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A morphological study of polypyrrole films grown on indium-tin oxide conductive glass

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In this study a detailed examination was carried out of variables that control the wrinkle morphology observed in *p*-toluenesulfonate doped polypyrrole films formed by electropolymerization on tin-doped indium oxide (ITO) coated glass using either methanol/water or water alone as solvents. Results are in agreement with an earlier study in which the porous nature of the substrate was identified as the most influential of the factors controlling the morphology. Other factors found to be important included: nature and size of the dopant ions, solvent, and concentrations of pyrrole and dopant. Examination of still-moist free-standing conductive films by light microscopy demonstrated that the wrinkles are not an artifact due to post-deposition shrinkage. © 1997 Elsevier Science Ltd

(Keywords: polypyrrole; indium-tin oxide glass; morphology)

INTRODUCTION

It is well known that doped polypyrrole (PPy) can be deposited electrochemically on a wide range of different types of conducting anodes[1,2] such as noble-metal coated base metals, graphite, glassy carbon, and also on commodity metals under certain conditions. Films have also been grown on optically-transparent conductive substrates such as tin-doped indium oxide coated glass (ITO). The transparency of thin polypyrrole films on such substrates allows their examination by various spectroscopic methods, leading to information regarding the doping levels, the mechanisms of doping/dedoping, thermal stability, etc. and can be utilized for a number of practical applications.

PPy can also be deposited on ITO as relatively thick, free-standing films. Systematic characterization of such thick films, doped with the *p*-toluenesulfonate ion (pTS) has been carried out in some detail by Mitchell and coworkers[3] and by Sutton and Vaughan[4]. It is evident from these studies that such films are generally poorer conductors than films prepared on noble metals, and that when deposited from aqueous media they exhibit a marked molecular anisotropy[3]. In addition, under certain sets of experimental conditions, the growth surface of these PPy films can display under scanning electron microscopy (SEM) unusual, undulating 'wrinkle' features, covered with small, randomly-distributed blister-like spots. In an earlier study Mitchell *et al.*[5] using aqueous solutions as the electrolytic medium found that larger wrinkles were formed with increasing electropolymerization potential. This is to be contrasted with a subsequent study by Sutton and Vaughan[6], who used water/methanol mixtures as solvent, and only found wrinkles in a limited range of solvent ratios. The term 'wrinkle' was, in fact, coined by Sutton and Vaughan. Here, it should be mentioned that earlier authors have used other terms such as: hillocks or mounds, mountain chains, wrinkles, interconnected fibrillar arrays and Y-shapes to describe such morphologies[7]. Our interest in wrinkles arose while studying PPypTS films grown in thin-layer cells deposited onto the non-conductive surface of poly(methyl methacrylate) (PMMA) where wrinkle morphology was also observed under certain conditions[8]. Since it was not possible to reproduce the PMMA surfaces used in the original series of experiments and since wrinkles were not formed regularly on all specimens of PMMA, it was decided to use ITO as an alternative substrate in a study of the variables that control the frequency, size and depth of wrinkles. In our search of the literature for examples of wrinkles in PPy films, we discovered that while this morphological phenomenon is not rare, no one has actually specifically studied the mechanism of formation of these interesting features or tried to relate the morphology of the deposited PPy films to the characteristics of the specific conducting substrate used.

It has been suggested that the origin of wrinkles may be due to shrinkage of PPy under vacuum during SEM examination[9] or due to the development of internal stresses[4,10]. Furthermore, it has been reported that wrinkles are hollow, rather than being solid formations[4,9]. While in an earlier publication[7] we drew attention to the similarity in wrinkle morphology of PPy films formed on ITO and PMMA and proposed a common formation mechanism on the two substrates, in this paper we will deal exclusively with films produced on ITO glass and describe a more comprehensive and detailed study considering a number of experimental parameters not previously reported by us.

In previous studies in which PPy has been electropolymerized on ITO substrate, there has been no report of characterization of the ITO itself. ITO has been, however, the subject of a number of studies in which it was shown that the morphology of the indium oxide/tin layer on glass or silica-coated glass depends on its

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*To whom correspondence should be addressed method of preparation, thermal history, and level of doping with tin[11–13]. In the present study it was deemed necessary to examine the surfaces of the ITO since we are endeavouring to relate the unusual features of the PPy film to the surface morphology of the ITO, which serves as anode.

EXPERIMENTAL

Two grades of indium-tin oxide coated glass (Donnelly Applied Films Corporation, USA) were used as anodes in this study. These had nominal surface resistivities of $75\,\Omega\ \mathrm{sq}^{-1}$ and $15\,\Omega\,\mathrm{sq}^{-1}$. We were informed by the Donnelly Applied Films Corporation that these two grades were prepared by reactive d.c. magnetron sputtering of heated substrates (temperatures not specified) from a 90% In–10% Sn metal target in an argon–oxygen atmosphere[14]. The $15\,\Omega\,\mathrm{sq}^{-1}$ ITO coated glass was prepared by direct deposition on glass and had a nominal ITO layer thickness of about 160 nm[14] while the $75\,\Omega\,\mathrm{sq}^{-1}$ ITO sample was prepared by deposition on silica-coated glass and had a nominal ITO thickness of 30 nm[14].

ITO anodes were typically prepared by cutting the glass to suitable size (active area = $3.5\,\mathrm{cm}^2$), degreased by Soxhlet extraction with 1,1,1-trichloroethane (AR Grade), followed by drying in a 60°C oven overnight prior to use. We have characterized the two grades of ITO by scanning electron microscopy (SEM), field-emission scanning electron microscopy (FESEM), and atomic force microscopy (AFM).

The following salts were used as electrolytes for the electropolymerization of pyrrole: sodium nitrate, sodium hexafluorophosphate, sodium tetrafluoroborate, sodium perchlorate, sodium dodecylbenzenesulfonate, sodium dodecylsulfate, sodium 10-camphorsulfate, and sodium *p*-toluenesulfonate. All these reagents, obtained as the best available grade, were used directly without further purification.

