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Morphological investigation by atomic force microscopy and light microscopy of electropolymerised polypyrrole films

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Abstract

Use of atomic force microscopy (AFM) together with light microscopy (LM) provides an ideal opportunity for studying the initial growth of wrinkles on polypyrrole films. In situ experiments, where continuous AFM image data acquisition was carried out during growth of thin polypyrrole films on indium–tin oxide (ITO) anodes, proved unsuccessful because the height changes occurring during the deposition proved to be too large to handle by the instrument cantilever and fell outside of the range of the *z*-piezo transducer. However, ex situ experiments have yielded valuable information on the earliest stages of film formation. Parallel in situ experiments where growth was followed by dynamic light microscopy imaging complemented the AFM study to yield a clear picture of the mechanism of formation of wrinkles. Additionally, the experiments confirmed that wrinkles are an integral part of the film and are not an artefact induced in films, consequent to shrinkage or drying out. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polypyrrole; Electropolymerisation; Atomic force microscopy

1. Introduction

It is well known that the morphology of free standing polypyrrole (PPy) films grown by electropolymerisation on solid anodes is heavily dependent on the characteristics of the anode, as well as on other experimental variables [1] such as dopant, solvent, applied potential, and post deposition chemical [2] and heat treatment [3]. It is important to understand the relationship between these variables and the morphology, since the latter frequently determines important film properties such as mechanical strength and conductivity. For most films there is a distinct difference in the morphology of the electrode-facing versus the solution-facing side. In other films, unusual features such as wrinkles are reported [4–6]. In some of our previous studies we have reported on wrinkle formation in polypyrrole films deposited on poly(methyl methacrylate) [4] and on indium–tin oxide (ITO) coated glass [7]. Previous literature reports exist of studies of in situ formation of polypyrrole or other conducting polymers by scanning tunnelling microscopy (STM) [8], and by atomic force microscopy (AFM) [9], as well as by optical microscopy at various stages of formation [10]. In the case of the scanning probe microscopy, experiments were generally conducted on the surface of a carbon [8] or on deposited gold substrate [9]. The initially-formed PPy is observed at a molecular level as helices [11] or as microislands at the earliest stages of deposition [9,12–14].

Relatively thick films produced by more extensive growth on ITO coated glass, as well as on metals have also been investigated [5–7]. The morphology of thick wrinkled films was studied by SEM [5–7,15] and has sometimes been complemented by X-ray scattering [5] and by Mossbauer spectroscopy [15]. In some recent reports scanning probe microscopy has also been used to deposit a conducting polymer on specific surfaces [16,17].

In this study we report on an attempt to observe the actual development of wrinkles in PPy films as they grow, i.e. in situ experiments. These will be supplemented by parallel light microscopy experiments which will provide data on thicker films, which are out of the range of AFM experiments. The major aim of all such experiments is to elucidate in detail how wrinkles and their associated blisters/holes are created during PPy film formation on certain anodes. These results are significant as well as practical, since the study will result in determining the variables that favour wrinkle formation. Thus by elimination of such conditions, smooth and relatively high conductivity films could be produced by simple manipulation of the experimental conditions.

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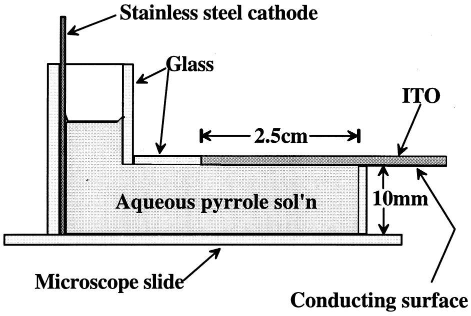

Fig. 1. Schematic diagram of the cell used in the light microscopy study.

