

Pyrrole-added Fe₂O₃ films by ultrasonic spray pyrolysis

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Fe₂O₃ thin films were grown by Ultrasonic Spray Pyrolysis from a 0.05 aqueous solution of FeCl₃ added with a small amount of pyrrole monomer. Films at different substrate temperature and pyrrole content were grown. They were characterized by using x-ray diffraction (XRD), infrared spectroscopy (FTIR) and atomic force microscopy (AFM). Results indicated that at low substrate temperature (approximately $\leq 200^{\circ}\text{C}$) the films mainly resemble the polypyrrole structure. At higher temperatures up to 400°C the trend is to form the hematite phase (Fe₂O₃) of iron oxide. Furthermore, the surface morphology exhibits nano-size features, which can be changed by using different pyrrole contents. This last feature could be useful for usage of the film as a gas sensor.

Keywords: Composite films; Polypyrrole and iron oxide; Ultrasonic spray pyrolysis

1. Introduction

New materials are still trying to be obtained with several cheap deposition methods. Recently, conducting polymer composites have generated tremendous attraction, and they have become one of the most active and promising research areas. The properties of the composites are quite different from the constituent components due to interactions at the molecular level. These materials are largely being used in nonlinear optics, electrochemical display devices, molecular electronics, sensors, electrical and magnetic shields and microwave absorbing materials. Unfortunately, so far the use of conducting polymers has often been impeded by their intractability. Consequently, much effort has been directed toward improving the tractability of organic conducting polymers using new methods. In these new methods, control of both microscopic and macroscopic structural homogeneity of the polymers is essential for the development of such materials with enhanced electronic, optical, and magnetic properties.

Two methods currently exist for improving the tractability of organic conducting polymer. One method involves mixing the conducting polymers of interest with a second inert material to form a conductive composite. In this way, the matrix material not only strengthens the composite but also serves to protect the polymer from ambient moisture as well as air. This type of approach toward improved tractability has been moderately successful, particularly in the preparation of sterically stabilized polypyrrole (PPy) colloids via dispersion polymerization. Since 1986, various research groups have reported the preparation of sterically stabilized colloidal dispersions of PPy incorporating either commercial polymers or metal oxide particles. Thin conducting films can then be fabricated from them. Although this approach significantly improves preparation of such materials, it still has shortcomings in obtaining the desired microscopic and macroscopic structural homogeneity.

The second method to improve the tractability of organic conductive polymers involves using a wide variety of host materials as templates including glasses, ceramics, and polymers for polypyrrole synthesis. The second method also provides an opportunity to control both the morphology and structure of the composite [1].

Even though, polypyrrole is one of the most used conducting polymers for application due to the good stability of its properties and because it can be easily synthesized as a homopolymer and also as a composite. The success of PPy applications depends on the improvement of the properties and the processability of this material. Therefore one of the main research goals is the correlation between the synthesis parameters and the molecular architecture of PPy in order to obtain the required properties for a specific application [2, 3].

In this paper we report the structural, optical and morphological properties of polypyrrol-iron oxide (PPy-Fe_xO_y) films, studied by using XRD, FTIR spectroscopy and AFM images.

2. Experimental section

a) Aqueous Solution Preparation

We made films from a 0.05M aqueous solution of FeCl₃, which is considered by many authors as an oxidative agent for polymerization process of pyrrole monomer [4]. The FeCl₃ reagent was weighed in an electronic balance, deionized water as a solvent was added in a beaker and the aqueous solution was stirred during about 10 min. 100 ml of solution were always prepared as a reference volume to aggregate the monomer. Then the pyrrole monomer was poured into the same glass. Finally, the whole solution is stirred continuously during 1 h. Meanwhile, the color changed from clear yellow to black, due to the polymerization process.

