In Situ Polyaniline Film Formation Using Ferric Chloride as an Oxidant

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ABSTRACT: *In situ* polyaniline (PANI) films were grown from an aqueous hydrochloric acid solution on glass substrates via the chemical oxidation of aniline using hydrated ferric chloride, $FeCl_3.6H_2O$ (FC). The effect of initial molar ratios of FC/aniline on the yield of PANI films was monitored using the quartz crystal microbalance technique. The morphology of the resultant polymer film and powder was examined using scanning electron microscopy. It was found that the film possesses a porous character; however, the polymer powder consists of small particles with interconnected nanofibers. The polymer powder formed in the bulk was characterized using the energy dispersive analysis of X-ray, the X-ray diffraction, and the thermal gravimetric analysis. A comparison between the PANI produced from FC and ammonium peroxydisulfate was considered and discussed. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2695–2700, 2012

Key words: conducting polymers; polyaniline; ferric chloride; thin films; morphology

INTRODUCTION

Polyaniline (PANI) has attracted considerable attention in the last decades due to its excellent environmental stability, good redox reversibility, and good electrical conductivity. These properties provide many applications in different fields including battery electrodes,[1,2] electrochromic devices,[3,4] photoelectric cells,[5,6] and light-emitting diodes.[7]

A great deal of attention has been paid to the deposition of a thin layer of conducting PANI on various surfaces.[7–10] MacDiarmid and Epstein[8] have reported that PANI may be deposited by *in situ* adsorption polymerization as a strong adhering film on a variety of substrates such as fibers, textiles, glass, gold, etc. The optimum reaction conditions for the synthesis of PANI are very important due to the high potential applications of the polymer.

The quartz crystal microbalance (QCM) has a wide range of applications in biochemistry, analytical science, and other fields.[11–14] Furthermore, QCM can be used concomitant with other techniques for instance, electrochemistry (EQCM), Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, ellipsometry, and atomic force microscope,

among others. In case of PANI studies, EQCM has been used to study redox reaction mechanism,[15] film formation,[14,16] ion transport within the PANI films,[16,17] and PANI film degradation.[18] The QCM technique concomitant with the chemical method has been used by Ayad et al.[19–24] to study the PANI and nanotubular PANI film formation. In those studies, ammonium peroxydisulfate (APS) has been used as an oxidizing agent. In addition, the relation between the molar ratio of APS/aniline and the yield of the PANI film deposition has been studied. It has been found that the yield has an optimum molar ratio of APS/aniline at $\sim 1.15 \pm 0.1$. This optimum value has been approximately obtained previously[25] by Armes and Miller during the polymerization of aniline in the bulk.

$FeCl_3$ can be either hydrated or anhydrous. Hydrated $FeCl_3$ dissolves in water without any thermal effect, differing from anhydrous $FeCl_3$. Cao et al.[26] have studied the chemical synthesis of PANI powder with ferric chloride (FC) as an oxidant, and they have showed that the molecular weight was lower than that of the APS-synthesized one. However, the electrical conductivity of the polymers synthesized with both oxidants was similar. Additionally, Yasuda and Shimidzu[27] have studied the chemical polymerization of aniline using FC in water at 35°C, and the elemental analysis of the produced PANI powder has been determined to be $C_{24}H_{19.1}N_4$ that is very close to the determined formula for the PANI synthesized using APS, $C_{24}H_{19.7}N_4$.

Furthermore, they have found that the redox potential of the oxidizing agent is not a dominant parameter. Moreover, the polymer synthesized using FC as an oxidant has been found to be soluble in polar organic solvents. FC has an advantage over APS that the former has an oxidation potential of 0.771 V, which is lower than that of the later 2.01 V. The low oxidation potential of FC reduces the side reactions during the polymerization.

Zhang et al.[28] have synthesized PANI fibers using FC as an oxidant in the presence of p-toluenesulfonic acid, β-naphthalenesulfonic acid, and camphorsulfonic acid as the dopants. They have mentioned that the structure of the oxidant, especially the oxidation/reduction potential affects the morphology and the size of the resulting polymer and the effect of the oxidant on the main chain structure of PANI nanofibers can be neglected. Zhu et al.[29] have synthesized PANI nanofibers using FC and salicylic acid as an oxidant and a dopant, respectively. Ma et al.[30] have synthesized PANI doped with dodecylbenzenesulfonic acid (DBSA) by emulsion polymerization using FC/APS as a composite oxidant. In addition, the effects of different parameters (such as the magnetic field intensities, the molar ratios of FC/APS, and the concentrations of DBSA) on the film growth rate of PANI have been analyzed by using the QCM technique. The polymerization conditions were optimized by cyclic voltammetry.