2. Experimental

Two sets of experimental conditions were used. Studies involving AFM imaging were carried out at Bristol University (Bristol, UK), while the optical microscopy experiments were performed at Macquarie University (Sydney, Australia). In all experiments one grade of ITO coated glass (Donnelly Applied Films corporation, USA) was used as an anode. It had a nominal surface resistivity of 75 Ω/sq. We were informed by the manufacturers of the ITO (Donnelly Applied Films Corporation) of the method of its preparation [18]. It involved use of the reactive DC magnetron sputtering deposition process with a 90% In–10% Sn target in an argon–oxygen atmosphere with the substrate heated to a temperature not specified by the manufacturer. Prior to use, ITO anodes were prepared by cutting to suitable size, and unless specified otherwise, degreased by Soxhlet treatment with 1,1,1-trichloroethane (AR grade), followed by drying in an oven at 60°C overnight. We have characterised the ITO by several techniques: SEM, FESEM, AFM and STM.

2.1. Atomic force microscopy experiments

For these experiments pyrrole (Aldrich, 98.0%) was purified by passing it through a short Al_2O_3 column [19] for immediate use. Sodium *p*-toluenesulfonate (Aldrich, 95%), and methanol (spectroscopic grade) and distilled water were used directly. All experiments were performed with a methanol/water mixture of 40/60 by volume as solvent. Electropolymerisations were carried out in a single compartment three-electrode cell consisting of ITO coated glass working electrode, and Pt wire counter- and pseudo-reference electrodes. Typical anodes were about 1 cm^2 and were provided with an electrical contact by means of a platinum wire attached with silver glue and superglue. A Ministat Precision Potentiostat (Thompson Electrochem Ltd, Newcastle-upon-Tyne, UK) was used to provide a constant potential at the working electrode. The atomic force microscope used was the Digital Nanoscope III, multimode AFM with a 12-micron scan tube. In situ experiments were performed with an adapted liquid cell, with the cathode and reference electrodes attached through the side hoses, and with the ITO anode wired to the magnetic disc support. The cathode and pseudo-reference electrodes used were both platinum wires. Prior to attempting in situ experiments, initial scouting ex situ experiments were performed with concentrations of pyrrole (Py) and sodium *p*-toluenesulfonate (pTS) of 0.1 M, in order to be able to estimate the most suitable concentrations of these reagents and applied potential that would lead to deposition of a thin film in about 1 h. These concentrations were reduced in subsequent in situ experiments to 0.05 M for both reactants, in an attempt to slow down the reaction so the polypyrrole growth could be monitored by the AFM. An applied potential of 0.7 V vs. the Pt pseudo-reference electrode was used. This value is considerably lower than values used by Sutton and Vaughan in their similar studies (1.2–3.0 V) [20]. At lower concentrations than 0.05 M of both reactants, no visible evidence could be found of film formation.

2.2. Light microscopy experiments

Pyrrole (Aldrich) was doubly distilled immediately prior

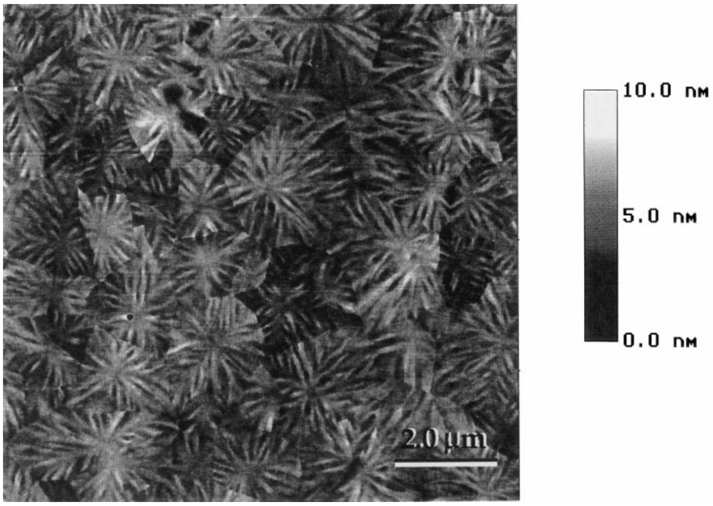

Fig. 2. An AFM image of ITO, 75 Ω/sq in the dry state.

