasma needle. Sinusoidal power was applied to the powered electrode with a maximum value of 8 kV and of frequency 29 kHz. The plasma jet system used in this employment is shown in Fig.1.

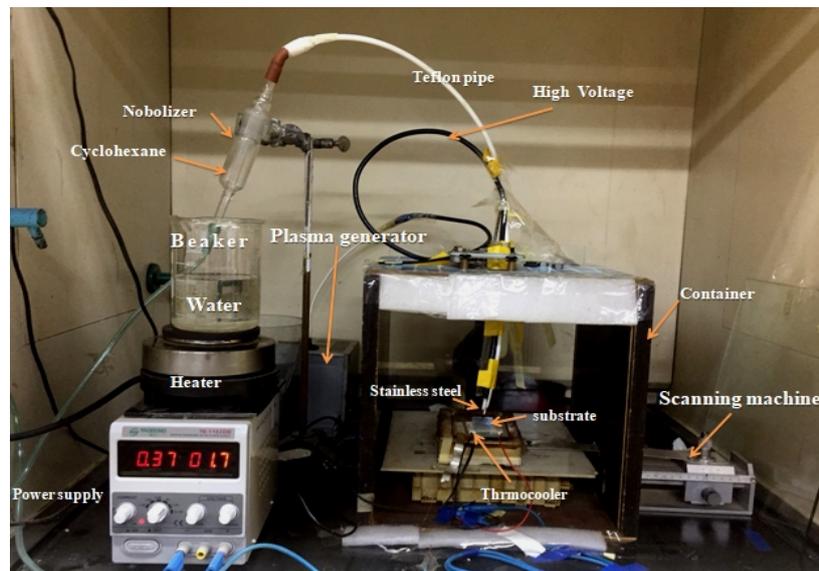


Fig.1: Image of the plasma jet system.

The XRD system (Shimadzu XRD-6000, Japan) was used to obtain the structural characteristics. Cu- α represent the source of radiation of wavelength $\lambda = 1.5418 \text{ \AA}$, voltage 40 kV, and current 30 mA. The scanning angle 2θ was diversifies from 5 to 80° with step size 0.0202° . To determine the chemical changes in the polypyrrole thin film the FT-IR was used. FT-IR- 8400S (SHIMADZU, made in Japan) was used to record the absorption of electromagnetic radiation by the sample in the range of wave number $(4000-400) \text{ cm}^{-1}$. UV-Visible spectrophotometer (MetertechInc SP-8001, with the range of wavelength 190 -1100nm) was used to detect the optical transmission spectra of the PPY films [3].

Optical Emission Spectra (OES)

Optical emission spectroscopy is a suitable test for the recognition of a number of characteristics of the plasma jet. The obtained emission spectrum of the plasma sources, at 1 cm away from the discharge pipe, in the wavelength range 300–500 nm is shown in Fig.2 in order to prove the excited N₂ species present in plasma plume. From the figure, it can be observed that the spectra of plasma jet which were recorded for different gas flow rates (0.5, 1 and 1.5) L/min, have the same peaks position. They belong to the same excited species with different intensities. That is expected because the atmospheric plasma jet working by Ar gas, and injected to the atmosphere which contain the same components. Electron temperature was measured using the value R_1/R_2 obtained from the optical spectrum. Fig.3 shows the plot between R_1/R_2 and T_e with different values of T_e . By apply the following equation [12]:

$$\frac{R_1}{R_2} = \frac{I_1/I_2}{I_3/I_4} \quad (1)$$

where I_1 , I_2 , I_3 and I_4 are line intensity (belong to N₂) for the wavelengths 381 nm, 427 nm, 392 nm and 409 nm, respectively. The values of $\frac{R_1}{R_2}$ were obtained are 9.13, 9.2 and 9.18 at flow rates of gas 5, 10 and 15 L/min, respectively. The average electron temperature is 1.978 eV [13].