Using the interfacial polymerization route, Huang and Kaner[31,32] have synthesized PANI nanofibers. This method requires different solvents with organic pollutants. In addition, Chiou and Epstien[33] have synthesized PANI nanofibers using APS in dilute chemical polymerization, but the yield of the produced nanofibers was small. That is important with respect to the mass production needed for PANI applications. Additionally, using this dilute solution, it is difficult to form in situ PANI films. To obtain nanofibrous films in both of the aforementioned methods, the dispersion of the produced nanofibers in organic solvents is required. Therefore, this study provides an easy and a noncontaminant route to obtain in situ porous polymer films. Such property imparts the film large surface area, rendering important class of new materials that can be used as promising candidates for sensors, energy storages, and electron field emissions.[34] The QCM technique was mainly used in this work to study the PANI film deposition and also to determine the optimum conditions for the formation of PANI films. Additionally, the effect of the molar concentrations of the reactants on the yield of the in situ PANI deposition onto the QCM electrode was studied. Besides, the properties of the polymer formed in the bulk were investigated. The morphology of the resultant polymer films and powder was examined using scanning electron microscope (SEM). Furthermore, the energy dispersive analysis of X-ray (EDX) for the PANI-FC film was measured. The X-ray diffraction (XRD) and the thermogravimetric (TGA) analysis were measured for the polymer powder formed in the bulk. Moreover, a comparison between the PANI produced from APS and FC was made and discussed.

EXPERIMENTAL

Chemicals

Aniline (ADWIC, Egypt) was purified by vacuum distillation and stored at 4°C. FC (BDH) and APS (WINLAB, UK) were used without further purification. Hydrochloric acid (ADWIC, Egypt) was used as received.

Preparation of solutions

Some experiments were made in which the aniline concentration was kept constant at 0.15M (0.1M hydrochloric acid solution), and the concentration of FC was varied (in 0.1M hydrochloric acid solution). The overall volume of reactants solution was 500 mL. The temperature of the solution was kept constant at 19 ± 1°C. The molar ratio (r) between FC and aniline was varied from 0.25 : 1 to 5 : 1.

QCM measurement for the in situ deposited PANI films

The solutions of FC and aniline in the acid medium were added to the reaction vessel. A total of 5 MHz-cut quartz crystal attached with a GW Frequency Counter, Model GFC-8055G was used. Details of the apparatus design and the procedure were described in earlier studies.[35,36] The mass per unit area of the PANI film (m' (g cm^{-2})), grown onto the gold electrode on the crystal surface, was determined from the change in its resonance frequency. The frequency decreases linearly with increasing the mass deposited on the electrode. The relation between the frequency change Δf (Hz) and m', was well established from the work of Sauerbrey[37] and is given by:

$$\Delta f = -(2f_o^2 / \sqrt{\rho_Q \mu_Q})\, m' \qquad (1)$$

where f_o (Hz) is the natural frequency of the quartz crystal, ρ_Q is the quartz density (2.649 g cm^{-3}), and μ_Q is the shear modulus (2.947 × 10^{11} N cm^{-2}). If the density of the PANI film ρ (g cm^{-3}) is known, the thickness of the polymer film ε (cm) can be determined from the relation:

$$m' = \rho\, \varepsilon \qquad (2)$$

The density of the PANI hydrochloride is taken to be 1.33 g cm^{-3}, as determined in other studies.[38]

PANI films can be obtained during the polymerization of aniline on rectangular glass supports. These supports were stuck onto an adhesive tape and introduced into the reaction vessel before the polymerization starts. Once the reactants are introduced to the vessel, the film grows simultaneously onto both the gold electrode of the QCM and the glass support. After 2 h of the polymerization process, the glass supports were removed from the reaction mixture, rinsed with 0.1M HCl and finally dried.

The PANI powder formed in the bulk solutions during the QCM experiments were collected, washed with 0.1M HCl, and finally dried for 24 h at 40–50°C.