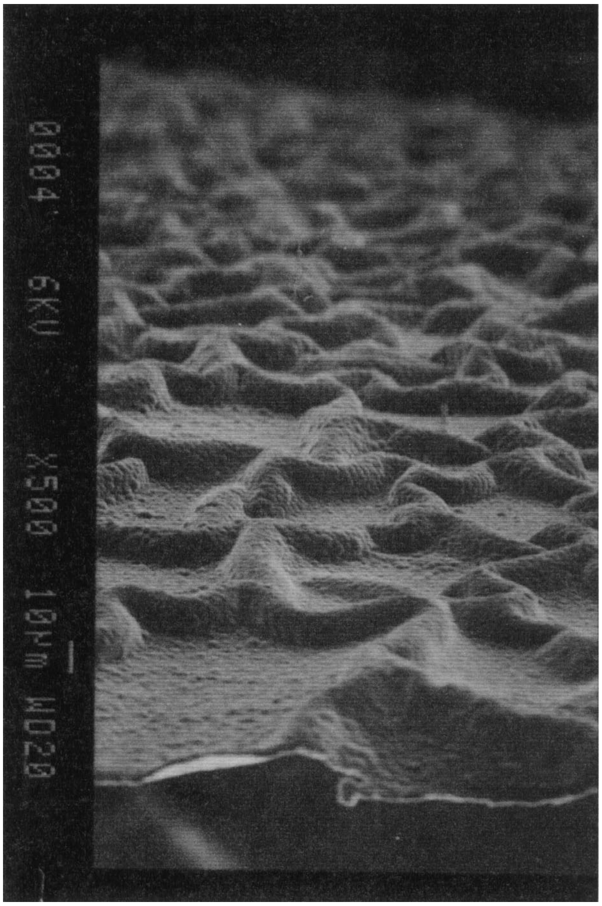

Fig. 3. An SEM micrograph of polypyrrole film formed on ITO, 75 Ω/sq (Ref. [21]).

to use. Unless stated otherwise, electrochemical depositions were carried out using pyrrole (0.25 M) and sodium *p*-toluenesulfonate (0.50 M) in a 40/60 (by volume) methanol/water mixture as solvent. The electrochemical cells were designed so that the conductive surface of the ITO anode faced horizontally down into solution, as shown in Fig. 1. A vertically positioned stainless steel plate served as the counter electrode. Electropolymerisations were carried out at an applied current density of 2.5 mA/3.5 mm^2, which in a comparable cell having a vertical ITO anode configuration, corresponded to an initial applied potential of 1.4 V (vs. SCE) which levelled off to about 1.2 V (vs. SCE) after 15 min reaction period.

Electrodes were allowed to equilibrate in solution for 15 min prior to the application of potential at the start of each experiment. The electrolyte solutions were unbuffered and no attempt was made to exclude atmospheric oxygen during film deposition.

Optical microscopy was performed with an Olympus BH2-UMA unit fitted with an epi-illumination system to allow operation in reflection mode. Magnification in the range 12.5–125 × was used. For static photographs, an Olympus PM-6 camera was attached to the microscope. For dynamic recording, the microscope was attached to a video camera feeding to a video cassette recorder and television monitor.

3. Results

3.1. Characterisation of ITO substrate

The pristine ITO was initially examined by AFM, both in the dry state and in a liquid cell prior to application of electrical potential. As shown in Fig. 2 the surface of ITO was observed by AFM to be covered by layers of spherulitic nature, about 1.5 nm high, with nuclei separated from each other by about 1.2–2.0 μm. The thickness of the ITO layer is reported by the manufacturers to be about 30 nm and our observations are in agreement. However, we cannot determine from the AFM images whether the entire conductive layer consists of sheets of spherulites stacked on top of each other, or whether it is only the region close to the surface which is spherulitic.

3.2. AFM ex situ experiments involving deposition of polypyrrole

This set of experiments included samples of PPy deposits produced in ex situ experiments at various advanced reaction times (greater than 1 min) corresponding to relatively thick films and then subjected to AFM examination. Out of a large number of runs performed we have chosen to describe a few selected examples of typical films. Regarding the various films examined by AFM, it was quickly realised from initial experiments that it would be impossible to observe the surfaces of thick films, since the area of the film that could be imaged was relatively small, only several square microns at best. With extremely thin, flat films, it is possible to observe larger surface areas of up to 10 μm^2. This is illustrated by a micrograph taken in an earlier study (carried out under identical polymerisation conditions), though not included in that publication [21], shown here as Fig. 3. This figure shows an SEM micrograph of a PPy film, deposited electrochemically on ITO, with the film surface tilted at an angle to the incident electron beam, allowing an estimation to be made of the height of the wrinkles. These wrinkles are about 10 μm high, that is, their height approximately equals the thickness of this film measured by a micrometer.