Pyrrole (Aldrich) was doubly distilled immediately prior to use. Unless otherwise stated electrochemical polymerization were carried out potentiostatically for various time periods at 1.20 V (vs. SCE) using pyrrole (0.1 M) and electrolyte (0.2 M) at room temperature. Electropolymerization was carried out in a single compartment glass vessel with the ITO working electrode, saturated calomel reference electrode (SCE) and stainless steel counter-electrode each positioned vertically. The electrodes were allowed to equilibrate in solution for 15 min prior to application of potential for each experiment. No attempt was made to exclude atmospheric oxygen during film deposition. After preparation, films were generally stripped off the ITO surface, washed thoroughly by rinsing with water and methanol, placed between glass slides to reduce curling and dried in a vacuum oven at 40°C for 3 days.

Morphological examination of the films was routinely conducted using a Jeol JSM-480 SEM unit at three sites on each PPy film corresponding to the top, the middle and the base of the ITO working electrode. When required, more detailed examination was carried out by atomic force microscopy (AFM) using a Park Autoprobe LS unit and field emission scanning electron microscopy (FESEM) using a Hitachi S900 unit or a Jeol 6300 unit. Energy dispersive spectroscopy (EDS) was performed using the Kevex light element quantitative X-ray analysis system and Kevex quantitative image analysis system connected to the Jeol 6300 FESEM unit. X-ray photoelectron spectroscopy (X.p.s.) was performed on a XSAM PCI X-Ray photoelectron spectrometer (Kratos) using a $\mathrm{Mg}K_\alpha$ X-ray source. Conductivity measurements were carried out with a four-probe device built by the university workshop.

RESULTS

Sets of experiments were conducted in an attempt to define the conditions under which wrinkles are formed. These are presented below in separate sections. However, initially it is important to discuss the characteristics of the ITO used as anode materials. Donnelly Applied Films Corporation have kindly provided us with AFM images of representative samples of the two types of ITO, shown in *Figures 1* and *2*, for the $75\,\Omega\,\mathrm{sq}^{-1}$ and the $15\,\Omega\,\mathrm{sq}^{-1}$ ITO grades, respectively. Both materials can be seen to have a surface morphology comprising of clusters of surface crystals oriented at right angles to the underlying substrate. These crystal clusters have a tapered appearance in the case of the $75\,\Omega\,\mathrm{sq}^{-1}$ ITO, with separation between the tips of about 0.2 μm. In the $15\,\Omega\,\mathrm{sq}^{-1}$ ITO, the crystal clusters appear to have a more rounded morphology and greater packing density than the poorer conducting sample. Depth profiles of the two samples indicate that the $75\,\Omega\,\mathrm{sq}^{-1}$ ITO has deeper microcrevices than the $15\,\Omega\,\mathrm{sq}^{-1}$ sample: maximum depth of 300 Å against 100 Å, respectively.

We have also obtained independently AFM images of the two types of ITO. The $75\,\Omega\,\mathrm{sq}^{-1}$ ITO, in *Figure 3*, exhibits an unexpected formation of interlaced patterns of ridges emanating from a central nucleus with gaps of about 0.2 μm between adjacent ridges. This structure has very recently been shown to be spherulitic, that is, the layers of crystals consist of spherulites stacked in layers[15]. The nuclei of these spherulites are about 2–3 μm apart. These structures appeared so unusual and unexpected that three separate samples of $75\,\Omega\,\mathrm{sq}^{-1}$ ITO glass were examined by identical AFM units in three different laboratories. These results were essentially reproducible. This unusal formation, however, was not observed on examining other specimens of $75\,\Omega\,\mathrm{sq}^{-1}$ ITO glass by FESEM, a technique which should have allowed the observation of the features in question. In contrast, the surface of the $15\,\Omega\,\mathrm{sq}^{-1}$ ITO, shown in *Figure 4*, does not display any such interlaced features, appearing as a predominantly flat surface on the scale of μm but covered with numerous ultra-fine needle-like structures on the sub-μm scale. The two sets of AFM images are mutually consistent if the spacing between the ridges (*Figure 3*) is considered to be the same as that between the crystals, viewed in the Donnelly micrograph (*Figure 1*).

In several series of experiments, comparison of the $15\,\Omega\,\mathrm{sq}^{-1}$ and $75\,\Omega\,\mathrm{sq}^{-1}$ ITO samples as working electrodes for polypyrrole electrodeposition was achieved by potentiostatic deposition at 1.20 V (vs. SCE) from identical electrolyte-containing pyrrole solutions. Since the average current density at the $15\,\Omega\,\mathrm{sq}^{-1}$ ITO working electrode was typically about 3.6 that at the more resistive $75\,\Omega\,\mathrm{sq}^{-1}$ ITO, a range of polymerization periods were investigated to enable comparison on the basis of total charge transferred.