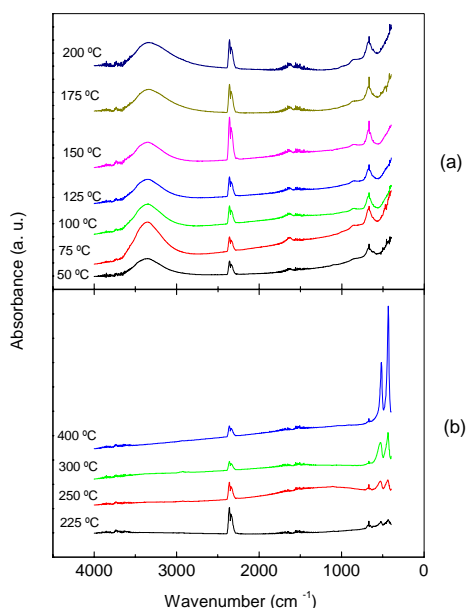


Figure 1. FTIR absorbance of samples deposited at different substrate temperatures (a) low temperature region ($\leq 200^\circ\text{C}$) and (b) high temperature region ($> 200^\circ\text{C}$).

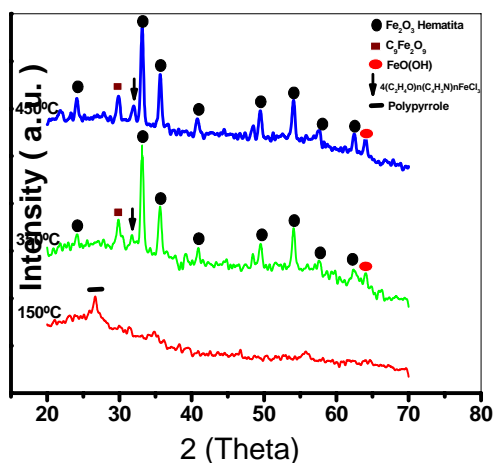


Figure 2. Shows the X-Ray Diffraction Spectrum of Samples Deposited at Different Substrate Temperatures.

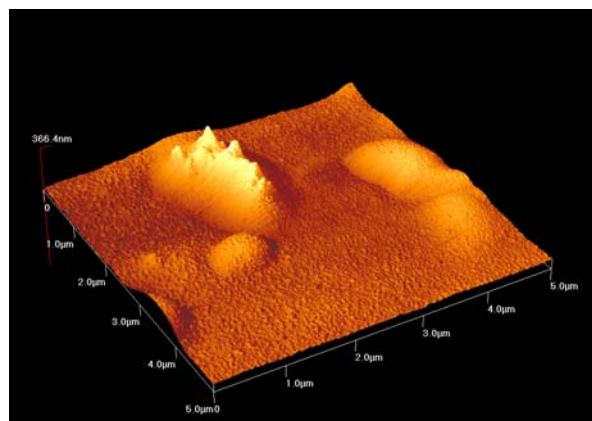


Figure 3. Film surface of a film on silicon substrate at 100°C , grown from a 2 pyrrole drops solution.

b) Substrate Preparation

Glass substrates were used to deposit the films. They were cut in pieces of 2 cm x 2 cm size. The cleaning was made leaving the glass substrates in an Extran-detergent solution to remove any content of grease. Then, they were rinsed in deionized (DI) water with ultrasonic cleaning until detergent was eliminated. Afterwards, rinses in acetone and DI water were performed.

Silicon substrates were also used due to their transparency to the IR radiation. Substrates of 1.5 cm x 1.5 cm size were cut. The cleaning process starts with Xylene for 5 min. Then ultrasonic rinses during 5 minutes in acetone and DI water follow. Finally, both glass and silicon substrates were kept in alcohol and prior to use they were dried with nitrogen gas.

c) Sample preparation

In order to deposit the thin films, a variety of techniques can be employed. In our case, the precursor solution is pulverized by means of an ultrasonic device and carried out by an inert gas (nitrogen). The substrate is supported on a stainless steel heater at a desired temperature. A series of samples varying the deposition temperature from 100°C to 400°C and also the amount of pyrrole monomer (Py) from 1, 2 and 4 drops in 100 ml of iron chloride solution were prepared. The deposition time was 5 min. and a gas flow of 5.9 l/min for all the samples was kept constant.