Polymerisations for the ex situ AFM experiments were performed with the ITO anode in either perpendicular or parallel position relative to the vertical cathode and the reference electrodes. However, it was noted that the parameter that mattered most was the relative distances between the three electrodes. Conditions were accordingly adjusted to provide the slowest growing deposit. This information was needed since during in situ experiments within the AFM set up the anode is placed horizontally.

Several independent experiments were conducted where polymerisation was allowed to continue for periods of 2, 4

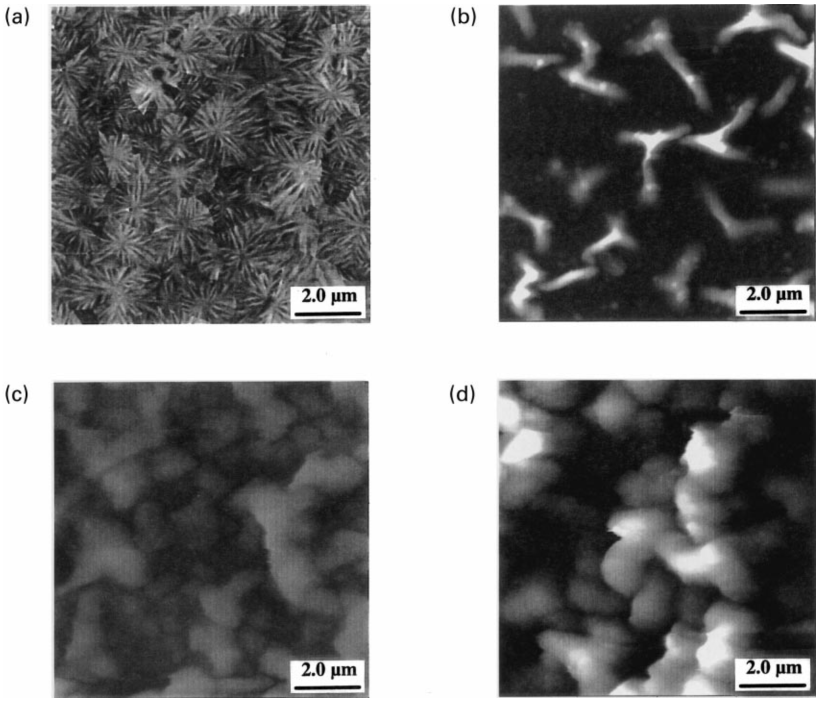

Fig. 4. An AFM image of: (a) ITO, before application of current in an ex situ experiment; (b) the solution-facing side polypyrrole film deposited on ITO, 2 min after application of current in an ex situ experiment; (c) The solution-facing side polypyrrole film deposited on ITO, 4 min after application of current in an ex situ experiment; (d) The solution-facing side polypyrrole film deposited on ITO, 6 min after application of current in an ex situ experiment.

and 6 min. In each case the films were washed in methanol, followed by water, then allowed to dry overnight. These films were then examined by AFM and their images are displayed in Fig. 4(b)–(d), while Fig. 4(a) displays the ITO surface prior to deposition. In these figures the *x*-axis is shown on the individual figures as a bar scale, whereas the height of the features displayed in the images, while not shown, corresponds to 10 nm, 1.0 μm, 2.5 μm, and 3.5 μm for Fig. 4(a)–(d), respectively. These are the maximum depth scales, but typically the film thickness was always less than the maximum, for example in Fig. 4(b) the depth range was 200–500 nm. Thus, it is seen that these are thinner films compared to that shown in Fig. 3.