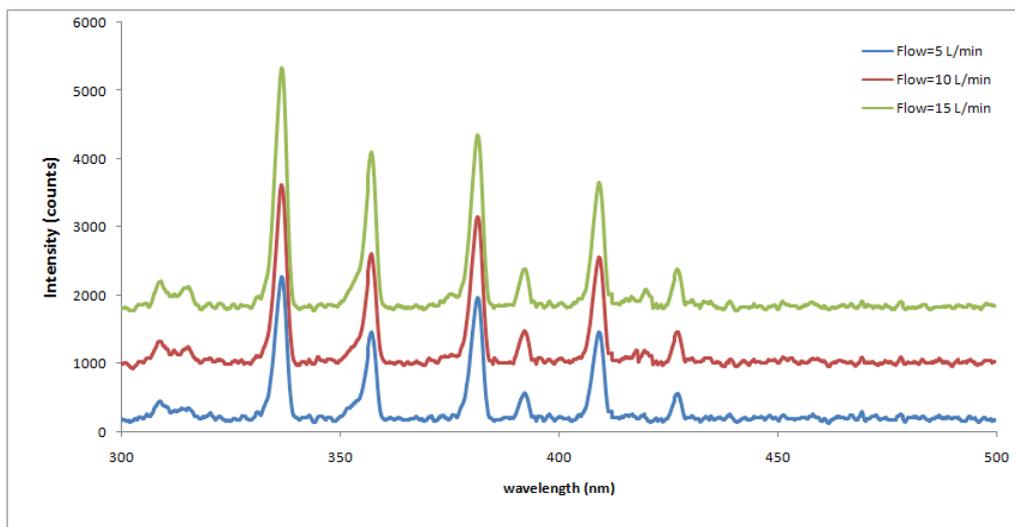


Fig. 2: Optical emission spectra (OES) in the range (300 - 500) nm as a region of wavelength for the proposed by Ar plasma jet.

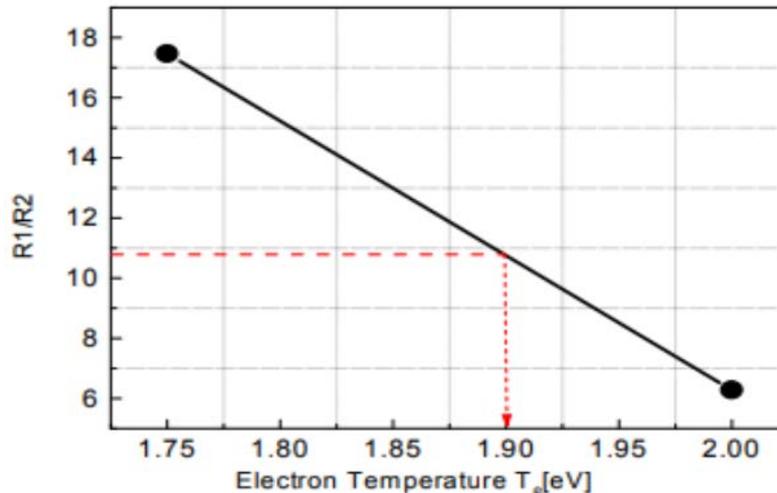


Fig.3: The plot between R_1/R_2 and T_e with different values of T_e .

Optical properties of PPY

The absorption spectra of PPY thin films was recorded over a wavelength range (300 -1100) nm at 25 C°. UV-Visible spectra of PPY thin films are shown in Fig.4. PPY thin films display absorption peaks at 464.1, 449.7 and 435.3 nm at different flow rates of argon gas (0.5, 1 and 1.5) L/min, respectively. The position of the peaks are in agreement with that reported in literature [8, 9]. At oxidation, the maximum peak shifts to shorter wavelength with a decrease in intensity. From the absorption spectra of polypyrrole thin films, it can be observed that, when the Ar gas flow rate is increased, the peaks shift toward higher energies. This indicates an increase in the thin film oxidation of polypyrrole film, so the thin film which prepared with 0.5 L/min flow rate was selected for the other tests because it is less oxidized [14].