3. Results and discussion

a) FTIR Spectroscopy Analysis

A comparison of the IR absorbance spectra of Polypyrrole-Iron oxide films deposited on silicon substrates at different temperatures are shown in Fig 1. These samples contain 2 drops of PPy in the solution. The observed bands indicate the existence of two temperature regions; samples with $T_s \leq 200^\circ\text{C}$ behave similarly (Fig. 1a) and those with $T_s > 200^\circ\text{C}$ show different bands (Fig. 1b). In all spectra the peak at 2358 cm^{-1} corresponding to atmospheric C-O absorption appears. In the low temperature region we see several absorption bands. The wide band at 3344.70 cm^{-1} and the small peak about 1640 cm^{-1} are associated to N-H and C-N stretching vibrations of polypyrrole respectively[5,6]. The small peaks near 671.9 cm^{-1} and 773 cm^{-1} are associated to C-H absorption [7].

Above 200°C the trend is to form the iron oxide phase according to the strong sharp peaks observed at fig.1 (b) which are placed at 433.52 cm^{-1} and 517.27 cm^{-1} , both belonging to iron-oxygen bonds [8]. Furthermore, in a closed look, the absorption band found in the low temperature region ($< 200^\circ\text{C}$) localized at 671.9 cm^{-1} still clearly appears in the spectra of samples at higher temperature. Besides, the peak at 1640 cm^{-1} seems to be widened and dominated by those of the Fe-O bond. Also,

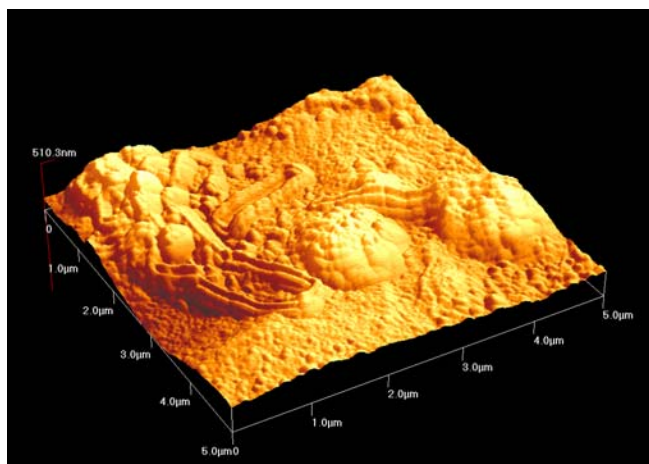


Figure 4. Composite film on a silicon substrate growth at 200 °C. The pyrrole content is 1 drop.

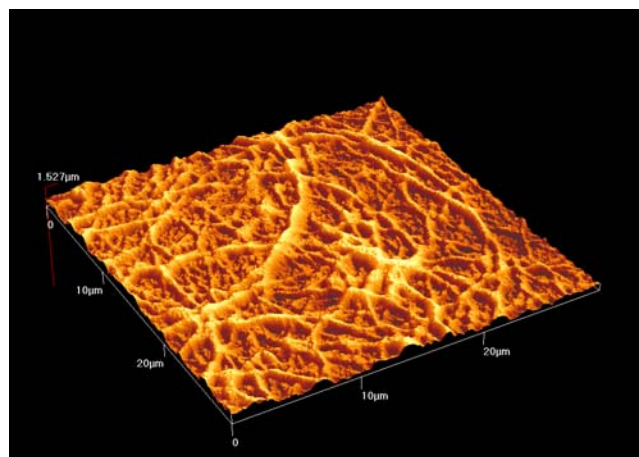


Fig.5. 1 pyrrole drop film deposited at 400°C upon silicon substrate.