In the case of the examination by AFM of most of PPy films formed in ex situ experiments, the ITO was glued to the magnetic disc while its other side was covered by the PPy film with its solution facing surface exposed. This procedure was necessary because the PPy films were insufficiently robust to enable them to be attached directly with superglue to the magnetic disk for imaging in the AFM. In

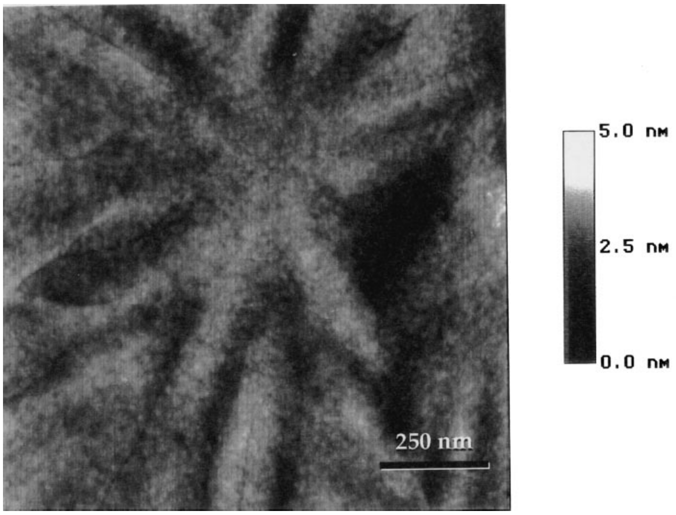

Fig. 5. An AFM image of ITO-facing side polypyrrole film deposited on ITO, 4 min after application of current in an ex situ experiment.

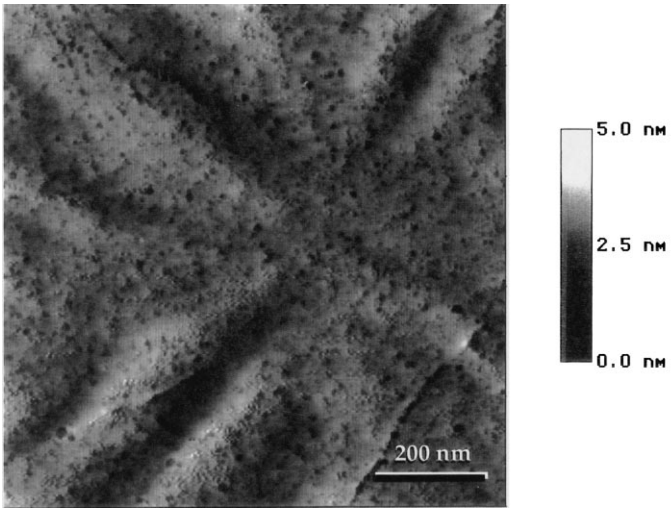

Fig. 6. An AFM image of the ITO surface after removal of the extremely thin polypyrrole film (shown in Fig. 5) by adhesion to the glue on the magnetic disc on the AFM probe.

the case of these thin films, these were so fragile that they tore if any attempt was made to remove them, however carefully, from the ITO. Therefore, it was only the solution-facing side of the PPy film which could be examined by AFM, with the film itself remaining still attached to the ITO. With the AFM used, it was not possible to follow further growth as the film thickens, since the maximum range of height and lateral dimensions observable by the particular AFM scan tube used were 5 μm and 12 μm, respectively, whereas the wrinkles are typically at least 50 μm across and 10 μm high. In contrast, as discussed below, light microscopy provides complementary information on the development of the larger morphological units that form, namely the wrinkles (which according to SEM data range in size from 5 to hundreds of microns [7,21]).