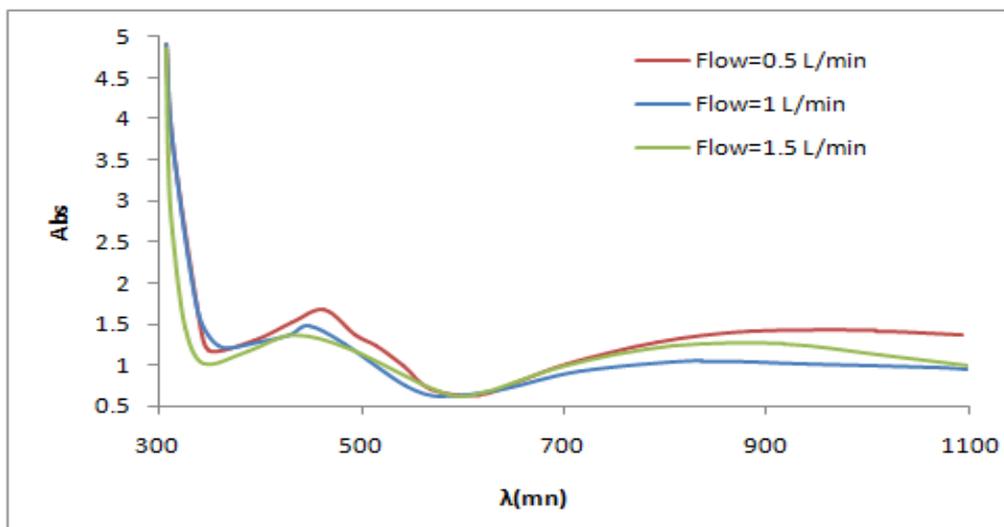


Fig.4: Absorption spectra of polypyrrole films at (0.5, 1 and 1.5) L/min argon gas flow rates.

The scanning electron microscope analysis

SEM test was used to recognize the polypyrrole morphology. The morphological features of the prepared polypyrrole have cleared that, in general, the polymeric evolution is like that of the crystallite form. Fig.5 shows a top view of the scanning electron microscope (SEM) image of polypyrrole thin film deposited on glass

substrates with argon gas flow rate of 0.5 L/min at room temperature. From this image, it can be observe that, continuous polymer layers was formed on the substrate. Regular spherical nanoparticles have been formed by plasma polymerization [6].

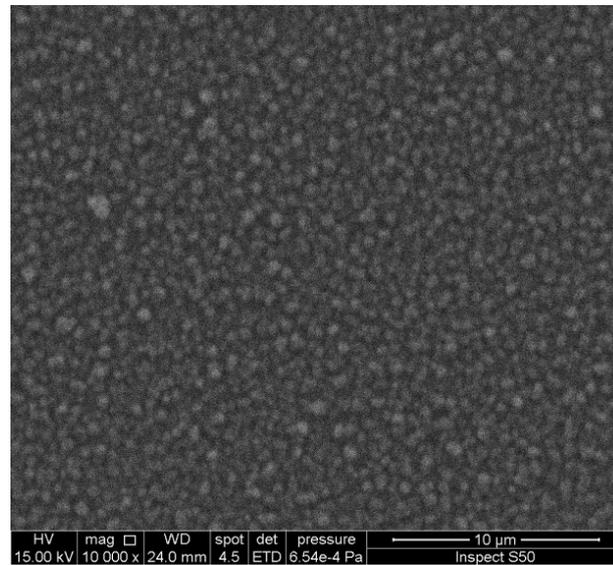


Fig. 5: SEM image of polypyrrole thin film.

X- ray diffraction patterns of PPY

The crystal structure of polypyrrole (PPY) was examined with X-Ray diffractometer. Fig.6 illustrates the XRD pattern of the of polypyrrole film which was synthesized on glass substrate with a flow rate of argon gas of 0.5L/min. In XRD pattern as a 2θ plot scanning from 5° – 80° , two broad peaks were observed at 11.8° and 23.9° denoting that the part of structural ordering of nano-dimensions, ideal of nano-structured polymers with low degree of crystallinity. There are a lot of turmoil embedded in the PPY array so the X-ray peaks are broad Gaussians. Also the higher order peaks are roughly frustrate [14].