Instruments

The SEM and the EDX measurements were performed using Hitachi S-4800 SEM. The PANI powder were dispersed in acetone and transferred onto Si wafer substrate. This substrate, in addition to the in situ PANI film grown onto the surface of glass substrate, was sputtered with a thin layer of Pt/Pd. The XRD characterization was performed by RIGAKU RINT2000. The TGA analysis for the PANI powder was made using Shimadzu TGA-50H thermogravimetric analyzer at a flow rate of 30 mL min^{-1} and a heating rate of 10°C min^{-1} under nitrogen atmosphere.

The electrical conductivity of the films was measured using the four-probe technique for seven different glass supports coated with PANI films. The current was applied to the outer electrodes, and the resulting voltage across the inner electrodes was measured using Keithley 617 Digital Multimeter. In addition, the electrical conductivity of the PANI powder, as compressed pellets (13 mm in diameter and 1–2 mm thick), was measured using the two-probe technique.

RESULTS AND DISCUSSION

QCM measurement for the course of polymerization

The oxidation of aniline with FC or APS can be easily followed by using QCM. The plot of m', during the PANI film deposition onto the gold electrode of the QCM, as a function of polymerization time, is shown in Figure 1(a). This is for a solution of a molar ratio (FC/aniline) = 1 using 0.06M aniline solution. The polymerization in the depletion periods ends with the formation of in situ PANI hydrochloride films. These films were in situ doped with chloride anions due to the presence of hydrochloric acid in the polymerization medium.
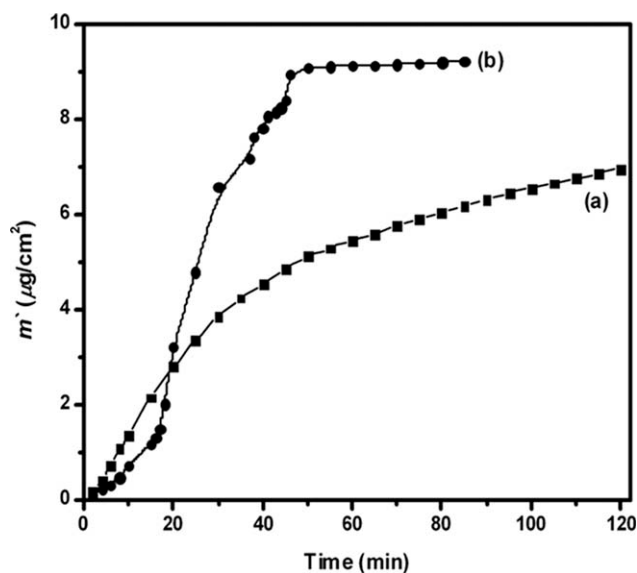

Figure 1 The relationship between m' and the time for the in situ PANI film deposition onto the gold electrode of the QCM on using: (a) FC and (b) APS.

It is expected that the first deposits of PANI must nucleate on the gold surface and give rise to a rather slow deposition rate. Following this induction period, the rate of deposition increases, and this can be evidenced by the increasing magnitude of the slope. Afterward, the rate attains a steady state as the deposition is finished due to the depletion of the monomer. It can be seen that there is no boundary differences between these stages, which indicates that the growth rate of the PANI-FC film was relatively low. However, for the PANI film obtained from a solution of 0.1M APS and 0.08M aniline in 0.1M hydrochloric acid solution, the three mentioned stages are more defined, and the growth rate of the film was found to be high, when compared with that of the PANI-FC film,[19] Figure 1(b). Therefore, it can be concluded that the course of polymerization using both FC and APS is different due to the difference in their oxidation/reduction potentials.

Furthermore, the effect of molar ratios of FC/aniline (r) on m' of the film deposition was studied. The aniline concentration was kept constant at 0.15M and the concentration of FC was changed and hence, r was varied from 0.25 up to 5. m' at different times of polymerization, for different solutions, were plotted against time, Figure 2. It can be seen that, m' increases with increasing r of FC/aniline.