In one experiment, by accident, the PPy film was inadvertently placed directly on the glue with the ITO above it. After the glue dried out the ITO/glass anode separated from, and fell off the PPy film, leaving behind the *ITO-facing side* of the very thin film facing upwards, deposited on the hardened glue, still intact and ready for AFM examination. Thus in this case an opportunity presented itself to examine the ITO-facing side by AFM. Fig. 5 displays this ITO-facing surface of an extremely thin section of film, which was originally observed by the naked eye as a light grey deposit. To ensure that the AFM image observed was genuinely that of the thin PPy film and not that of the spherulites stripped off the ITO-coated glass, on which this specific film was grown and to which it was originally attached, the glass surface from which the film was removed was itself re-examined by AFM. It appeared identical to other samples of clean ITO-coated glass, without any regions which would correspond to the stripping of a thin surface layer, as demonstrated in Fig. 6. Finally, the electrical resistance of this glass was measured and found to be similar to other samples of clean ITO-coated glass taken from the same sheet and again no difference in resistivity was found. This has led us to the conclude that the image of a spherulite displayed in Fig. 5 is indeed a replica of an ITO spherulite reproduced in the PPy film. The image suggests that at least in the very earliest stage of film formation, the spherulites observed on the ITO surface initially do serve as templates on which PPy begins to form as an extremely thin layer of film. However, as is seen in Fig. 4(b), at a later stage these deposits are followed by the development of elongated grains or fibre-like structures arising from some of the inter-spherulitic spaces/crevices or from specific sites, possibly of better conductivity than their surroundings. Later, these grow further out of the plane of the ITO substrate to form complex, Y-shaped units, eventually linking up and forming wrinkles, as will be shown in the sequence of images from the light microscopy work. The above result suggests that placing the film directly on the glue may be developed as a new technique for viewing very thin and fragile films on the electrode-facing side of the anode.

3.3. AFM in situ experiments involving deposition of polypyrrole

These experiments aimed to produce very thin PPy films within the AFM liquid cell at very early stages of polymerisation. In such experiments the ITO surface was observed continuously, before and immediately after being covered by the electrolyte/pyrrole solution in the cell, then after current application, at regular intervals of about 1 min, the minimum time required for a complete scan of the selected area. With the passage of time, the surface appeared to become very slowly covered with a PPy deposit. However, this very early growth was extremely slow and there was still no evidence of the structural features seen in thicker films, as shown previously in Fig. 4(b)–(d). In a typical in situ experiment, during the first 12 min no significant