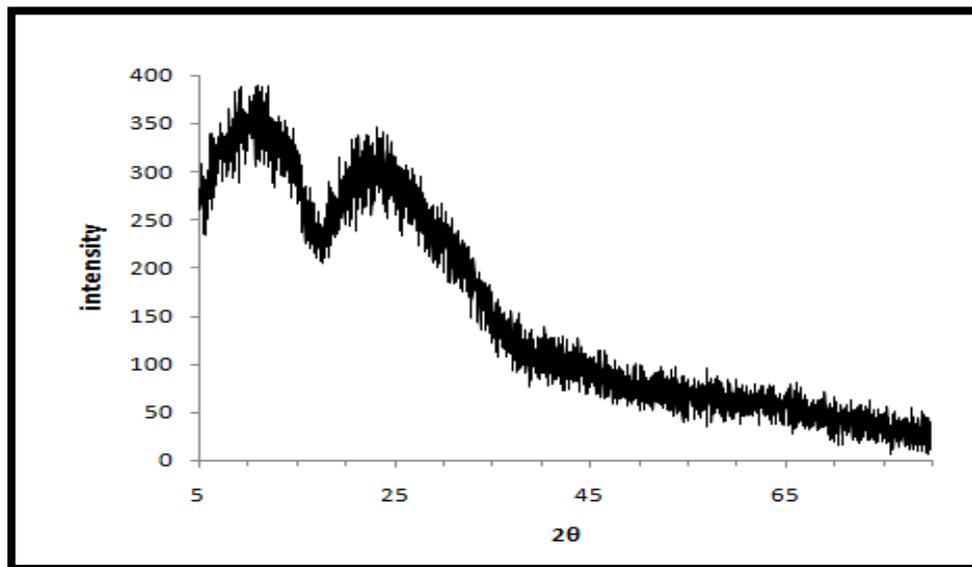


Fig.6: XRD pattern for polypyrrole film at 0.5 L/min argon gas flow rate.

FTIR analysis

The Fourier transform infrared spectroscopy (FTIR) spectrum of polypyrrole is shown in Fig.7. Thin film was prepared on quartz substrate with argon gas flow rate of 0.5L/min and the distance from the slide to plasma tip was 2.5 cm. FTIR spectrum was performed by the transmittance technique. As shown in FTIR spectrum, the peak at 3250 cm^{-1} represents the N–H stretching, the peak at 2959 cm^{-1} refers to stretching absorption of C–H and the peak at 2214 cm^{-1} refers to (–C=H) aliphatic vibration. Another peak at 1689 cm^{-1} represents the C=C double bond peak that has double bond obtaining π electrons. Also one can see peaks at 804 cm^{-1} and 731 cm^{-1} . The presence of these related peaks confirms the prosperous formation of polypyrrole film with perfect electrical conductivity which will be enhanced by doping hauler electrons [3].

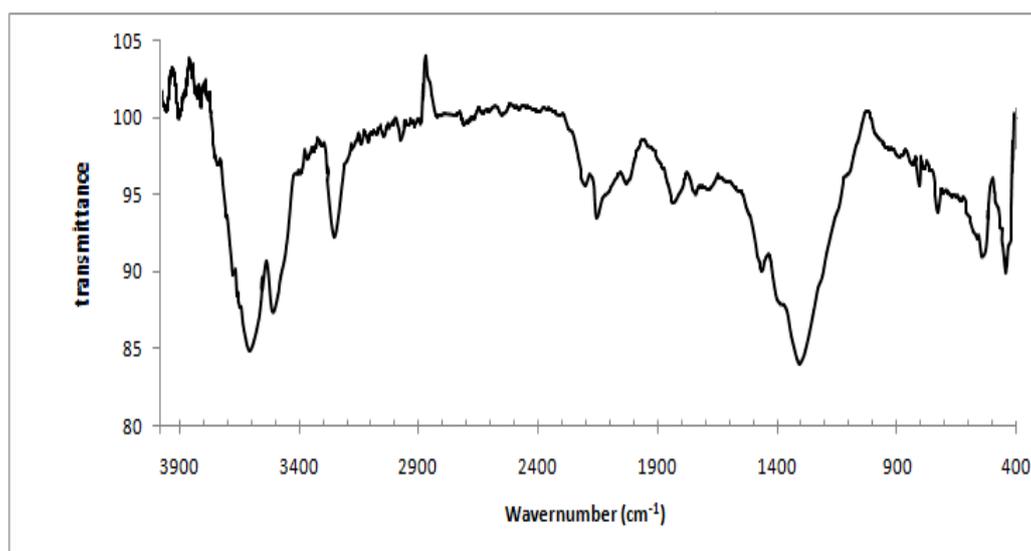


Fig.7: Fourier transform infrared spectroscopy (FTIR) spectrum of polypyrrole thin film.