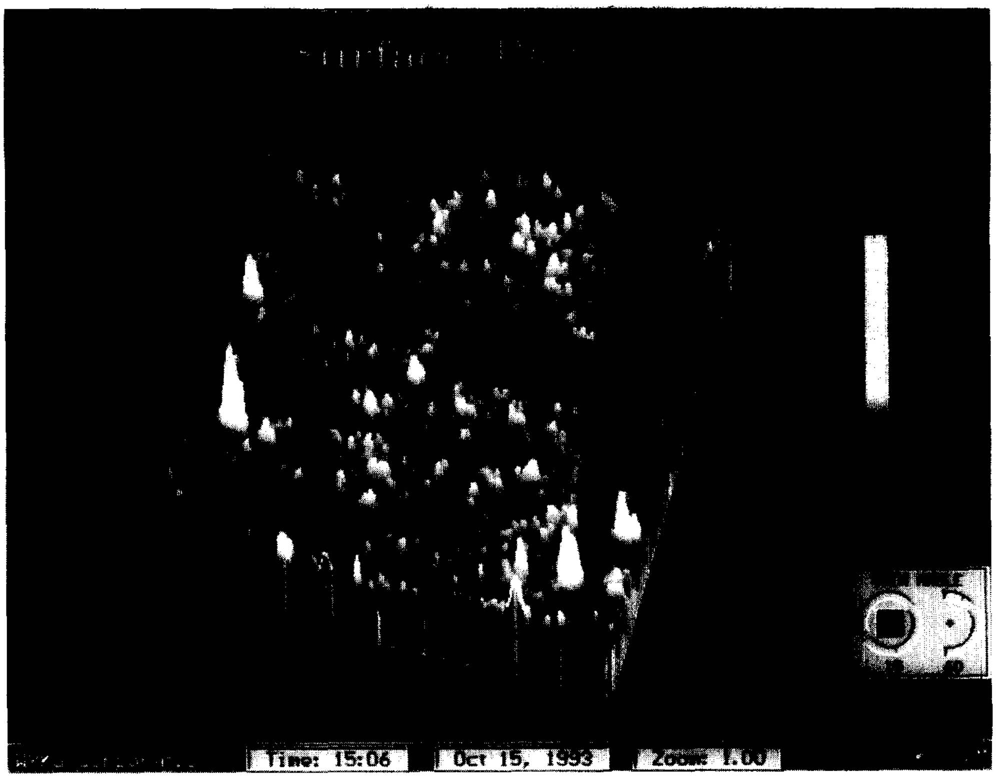


Figure 1 10 × 10 μm AFM image of 75 $\Omega\,sq^{-1}$ indium-tin oxide coated on glass provided by manufacturer (Donnelly Applied Films Corporation, USA)

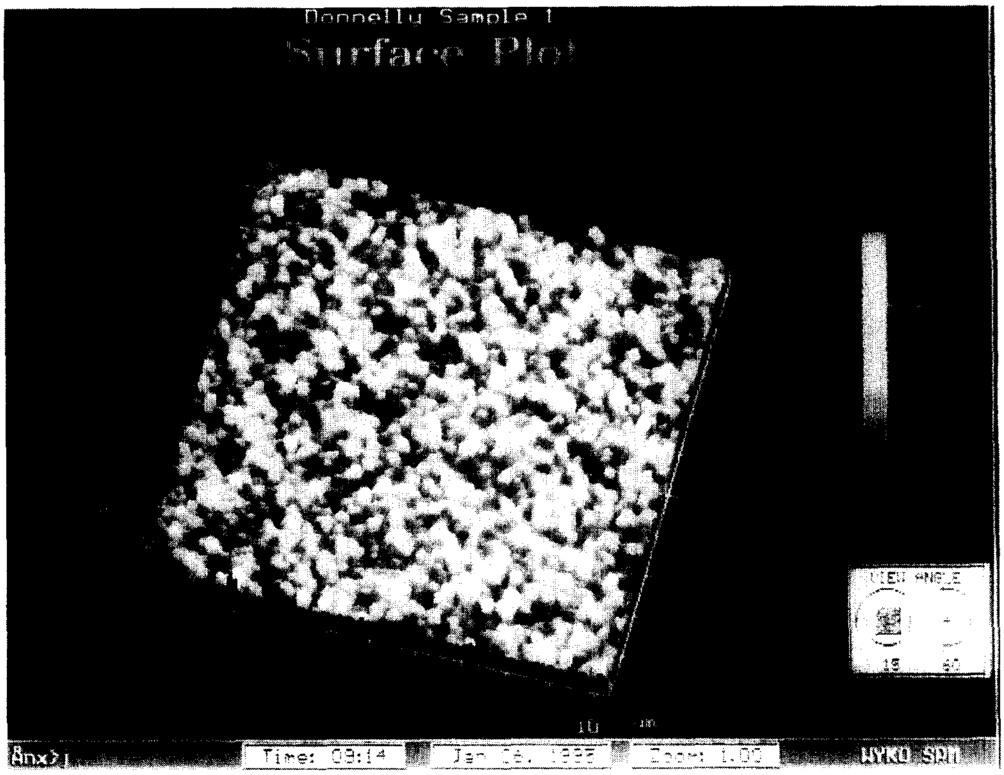


Figure 2 10 × 10 μm AFM image of 15 $\Omega\,sq^{-1}$ indium-tin oxide coated glass provided by manufacturer (Donnelly Applied Films Corporation, USA)

After deposition, films were treated in the manner described previously and depending on the film thickness and the surface to be examined (ITO- or solution-facing), were either left attached to the ITO, peeled off the ITO using adhesive tape or separated as free standing films from the ITO using a scalpel.

Films grown on the 15 $\Omega\,sq^{-1}$ ITO exhibited a lower frequency of wrinkles and a corresponding smaller number of pits/blisters per unit area than films deposited on the 75 $\Omega\,sq^{-1}$ ITO. It should be mentioned here that the concave-shaped 'pits' (diam. < 1 μm) observed on the ITO-facing surface of the PPy films appear to be the same structures as the convex-shaped blisters observed on the solution-facing PPy surface.