In a previous investigation,[19] the PANI film deposition was studied using APS in aqueous hydrochloric acid medium. It was found that the film degrades at molar ratios of APS/aniline > 2. This was attributed to the existence of an excess APS, which over oxidizes the formed PANI films. This degradation was not observed in this work at different molar ratios of FC/aniline. Therefore, the course of
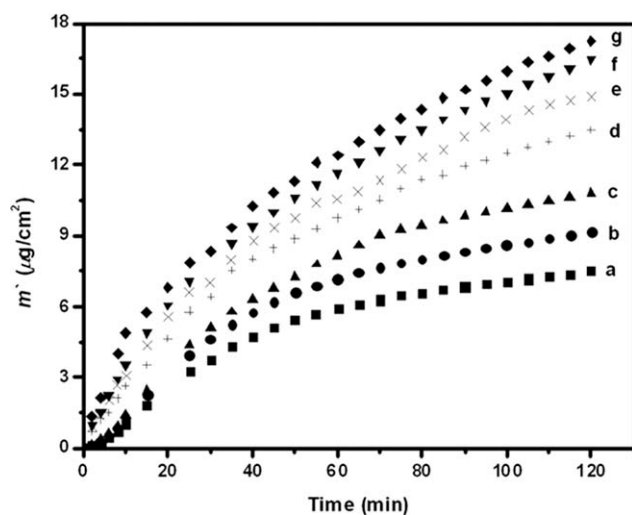
Figure 2 Relation between m' of the PANI film and time at different molar ratios of FC/aniline: (a) 0.25; (b) 0.5; (c) 1; (d) 2; (e) 3; (f) 4; and (g) 5.

oxidative polymerization of aniline using FC and APS was found to be different, which can be explained on the basis that both of APS and FC possessed different oxidation/reduction potentials and also APS in aqueous solution is considered as one of the strongest oxidizing agents.[39]

The morphology of the *in situ* PANI film and powder formation

The morphology of the *in situ* PANI films and the polymer powder formed in the bulk, using FC was examined using SEM technique and is presented in Figure 3(a,c). A close inspection of the image shows that PANI-FC film is actually porous, Figure 3(a). However, Figure 3(c) shows that the polymer powder composed of small particles with interconnected nanofibers and has a sponge structure. For comparison, the SEM images of the PANI film and powder samples synthesized by using APS were measured and are shown in Figure 3(b,d). The PANI-APS film has a smooth topography; however, the powder consisted of course and irregular particulates of different sizes.

The EDX for the PANI-FC film was measured, Figure 4. The spectra revealed that the PANI-FC film contains Fe atoms. This is consistent with the results of Yasuda and Shimidzu,[27] who studied the chemical polymerization of aniline using FC. The concentration of Fe in PANI was measured with an ion-coupled plasma spectrometry and showed that the polymer contains 150 ppm Fe, which includes Fe^{+2} and Fe^{+3}.
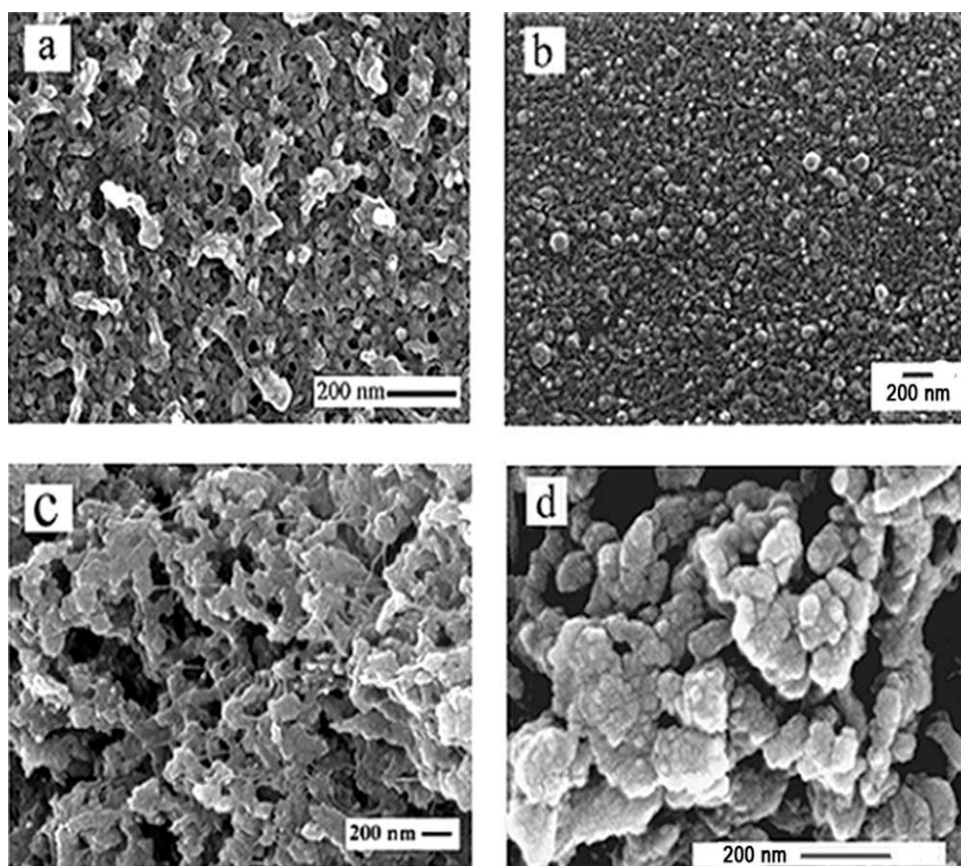