Raman analysis

The Raman spectroscopy technique was used to study the molecular structure of the nanoparticles of polypyrrole. The scattering phenomena is the principle of Raman spectroscopy so that the analysis of insoluble samples could be done. The Raman analysis was done on the polypyrrole thin film after preparation. This permits to obtain the distinctive spectrum of polypyrrole. Raman spectra were obtained using a Stellar Net Raman-HR-TEC-1064 spectrometers by the two different wavelengths of laser (785/1064 nm) employing a Nd:YAG laser of 499mWatt. Raman spectrum of polypyrrole as shown in Fig.8 depicts the most important peak at 1550 cm^{-1} which represents C = C symmetry stretching. The double peak at 1400 and 1342 cm^{-1} is related with the ring-stretching vibrations of polypyrrole. There are two peaks at 1330 and 1400 cm^{-1} assigned to be the inter-ring (C–C) stretching. The vibration at these peaks is recognized to a ring deformation mode (δ) ring. There are two peaks at 920 and 930 cm^{-1} related to the ring disfigurement related with dication (dipolaron) and radical cation (polaron), respectively. The band with double peaks at 1010 and 1065 cm^{-1} is ascribed to the C-H in plane disfigurement. In addition, from Raman spectrum of polypyrrole it can be seen, there is peak at about 1720 cm^{-1} demonstrating that the polymer is faintly over oxidized [4].

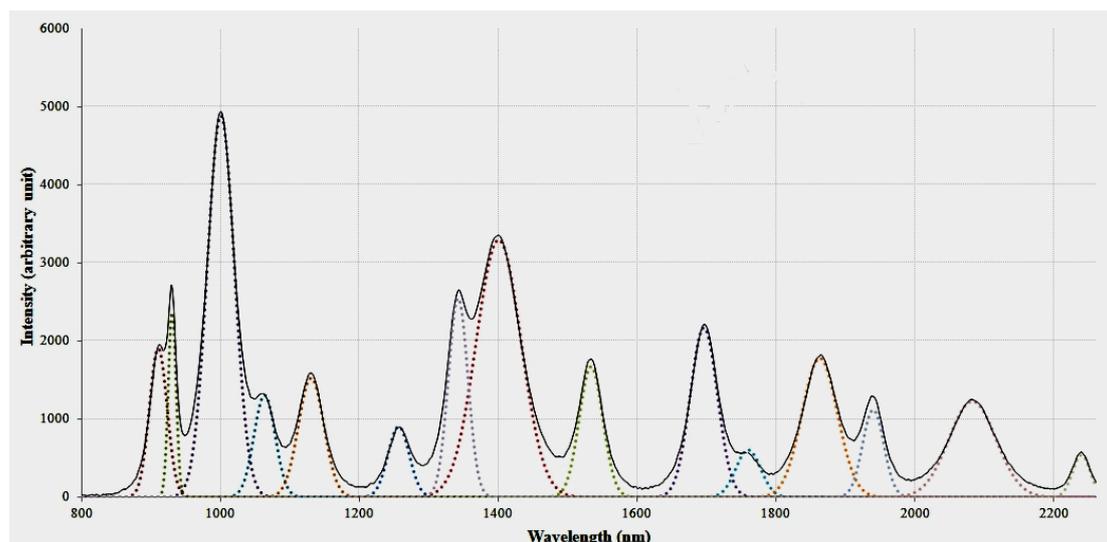


Fig.8: Raman spectra of polypyrrole film.

Conclusions

polypyrrole (PPY) thin films were synthesized successfully using an advanced atmospheric pressure plasma polymerization method. The properties of the prepared polypyrrole films were enhanced because of regulating the gas flow rate to 0.5 L/min and using input power of 8kv during plasma polymerization. UV- spectra of polypyrrole thin films showed that, the peak shifts toward the lower wavelength this indicates an increase in the thin film oxidation of polypyrrole film. XRD technique showed a semicrystalline pattern for polypyrrole (PPY) thin film. Concerning the morphology of polypyrrole thin film, a spherical-shaped topographic structure were obtained. Using FTIR spectra, it was easy to recognize distinctive absorption bands concerning functional groups and chemical bonds that exists in polypyrrole (PPY) structure, which give it its structural and organic chemical properties. The Raman spectrum of polypyrrole showed eight main bands at 1550, 1400, 1342, 1330, 1065, 1010, 920 and 930 cm^{-1} . These bands are assigned to modes of perfect polypyrrole.

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