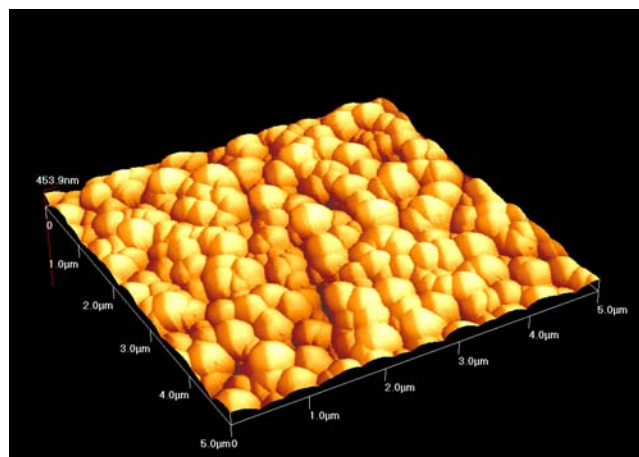


Fig.6. Film with 1 pyrrole drop grown at 400 °C upon a glass substrate.

the peak of N-H absorption practically disappears. These results suggest that polypyrrole-like material keeps its chemical structure at temperatures less or equal to 200 °C, but once the temperature surpasses this limit, only some bondings of the polypyrrole are kept and the iron-oxide structure dominates within the film.

The above behavior was observed for pyrrole contents of 1, 2 and 4 drops in the solution.

b) XRD

In figure 2, diffraction spectra corresponding to films grown at different substrate temperatures and containing 4 drops of pyrrole monomer in the solution are shown. The evolution of the film material as the substrate temperature increases from 150 °C to 350 °C and then to 450 °C is illustrated.

At the bottom of this figure the diffraction spectrum for a film deposited at a substrate temperature of 150°C is seen. In this spectrum the wide diffraction peak localized at $2\theta = 25.6$ degrees illustrates the presence of polypyrrole bearing an incipient ordering [9] but dominating on the other small peaks. At higher substrate temperatures (350 °C and 450 °C) more peaks appear larger, making evident a polycrystalline structure. As indicated, most of these diffraction peaks correspond to the hematite phase (α -Fe₂O₃) of iron oxide (87-1165,2000-JCPDS). A few are due to the existence of some organic species like C₉Fe₂O₉ (21-1141,2000-JCPDS) and 4(C₂H₄O)_n(C₄H₃N)_nFeCl₃ (49-2055,2000-JCPDS) and also to FeO(OH) iron hidroxide species (81-0464,2000-JCPDS). The organic components are remaining materials after degradation of the chemical structure of polypyrrole under the effect of oxidation.

c) AFM images

One of the interesting characteristics of the films fabricated is the variety of surface morphologies obtained under different growth conditions and substrates.

According to the former measurements, at low substrate temperatures an amorphous-like structure is expected. This is confirmed by the featureless surface morphology shown in Fig. 3, corresponding to a sample grown at 100 °C upon silicon, which contains 2 drops of pyrrole.

In Figure 4, the surface morphology of a film with 1 drop Py growth at 200 °C on silicon is shown. This time, features that can be related to traces of polypyrrole structures defined on an amorphous-like matrix exhibit some ordering of the organic component. In this case the sample is not homogeneous. As mentioned above, this is the limiting temperature prior to starting the degradation of polypyrrole.

At 400 °C different morphologies are observed in figures 5, 6 and 7. For instance, a film with 1 Pyrrole drop grown on silicon exhibits a regular ordering (Fig. 5) with particles of about 200-300 nm lateral size and height variations within 460 nm.

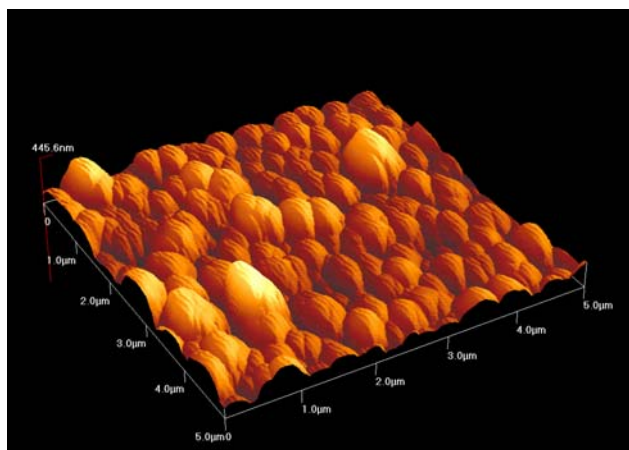


Figure 7. Film on glass substrate at 400 °C, grown from a 4 Pyrrole drops solution.