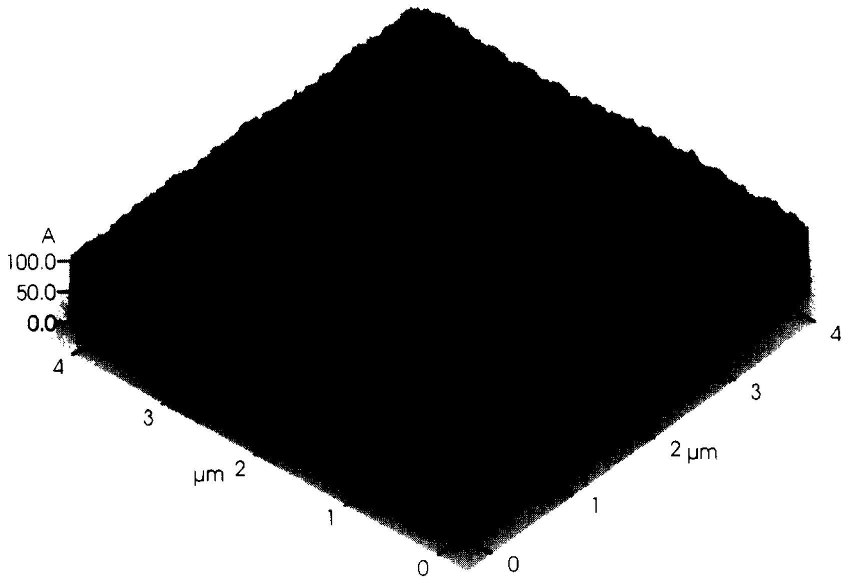
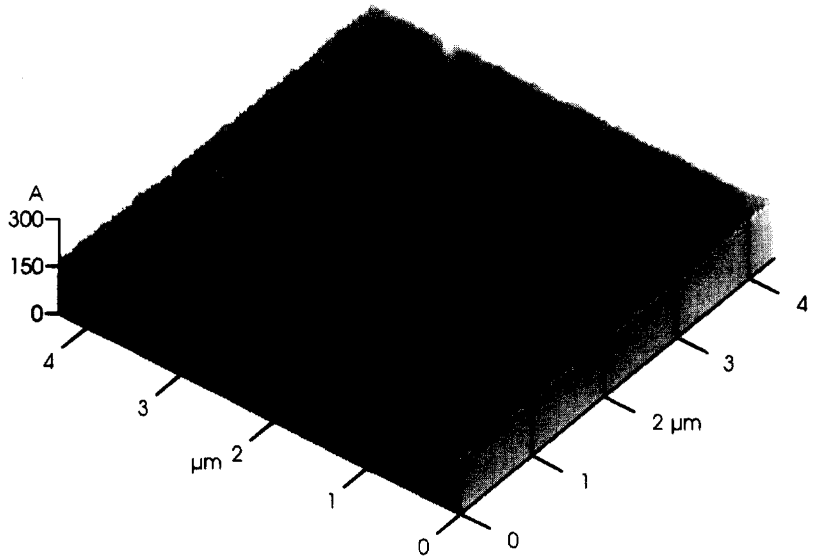


Figure 3 4 × 4 μm AFM image of 75 Ω sq^{-1} indium-tin oxide coated glass obtained independently of manufacturer



Influence of nature of dopant on wrinkle size

Replacing the pTS anion with dopants spanning a range of molecular shapes and sizes, was the theme of this set of experiments. Polymerization was conducted at 1.20 V (vs SCE) for 5 min in each case on the 15 Ω sq^{-1} ITO, in 40/60 parts by volume methanol/water mixtures, with pyrrole and dopant concentrations of 0.1 M and 0.2 M, respectively. The dopant ions used were: *p*-toluenesulfonate, nitrate, tetrafluoroborate, perchlorate, hexafluorophosphate, dodecylbenzenesulfonate, dodecylsulfate and 10-camphorsulfonate.

With the small, compact inorganic dopants (nitrate, tetrafluoroborate, perchlorate, hexafluorophosphate) small wrinkles were found on the ITO-facing surface upon examination by SEM. Wrinkle size is taken here as a semi-quantitative estimate of the average width (diameter) of wrinkle units/cells on the ITO-facing side of the film. Photomicrographs of two such films, prepared with NO_3^- and PF_6^-, are displayed in *Figures 5* and *6*, respectively. Even between films grown in solutions containing small anions, differences in wrinkle size and distribution can be observed. Thus films prepared with the other two small inorganic anions, BF_4^- and ClO_4^- (photomicrographs not shown), display similar morphologies but with a somewhat more irregular distribution of wrinkle sizes. In terms of size, the nitrate-doped film exhibited wrinkles having larger width and variation (average diameter 10–20 μm) than films doped with the other small anions (average diameter of 5–10 μm). In contrast, as shown in *Figure 7*, very large wrinkles (30–100 μm) were found in the film doped with the dodecyl sulfate ion. Wrinkles, however, were absent from the films prepared with the two largest dopants in the supporting electrolyte, namely, the 10-camphorsulfonate and the dodecylbenzenesulfonate anions.

The conductivity of the PPy films prepared with the various dopants is displayed in *Table 1*, with the best conductivity being noted for the sulfonate/sulfate-containing anions. *Table 1* also lists the level of doping of the individual films estimated from the XPS elemental analysis on both sides of the individual films together with the corresponding film thickness measured by micrometer. The most heavily doped films with the


Figure 5 SEM micrograph of the ITO-facing surface of a PPy film prepared in 0.2 M $NaNO_3$ in 40/60 $MeOH/H_2O$. Substrate: 15 Ω sq^{-1} ITO


Figure 6 SEM micrograph of the ITO-facing surface of a PPy film prepared in 0.2 M $NaPF_6$ in 40/60 $MeOH/H_2O$. Substrate: 15 Ω sq^{-1} ITO

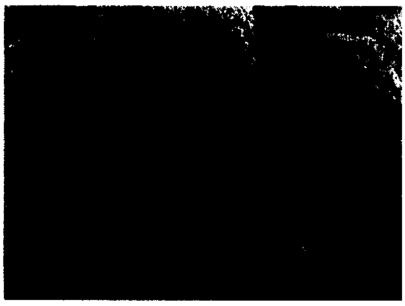


Figure 7 SEM micrograph of the ITO-facing surface of a PPy film prepared in 0.2 M NaDS in 40/60 $MeOH/H_2O$. Substrate 15 Ω sq^{-1} ITO. (Note different scale to that in *Figures 5* and *6* above)

relatively high conductivity were also found to be the sulfonate/sulfate-containing anions.