Figure 3 SEM images of (a) PANI-FC film, (b) PANI-APS film, (c) PANI-FC powder, and (d) PANI-APS powder.
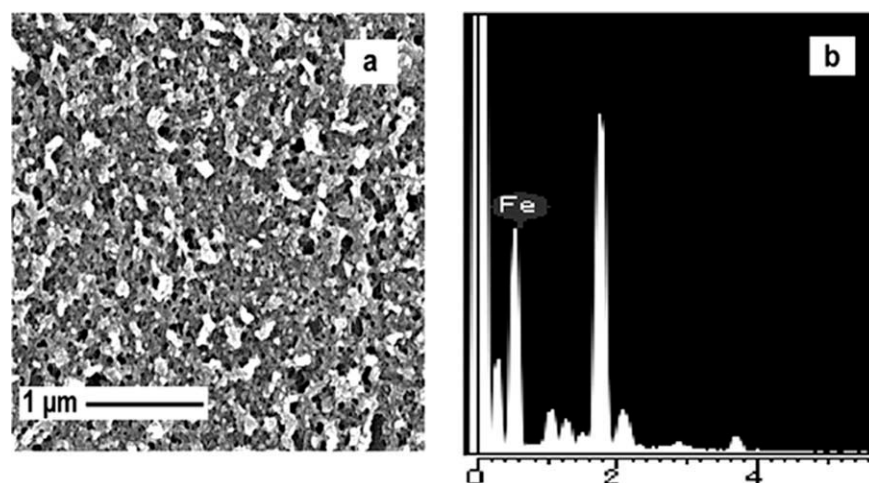
Figure 4 EDX images of the PANI-FC film.

XRD

The XRD can be used to check the crystallinity of the polymer. XRD pattern of the PANI-FC powder sample is shown in Figure 5. The figure reveals that PANI-FC powder has some degree of crystallinity. Three diffraction peaks appear in the spectrum region; the first centered at $2\theta = 25°$ and is more prominent than the other existed peaks at $2\theta = 20°$ and $15°$, but amorphous region is the main body. Thus, Figure 5 also indicates that the crystallinity of the PANI-FC is higher than that of the PANI-APS, which may be attributed to the lower oxidation/reduction potential of FC that results in slow growing structures controlled by accretion or elongation process.[28,40]