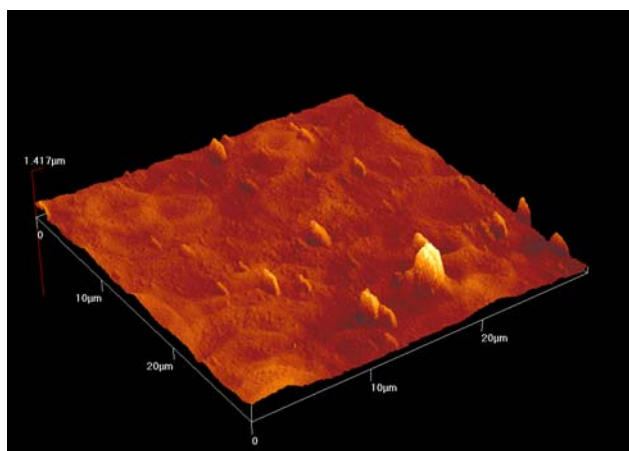


Figure 8. Image of a 1 drop Py sample deposited on glass substrate at 400 °C showing large peaks indicating some trend towards preferential vertical growth.

On the other hand, a filamentary surface structure coming from 1 drop Pyrrole solution with height variations within 1.6 microns is obtained on glass substrates (Fig. 6). The solution in this case was heated at near 70 °C besides being stirred during preparation.

A film grown from a solution with 4 Pyrrole drops upon silicon substrate is shown in Fig. 7. The formation of well ordered particles between 200 and 400 nm is clearly seen. The height variation is around 450 nm. An additional feature can be noticed. It consists of some line patterning upon the whole surface of such particles. This seems to be a feature of an organic-like layer extended possibly around the total surface of each particle within the film.

Another feature noticed mainly in larger area images of our samples (30 x 30 μm²) is shown in Fig. 8. It consists of large vertical peaks. These reflect some trend to vertical growth of the films. The tendency of this vertical behavior is in accordance with the general observation that the solution does not act uniformly over the substrate so iron oxide grows in the form of separate features (small columns, spikes, needles). It was formerly suggested that this kind of growth of iron oxide is associated to the

existence of HCl vapour in the growth ambient arising as a product when the precursor agents react in the system. This type of vapour does not permit the lateral growth due to Cl⁻ containing species [10].

The variety of surface morphologies that can be produced by spray pyrolysis can be an important factor for usage of these films for gas sensor and some other applications.

4. Conclusions

Polypyrrole (PPy)-iron oxide composite films could be prepared by a simple method: ultrasonic spray pyrolysis. FeCl₃ was used both as a source for the iron oxide and oxidant agent for the pyrrole monomer in an aqueous solution. From FTIR and XRD studies it is found that at low substrate temperatures (<200 °C) the polypyrrole structure dominates within the film. At higher temperatures up to 400 °C, the polypyrrole structure is degraded, leaving instead iron complexes such as C₉Fe₂O₉ and 4(C₂H₄O)_n(C₄H₃N)_nFeCl₃. Then the hematite phase (Fe₂O₃) of iron oxide becomes the dominating structure within the film. AFM imaging shows different surface morphologies after using different amounts of pyrrole monomer substrate type and temperatures. At low temperature the amorphous-like nature of the film is confirmed, while at middle temperature (200 °C) some inhomogeneity of the film is seen. At 400 °C different morphologies were obtained. A filamentary surface structure can be obtained, defined by the organic content. Also a surface bearing well ordered nano-sized (200-400 nm) particles was observed. In this last case, an apparently organic cover layer results when the pyrrole amount is increased. When the hematite structure dominates, some trend towards preferential vertical growth is observed. This is due to the acid medium during film growth. These properties can be used in the application of the films as gas sensors.

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