Doping/dedoping of PPy films

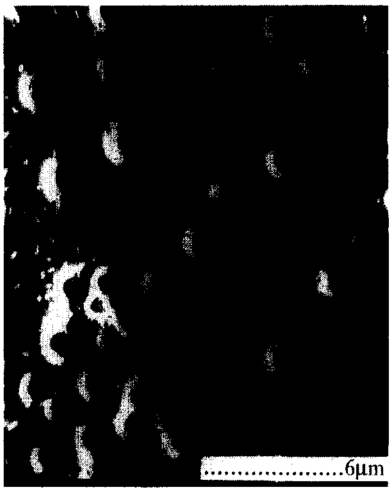
In these experiments it was of interest to reduce (dedope) oxidized PPy films possessing wrinkle morphology in order to learn to what extent the wrinkles size is influenced by the incorporation of counterions during the formation of the conducting film. Earlier, we had postulated[16] a mechanism describing the formation of wrinkles as arising from the introduction of dopant ions into the film, causing the undoped (electrically neutral) film to expand. This seemed reasonable since the dopant fraction of the film must be considerable, typically being about 40% by weight (based on a molar doping level of 25% in the case of pTS).

To generate wrinkled films, growth of PPy was conducted under similar experimental conditions to those used by Sutton and Vaughan[6], i.e. a constant potential of 1.20 V (vs. SCE) on ITO electrodes held vertically in a 40/60 methanol/water solvent mixture containing 0.1 M pyrrole and 0.1 M (or 0.2 M) NapTS. The dried films were characterized by conductivity, SEM, and by XPS surface element composition. An SEM micrograph of the ITO-facing surface of a PPy film, grown in 0.2 M NapTS solution, is shown in *Figure 8*. From this figure it is evident that the average diameter of the 'pits' distributed apparently randomly on the wrinkles is about 1 μm. Lower magnification images (not shown) revealed the average wrinkle widths were of the order of 100 μm. Another section of the same film viewed under the FESEM, displayed in *Figure 9*, revealed numerous needle-like structures scattered around the holes. These needles were originally suspected of being indium oxide crystals, stripped off the glass as the film was peeled away from the ITO surface. Examination of these crystals by EDS analysis has revealed that they were not indium oxide crystals but rather that they contained N, S, and Na, with $N/S = 3.57$ and $Na/S = 0.19$. This elemental analysis precluded the crystals from being fragments of the ITO layer, and suggests that these may be oligomeric pyrrole species, perhaps in the form of a sodium salt. By photographing areas around the 'pits' at several tilt angles (5, 10, 40°) we

Table 1 Properties of PPy films prepared in 0.2 M of various dopant anions in 40/60 $MeOH/H_2O$

Anion/dopant	Elements/X.p.s.	Film surface	N : Z atomic ratio	Thickness (μm)	Conductivity (siemens cm^{-1})
p-Toluenesulfonate	N, S	Solution-facing	2.6/1	15	2.7
		ITO-facing	2.6/1		
Dodecylsulfate	N, S	Solution-facing	2.0/1	16	2.0
		ITO-facing	1.1/1		
Dodecylbenzenesulfonate	N, S	Solution-facing	n.a.	8	1.8
		ITO-facing	4.3/1		
Hexafluorophosphate	N, P	Solution-facing	4.8/1	6	0.8
		ITO-facing	4.1/1		
Perchlorate	N, Cl	Solution-facing	4.9/1	14	0.5
		ITO-facing	5.4/1		
Nitrate	n.a.	n.a.	n.a.	15	0.4
Tetrafluoroborate	N, B	Solution-facing	4.5/1	5	0.3
	ITO-facing	4.7/1			
10-Camphorsulfonate	n.a.	n.a.	n.a.	5	0.1

Figure 8 SEM micrograph of the ITO-facing surface of a PPy film prepared in 0.2 M NapTS in 40/60 MeOH/H_2O. Substrate: 15 Ω sq^{-1} ITO



tentatively concluded that these features are mostly holes rather than surface protrusions. In the thicker films on the solution-facing side, cauliflower-type features were found, of the type usually reported for PPy films.

Electrochemical dedoping

As the first approach to dedoping, electrochemical dedoping of each free-standing PPypTS film was carried out by sandwiching the films between two ITO plates (which collectively served as the working electrode[17]), immersing in 0.1 M NapTS solution, and applying a potential of −0.7 V (vs. SCE) for 20 min. As a result, the conductivity of a film grown in 0.1 M NapTS for example, decreased from 1.2 S cm^{-1} to 0.003 S cm^{-1}. XPS analysis of the 'neutral' film confirmed the expectation of an increase in the N/S ratio, which rose from 1.6 in the oxidized state to 5.3 in the reduced state. Additionally, there was no evidence for the presence of sodium ions in the surface layers of the reduced film, as might have been expected[18] if the dedoping process had involved simultaneous incomplete removal of tosylate anions accompanied by partial replacement of the lost positive charges by influx of sodium cations into the film. A SEM micrograph of an electrochemically dedoped film prepared from 0.1 M NapTS solution is provided in *Figure 10*. It shows that the dedoping process causes the wrinkles to flatten out and for cracks to appear, leaving behind a smooth surface, with the 'pits' intact in their original locations on the film.