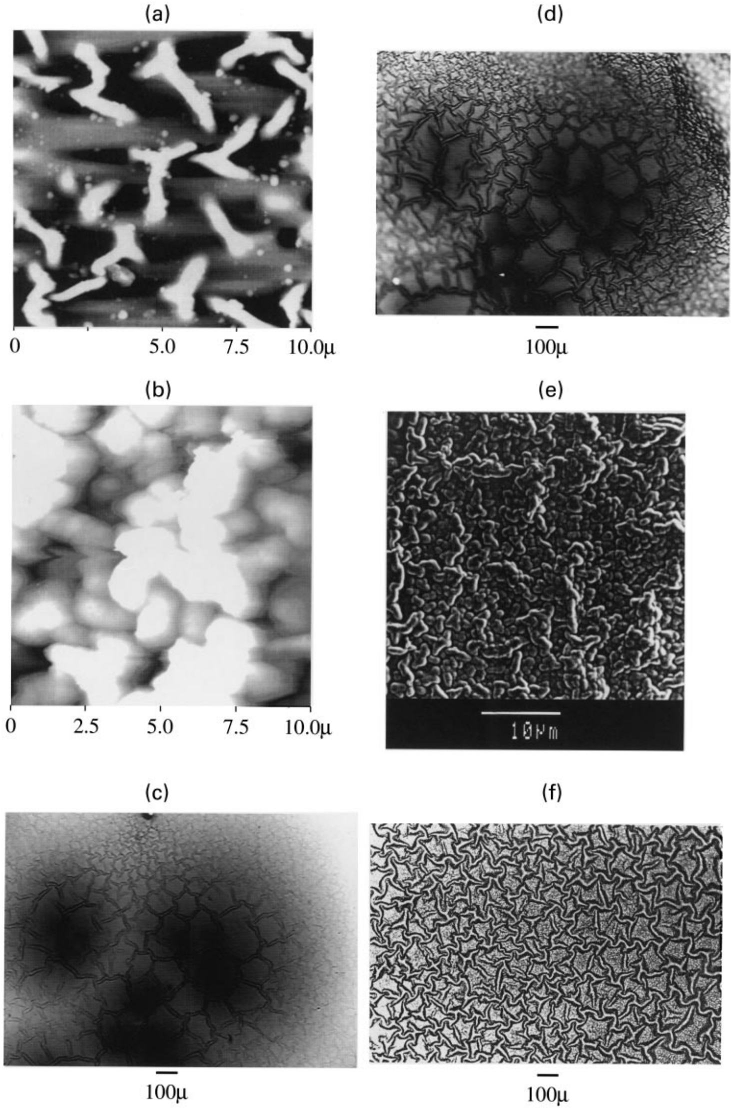

Fig. 7. An overall scheme showing the development of wrinkles in the early stages of polypyrrole film formation, using three different techniques, not in strict time sequence. (a) An AFM image of the solution-facing side polypyrrole film deposited on ITO, 2 min after application of current in an ex situ experiment; (b) an AFM image of the solution-facing side polypyrrole film deposited on ITO, 6 min after application of current in an ex situ experiment; (c) a light microscopy micrograph of a polypyrrole film grown on ITO for 3 min; (d) a light microscopy micrograph of a polypyrrole film grown on ITO for 11 min; (e) an SEM micrograph of a polypyrrole film grown on ITO for 15 min; (f) a light microscopy micrograph of a polypyrrole film grown on ITO for 12 min.

change was noted until suddenly a set of parallel lines appeared across the field of view and the surface became rapidly covered with large particles. It was not clear what caused this change, specifically there was a possibility that the specimen had moved slightly due to the swelling/expansion of the liquid cell O-ring surrounding the ITO sample or to some other subtle change. Hence, the ITO anode was then moved very slightly to another site, and observation was continued, but without success. With the liquid cell used it was difficult to move the ITO-supported magnetic disc more than a very short distance, without the liquid contained in the cell draining away. Further observation of the surface up to 30 min has revealed little regular growth. After 30 min the applied potential was switched off because there was a dramatic and abrupt change to the image, resulting from the appearance of a very large and tall object on the site. Following this event, the film thickness increased too rapidly for the AFM to cope with, resulting in the cantilever being dislodged. It could only be guessed that this was a newly-created nucleating centre, or that the PPy growth had just reached the site of the cantilever. An alternate explanation of the abrupt change in the form of the image could be due to the arrival of a minute gas bubble formed during the reaction. Either way it became obvious that unless the rate of growth of the film could be controlled, imaging would be impossible. Further observation of the surface has revealed little regular growth, if any. The potential was reapplied some time later and still no further change was noted. No changes were noted even when the potential was reversed, unlike the situation in the study reported by Li and coworkers [9].

In conclusion, it became clear that the main problems with the in situ AFM experiments, observing formation of very thin films are: (1) nucleating centres are formed at random and this makes it impossible to locate such a spot for AFM monitoring, and (2) the rate of growth is too fast. Possible improvement of the situation might have been achieved with the use of a large scan tube of 230 μm, which was unavailable to us at the time of the experiment. However, even with the large scan tube it would have been impossible to observe one complete small wrinkle develop. In further in situ runs, attempts were made to slow the rate of deposition by decreasing the concentrations of the reagents and by dropping the potential to below 0.7 V. Neither of these approaches succeeded, resulting either in no deposition or such a slow deposition that no change could be detected. STM has been used to study the formation of extremely thin films on ITO and may have been more successful if applied in this situation [22].

3.4. Light microscopy ex situ experiments involving deposition of PPy

Experiments were carried out in a cell, described schematically in Fig. 1. Experiments were timed with a stopwatch and were allowed to run until the film features became too thick and too dark to be clearly observed. In a typical experiment, images after specific times were selected and photographed off the TV monitor. The earliest photograph was taken at 10 s, followed by others showing further growth up to 14 min. In Fig. 7(f) is shown a film, photographed in transmission mode, taken after 12 min of growth, at which stage it is possible to discern the surface clearly as consisting of a network of interconnected cells and with identical features to those previously observed by us using SEM [21]. A set of images summarising the various stages in wrinkle formation, obtained by AFM, light microscopy and SEM, is in a sequential form in Fig. 7(a)–(f).