Thermal properties

The thermal properties of PANI were investigated by TGA analysis. Figure 6 shows the thermograms of two PANI powder samples using APS (a) and FC (b) as oxidiz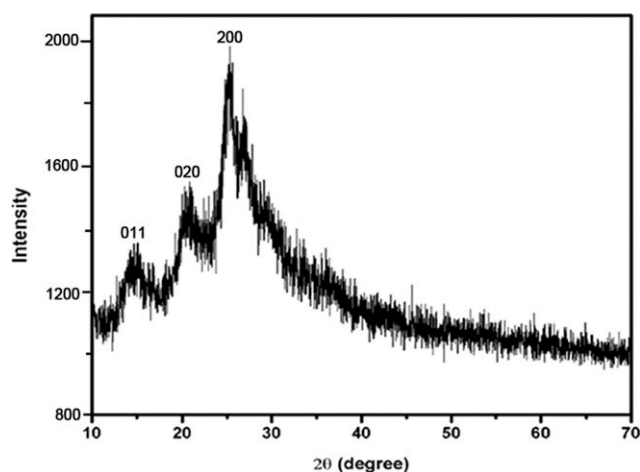ing agents. It can be observed that the weight loss, in both samples, is a multistage process. The first weight loss before 120°C is attributed to the loss of water molecules from the sample. The amounts of weight loss owing to the evolution of water are 7.9% and 7.8% for samples (a) and (b), respectively. The second stage observed within the temperature range of 120–300°C is assigned to the removal of dopant molecules from the polymer structure.[41] The amounts of weight loss attributed to the evolution of the dopant molecules are 9.26% and 8.6% for samples (a) and (b), respectively. The weight loss observed between 300 and 700°C after the removal of the dopant molecules corresponds to the degradation of the polymer chain.[42] PANI-FC exhibits a higher degradation rate than PANI-APS, and hence, the former is less thermally stable than the latter. The reduction of the oxidant potency from APS to FC makes the film growth rate of PANI relatively low in the case of FC.[30] In addition, it has
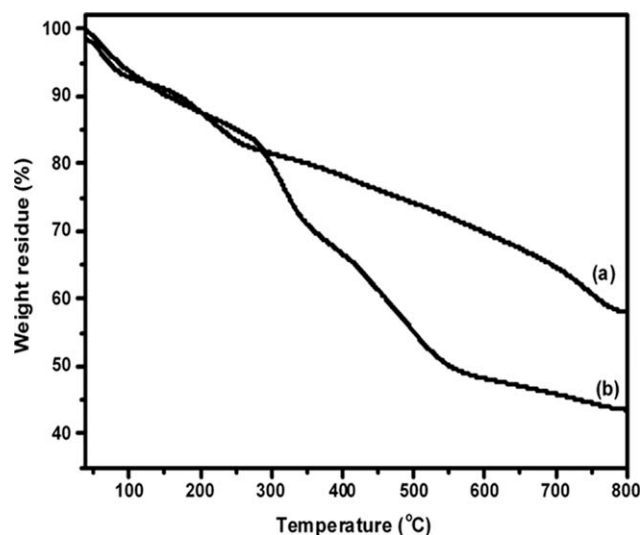

Figure 5 XRD pattern of the PANI-FC powder sample.

Figure 6 TGA curves of the PANI powder samples using: (a) APS and (b) FC.

been stated that FC produced PANI with a large fraction of oligomers.[26] Moreover, the lesser thermal stability of the PANI from aniline and FC may be due to the presence of the Fe traces. Those traces, probably, catalyzed a thermal destruction of this PANI. All these factors contributes to the lower thermal stability of the PANI synthesized with FC.

The electrical conductivity of PANI films and powder

The electrical conductivity of the PANI-FC films grown onto glass supports from the solutions of $r = 1$ in $0.1M$ hydrochloric acid, was measured using the four-probe technique. The films have conductivity in the range $0.63–0.85$ S cm^{-1}. However, the conductivity of the pressed PANI-FC power measured using the two-probe technique was found to be 7×10^{-3} S cm^{-1}.

To understand the effects of oxidants on the conductivity of PANI films, the conductivity of the *in situ* PANI films determined in previous studies[43] using APS as oxidant in aqueous $0.1M$ hydrochloric acid are recorded for the sake of comparison. The films have conductivities in the range $11.83–15.63$ S cm^{-1}, which are larger than that of the PANI-FC films in this investigation. This can be illustrated on the basis of the reduction of the oxidant potency from APS to FC, which makes the film growth rate of PANI relatively low in the case of FC. Furthermore, the low conductivity of the PANI-FC may be due to the lesser content of the quinonimine structures (oxidized form) in this PANI, that is, the conjugation extent of a macromolecule of this PANI is lesser than the conjugation extent of a macromolecule of PANI from aniline and APS. Therefore, a low conductivity of the PANI-FC was obtained, and this coincides with a previous study by Ma et al.[30]

CONCLUSIONS

In situ porous PANI films were grown from the chemical oxidation of aniline using FC in aqueous hydrochloric acid solution. The yield and hence the thickness of the deposited films increases with increasing the molar ratios of the FC/aniline without any caution concerning the over-oxidation due to the oxidant increase. The porous character of the produced films may find better sensor sensitivity to volatile organic compounds. This is attributed to the high surface area of the porous structure and the easy vapor diffusion in comparison with the compact PANI film. The EDX measurement revealed that the PANI-FC film is contaminated with some Fe atoms. The thermal stability and the electrical properties of PANI-FC are less than the PANI obtained from APS.

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