Chemical dedoping

A second method of dedoping consisted of immersing doped $PPyNO_3$ in a 2 M NaOH solution for 8 h. Qian has reported that conducting $PPyNO_3$ and also $PPyClO_4$ film grown on ITO and left immersed in 1 M NaOH for 8 h resulted in larger wrinkles shrinking to smaller ones, due to the de-intercalation of the anion[19]. In our experiment, which was basically a duplicate of the above procedure using $PPyNO_3$ film electrodeposited from MeOH/H_2O, we found inconclusive results. In the doped film itself, there was a lack of uniformity in wrinkle size, consequently in the NaOH-treated film, although there were many small wrinkles, it was not possible to definitely attribute the reduced size of the NaOH treatment. It is unfortunate that in his paper Qian did not specify whether the NaOH-treated film was taken from the same area of the untreated sample. So, in conclusion, although we found no evidence of wrinkle size reduction upon 2 M NaOH treatment, this may accord with Sutton and Vaughan's hypothesis[6] that different polymerization mechanisms (and hence structures) may be associated with deposition from aqueous and aqueous methanol solutions. That is, Qian's films deposited from aqueous solution may be more susceptible to reorganization of the morphological units associated with wrinkles than our aqueous/methanol-based films. This point warrants further investigation.

Film development in the early stages of growth in methanol/water

Ideally, it would be highly instructive to examine the developing PPy film by stripping off layer after layer, starting from the solution-facing surface and examining each layer by SEM and XPS Intuitively, it is obvious that the initially-formed film must be different from that formed at a later stage, because initially the film grows on a more conductive surface (ITO) than the doped PPy itself. Studies of the early stages of film growth indicate that a high level of alignment is present in these cases[20,21] but which is subsequently lost with further thickening of the film. Since a layer-by-layer stripping process is not practical, an alternative approach is to prepare films at several stages of development, after a specific quantity of charge has been passed through the electrochemical cell. Such a procedure is described below.

In a series of experiments, pyrrole (0.1 M) in 40/60 methanol/water solution containing NapTS (0.2 M) was polymerized onto 75 Ω sq^{-1} ITO under potentiostatic control (1.20 V vs. SCE) resulting in isolated spot-like deposits at very early stages of formation which coalesce to become continuous thin films at longer reaction times. Typically, electropolymerization was carried out for 20, 40, 60, 90, 120 and 300 s, so as to deliver increasing amounts of charge (ranging from 0.10 to 2.5 C).

Observations by SEM of the solution-facing side of the resultant thin films was conducted, in the case of the thinner films, on material still attached to the ITO surface. Films formed in the very early stages (at times shorter than 120 s) cracked severely on drying so their micrographs are not shown. Only after 120 s was it possible to obtain reasonable micrographs, as for example in *Figures 11a–c*. In *Figure 11a* it is possible to discern the early stages of wrinkle formation. On the left of the area shown in the micrograph, blister-like structures are shown protruding from the ITO-facing side, and at the right it is seen that some of those blisters

Figure 10 SEM micrograph of the ITO-facing surface of a PPy film prepared in 0.1 M NapTS in 40/60 MeOH/H_2O and electrochemically dedoped. Substrate: 15 Ω sq^{-1} ITO

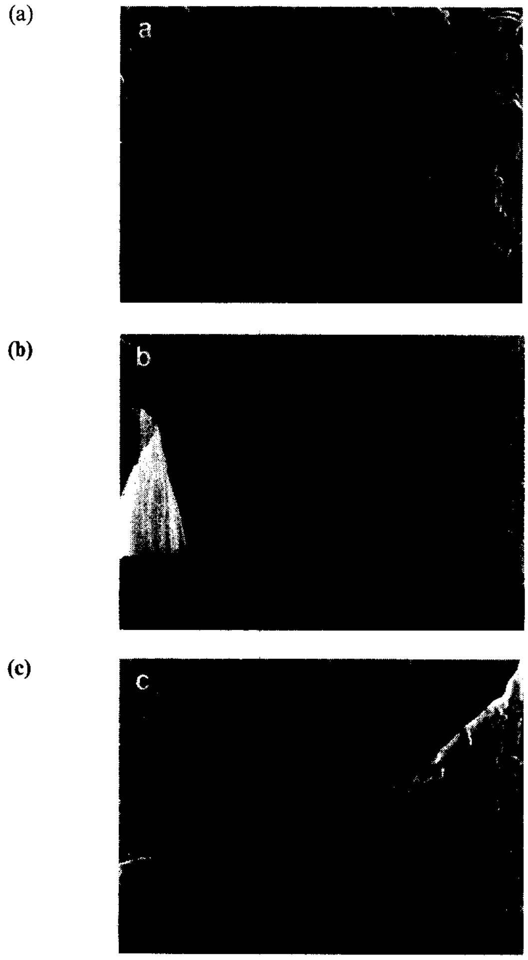


Figure 11 SEM micrograph of the ITO-facing surface of a PPY film prepared in 0.2 M NaPTS in 40/60 MeOH/H_2O on 75 Ω sq^{-1} ITO: (a) a site showing transition in surface morphology from simple blister-like structures (left-hand side) to more complex structures consisting of blisters overlaid by horizontal tube-like strips, (b) a section of torn film revealing underlying blister-like structures still attached to the ITO surface, (c) same site as (b) at higher magnification

have been covered by horizontal tube-like strips. We believe that this latter horizontal deposition of a polypyrrole layer parallel to the ITO surface leads to the creation of complete wrinkles. In *Figure 11b* is seen a section of torn film, which under greater magnification in *Figure 11c* reveals blister-like structures still attached to the ITO surface. At still greater magnification, shown in the FESEM micrograph displayed in *Figure 12*, the surface of the developing wrinkles is seen to be covered with nascent cauliflower-shaped structures, commonly found on the solution-facing side of PPy films. An excellent example, similar to that in *Figure 11a*, of the early stages of formation of a wrinkle is provided in a recent publication by Sutton and Vaughan (Figure 3b in ref. 4).

Effect of pre-treatment of ITO in water and in methanol

Some experiments were conducted on the low resistivity ITO glass after it had been soaked (a) in water (b) in methanol for 24 h. The idea behind this experiment was to check whether the water or the methanol modify the surface of the ITO in some way, possibly by leaching out amorphous indium oxide, already known to be slightly soluble in acid[22]. However, PPy films prepared on such treated surfaces failed to produce a distinctly different morphology.