4. Discussion

From the combined observations of film formation on ITO arising from the AFM and the light microscopic studies, the following general picture emerges for wrinkle formation in PPy films. Electropolymerisation begins as soon as an electrical potential is applied to the ITO anode immersed in the solution containing electrolyte and pyrrole. From the evidence that Fig. 5 provides, of an initially-formed film covering an ITO spherulite, it is seen that the initially deposited featureless film covers the ITO spherulitic surface, replicating it. However, even at this very early stage other features—small black spots are visible on the AFM micrographs. They range in the size between 5 and 10 nm and appear to be randomly distributed at typical distances of 50–100 nm apart. From the in situ experiment, illustrated by Fig. 4(b), it is possible to identify these spots as sites of torn-off fibres or heavy film growths on areas of high conductivity on the ITO substrate, which eventually develop into substantial elongated granules initially growing vertically out of the ITO surface and eventually in parallel to it. These, according to Fig. 4(c), at a more advanced stage of growth, expand to between 0.5 and 1 μm. Once such structures grow and protrude beyond the ITO surface, they branch out, continuing to expand but in a direction parallel to the surface rather than at right angles, eventually developing into Y- or T-shaped units. Later, as the number of Y-shaped units increases, neighbouring sites link up to form polygon-shaped cells of varying size (Fig. 7(c) and (d)). Beyond this stage, AFM ceases to be useful, while at the same time, this is the earliest detectable stage of film development observable by light microscopy. It is of interest to note that such cells have also been observed by SEM at an early stage of film formation in an earlier study [21], but have been dismissed at the time as some surface impurities.

The parallel experiments of film growth observed by light microscopy now indicate that the initially formed dark/black spots, visually observed on the ITO before film formation are, in fact, clusters of cell-like structures. It appears that the areas bound by larger cells (2000–3000 μm) are darker and grow faster than the areas contained within the smaller cells (100–300 μm). This may be explained by the probability that the smaller cells are bound more tightly to the ITO surface by the greater density of elongated granules to the ITO surface and are therefore less easily pushed away from the surface during growth. Once the film is thick enough to be removed from the surface, blisters/holes are revealed and we suspect that these are the broken ends of the fibres, which leave an imprint on the film. Sections of the film bound by larger cells puff up and rise away from the ITO surface to a greater extent than those in smaller cells during the course of film thickening due to incorporation of dopants. Eventually all cells thicken up and develop into the wrinkle surface, familiar from the previous SEM studies [21], with wrinkle cell areas ranging between 50 and 100 μm in size. The original elongated fibres and the Y-shaped units which develop from them then finally become the cells' boundaries. Thickening of wrinkles is attributed to combined growth and enhanced levels of doping which must occur during reorganisation of the polymer chains in the film structure, when additional areas of conjugated segments of chain approach each other, thus resulting in additional dopant ions becoming incorporated into the volume of the wrinkles. From the micrographs, it is seen that the apex of wrinkles projects further away from the surface with the passage of time.

It is pertinent to make some further observations on wrinkle morphology, which pertain to our previous studies. In the dedoping experiments we described in a previous publication [7], the dedoped samples retain their cellular appearance, but are flattened, presumably due to undergoing the opposite process to that experienced during growth, namely, loss of dopant. The borders between flattened sections still retain blisters or holes which are the original tubular structures on which the framework of cells developed.

In an unreported experiment, one of the authors (J.S.S.) and co-workers [23] have found in another type of an in situ experiment in which the growth of a PPy film on ITO was followed spectroscopically at different potentials, that the size of the absorption peaks associated with polarons and bipolarons decreased when the potential was switched off, presumably due to partial dedoping. In view of our previous experience with dedoping of thick films (thickness about 10 μm), where it was found that loss of dopant caused by the application of reduction potential to the film over a period of time also resulted in the collapse of the wrinkles [7], we might have expected to have observed a change in wrinkle size on switching off the potential. This has not been observed in this study either optically, or by AFM. A plausible explanation for the discrepancy between the two cases could be that the films observed spectroscopically were extremely thin (only about 100 nm or less) and subtle changes in these were detectable, whereas in relatively thicker films this becomes impossible.

5. Conclusions

Development of wrinkles in a growing polypyrrole film, monitored by AFM and light microscopy, illustrated without a doubt that wrinkles are not an artefact of the handling processes of films but are associated with growth on ITO substrates. Our previous studies have suggested that wrinkles are also found in polypyrrole deposited on other substrates and are uniquely associated with growth on a porous substrate. The same most probably applies to some other polymers for which wrinkled surfaces have been reported. Understanding the origins of wrinkles allows us to produce or eliminate them at will, depending on the requirement of the application.

Acknowledgements

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