Water vs. methanol/water mixtures as solvent

With low concentrations of pyrrole (0.1 M) and NapTS (0.2 M) in water, when electropolymerization was conducted potentiostatically at 0.8 V (vs. SCE) none of the films formed displayed a wrinkle morphology, even after a reaction time of 1 h. In contrast, upon increasing the concentrations of both pyrrole and NapTS to 0.25 M and 0.8 M, respectively, as was used by Mitchell and Geri[5], a coherent film with wrinkles became visible after only 300 s. However, when a mixture solvent water/methanol 40/60 was used, wrinkles were formed even with low concentrations of pyrrole (0.1 M) and NapTS (0.2 M) and electropolymerization potential of 0.8 V (vs. SCE). This experiment suggests that wrinkle formation in water as a solvent can happen but requires high concentrations of pyrrole and its dopant, perhaps because these increase the growth rate in water.

Observation of PPy films using optical microscopy

In this experiment, PPy films were once again produced potentiostatically at 1.20 V (vs. SCE) in a mixed solvent of 40/60 methanol/water with concentrations of pyrrole (0.1 M) and NapTS (0.2 M). The resultant films were left on the ITO anode and were intentionally kept moist up to the time of their examination under a light microscope. It was found that films deposited on ITO substrate under these conditions displayed wrinkle morphology (see *Figure 13*) whereas films deposited on stainless steel under similar conditions appeared essentially featureless.

This experiment proves that wrinkles are not just an artifact of the film treatment or due to shrinkage under vacuum.

DISCUSSION

In the present study, an extension of an earlier study into the growth of polypyrrole films on ITO surfaces[7], a number of experimental variables were examined with a view to determining how they affect the development and morphology of the conductive films. The influence of the conductive layer of the ITO-coated glass on the growth and morphology of PPy films is of interest, since this factor has not been specifically investigated previously.

As demonstrated by AFM and FESEM, the two grades of ITO investigated ($75\,\Omega\,\mathrm{sq}^{-1}$ and $15\,\Omega\,\mathrm{sq}^{-1}$) have in common porous surface morphologies and it is this characteristic which appears to be the major factor in determining the morphology of the PPy films formed on these anodes. In contrast, PPy films formed under identical conditions on smooth stainless steel anodes, in a control experiment, were free of wrinkle morphology.

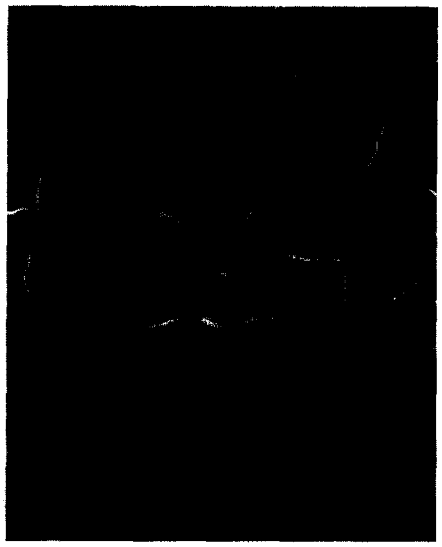


Figure 12 FESEM micrograph of a site near that shown on the left-hand side of *Figure 11a* showing the development of nascent cauliflower-like structures

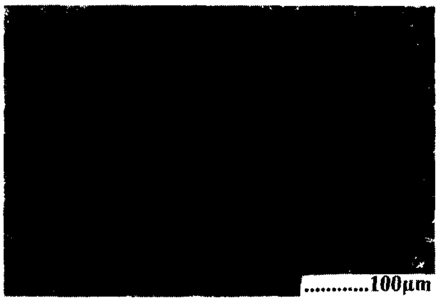


Figure 13 Optical micrograph of the solution-facing surface of a still moist PPy fim prepared in 0.2 M NapTS in 40/60 $MeOH/H_2O$. Substrate: $75\,\Omega\,\mathrm{sq}^{-1}$ ITO

The $75\,\Omega\,\mathrm{sq}^{-1}$ ITO specimens with the thin ITO coating [30 nm (*Figure 1*)] appear to be far more structured with grains organized as spherulites. It is of interest that the size of the wrinkles formed in PPy film grown on the ITO do not correspond to the size of these spherulites (see, for example, *Figure 3*). Had this been the case, it would have been quite obvious that wrinkles are merely imprints of the underlying template. ITO with the thicker conductive layer (160 nm, *Figure 2*) lacks the detailed structure of the less conductive specimen. Related reports by Bedekar *et al.* on the influence of the thickness of the conductive layer in a related substrate, SnO_2:F coated glass, on the formation and morphology of poly(*o*-anisidine)[23] and polyaniline[24] films largely parallel our findings.

From the examination of the effect of the nature and size of dopants on the properties of deposited PPy films, it appears that for the range of small, compact inorganic dopant anions studied (nitrate, tetrafluoroborate, perchlorate and hexafluorophosphate), except for the nitrate ion giving rise to somewhat larger wrinkles, the conductivity and morphology are essentially independent of the nature of the ions, as indicated in *Table 1*. Of the large dopant ions, the *p*-toluenesulfonate resulted in small wrinkles whereas the dodecylsulfate resulted in very large wrinkles; the dodecylbenzenesulfonate anion, and the 10-camphorsulfonate anion on the other hand resulted only in smooth films.

It is possible that the dense compact wrinkled structure found in films doped by the nitrate and *p*-toluenesulfonate anions are associated with the planar nature of these ions, resulting in the dopant ions being packed more effectively within the PPy matrix. Such observations are consistent with the previously proposed mechanism for formation of wrinkles[7]. That is, if doped polymer begins to form following nucleation within the micro-pores or spaces between grains of indium oxide, when large or rigid dopants are used, nucleation would tend to occur on or near the grain tips of the ITO crystals rather than within the micro-pores or spaces between indium oxide grains. As a consequence, smooth and featureless films will result. In the case of the dodecylsulfate ion, however, it may be that the anion is sufficiently flexible to be able to be accommodated within the growing PPy film, which nucleates within the ITO pores.

Examination of the consequences of electrochemical dedoping of films grown with one specific dopant, *p*-toluenesulfonate, led to rather interesting findings. The undulations in the film comprising the wrinkles disappeared and were replaced by cracks. However, the blisters/pits on the wrinkle surface remained in their original positions relative to the wrinkles. Reduced conductivity and increased N/S ratio confirmed that the film had indeed been dedoped. From past experience we know that complete electrochemical dedoping of other than extremely thin PPy films is difficult, possibly impossible to achieve[17,18]. The appearance of cracks in the dedoped films is likely attributable to shrinkage produced by the removal of dopant ions, which take up a considerable volume of the film. Li *et al.*[20], in an *in situ* AFM study of surface morphology of PPypTS film deposited on gold, also reported film cracking and loss of order following application of a reduction potential (-1.0 V vs. Ag/AgCl) to the film. They attributed these changes to the diffusion of the dopant ions. Control experiments in which light microscopy was used to view freshly made, still-moist PPy films, ruled out the possibility that wrinkles are created post film formation, possibly, for example, as the result of shrinkage during drying under vacuum.

Chemical dedoping of $PPyNO_3$ by treatment with NaOH, on the basis of Qian's reports[19] would have led us to expect a reduction in wrinkle size. As noted in the Experimental section we have not found sufficient overall reduction in wrinkle size in our samples. The fact that the NaOH treatment can be used to dedope polypyrrole is established and beyond question. However, the failure to find morphological evidence for it could be traced to our films being thicker than those reported by Qian or possibly due to more fundamental compositional/structural differences arising from our films being deposited from methanol/water solutions whereas those of Qian were deposited from water. It is possible that we may have been able to produce a more substantial reduction in wrinkle size by preparing thinner films and by using either more concentrated NaOH solutions or longer treatment periods than the 8 h.

By following the formation of films by SEM after various quantities of charge have been passed, we have gained an insight into how a PPy film develops. With very thin films grown in methanol/water mixtures, micrographs were of doubtful value because of severe cracking of the films after drying. The first useful micrograph was obtained with a film grown for 120 s on the $75\,\Omega\,\mathrm{sq}^{-1}$ ITO. This micrograph not only shows both the domes growing, protruding and arising from the ITO microcrevices, but also reveals how wrinkles are formed. Formation of a horizontal layer relative to the anode occurs when continued growth proceeds in solution at right angles to the domes, at their tips and in parallel to the plane of the ITO surface. This micrograph supports the previously described hypothesis for the mechanism of formation of PPy on ITO[7].

We have confirmed the findings of Sutton and Vaughan[6] that wrinkles are not obtained on ITO in aqueous solution with relatively low concentration of pyrrole and *p*-toluenesulfonate. We have taken this further and have demonstrated that wrinkle formation becomes possible with higher concentrations of pyrrole and *p*-toluenesulfonate. When the concentrations of reactants are greatly increased, as in the experiments reported by Mitchell and Geri[5], we do observe wrinkled films in aqueous solutions.

The following mechanism is therefore proposed for the growth of PPy films on ITO in 40/60 methanol/water mixtures. Following the application of a potential to the ITO anode, pyrrole oligomers begin to accumulate on the surface and in the inter-crystalline crevices which then serve as nucleation sites. Growth then proceeds in the manner suggested schematically in *Figure 9* of our previous paper[7]. Initially, the growth proceeds approximately at right angles to the anode, generating fibrils. Once they grow longer than the microcrevices in which they were created, fibrils from neighbouring microcrevices project beyond the ITO layer and join fibrils growing in solution and depositing in a parallel orientation to the ITO surface, eventually forming a coherent layer parallel to the anode and embedding all the fibrils within the film. Further growth of thick films eventually result in a cauliflower morphology. When the film growth is stopped and the film is stripped off the ITO anode, the tips of the fibrils still attached to the ITO surface are snapped off leaving behind holes on the wrinkle surface. PPy films produced on ITO possess the structural features that would be predicted on the basis of the proposed mechanism. Also, the ease with which such films are peeled off the anode is also consistent with the postulated fibrillar attachment of the PPy film to the ITO electrode.

In other studies where gold-plated stainless steel[9], titanium[25] and Pt-plated titanium anodes[26] resulted in wrinkle morphology, the existence and origin of holes or microcracks on the anode surface itself is speculative. However, these may have been formed after repeated use of the same anode, this practice resulting in pitting of the surface, creating a large number of minute holes.

In conclusion, it appears that the presence of microcrevices on the anode surface is a prerequisite for the formation of wrinkles, while the nature of the surface itself is of less importance. Additionally, the nature and size of dopant ions within the film are also implicated in the formation of wrinkles, as demonstrated in the dedoping control experiments. What determines the distance between wrinkles and their depth is difficult to assess at this stage of understanding, but it is likely to be those same factors, which are responsible for the periodic variations in length of the postulated fibrils. In the case of ITO substrates, slight fluctuations in the level of Sn distributed on the ITO surface are likely to play a part in determining the nucleation sites. The range of film thickness for what wrinkles have been observed both in this and in the other studies is $10-80\,\mu\mathrm{m}$. Thus, the thickness of the film, *per se*, does not appear to be an important factor in the development of wrinkles. Consequently, it seems unlikely that stresses developed in the film after stripping it off the anode are responsible for the wrinkle formation, since wrinkles are not generally observed on thin films prepared on Pt or other metal anodes.

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