Electrochemical synthesis of polypyrrole macro-tubes on aluminum substrate

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Abstract

A novel structure of conductive polymer films was synthesized by electropolymerization on aluminum substrate under potentiostatic condition at a relatively high applied potential. A thick film of polypyrrole was electrodeposited onto aluminum substrate from an aqueous electrolyte solution of $NaNO_3$ with pH 12 by applying a constant potential of 2.0 V versus SCE. This polypyrrole film has a good stability with strong adhesion to the substrate surface. However, the morphological structure of the film is different from those previously observed for conductive polymers. Large tubes (ca. 100–200 μm in diameter) are formed, which are spiraled around the cylindrical substrate electrode. Although, the internal channels of these polypyrrole macro-tubes are very wide, the polypyrrole synthesized is sufficiently dense, guaranteeing excellent mechanical stability for this novel morphological structure. On the other hand, such large walls of the macro-tubes have nano-structures.
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1. Introduction

Possibility of electrochemical synthesis of conductive polymers on aluminum substrate has been investigated by different research groups including ours [1–8]. Similar to typical studies of conductive polymers, these investigations are devoted to study of electropolymerization process. In a different strategy, we proposed enhanced stability of conductive polymers deposited on aluminum substrate [1,2]. Thus, such stable polymer films are excellent hosts for enzyme immobilization to fabricate biosensors, since gradual removal of enzyme is a main draw back in conductive polymer-based biosensors.

It has been discussed that the excellent stability of conductive polymers electrochemically synthesized on aluminum substrate is due to the formation of a passive layer as a result of interfacial oxidation of the metallic substrate [9]. However, no attention has been paid to study of morphological structure of conductive polymers growth on aluminum substrate. Following an extensive study of morphological structure of conductive polymers elec-

trodeposited on aluminum substrate under various experimental conditions, we found a particular case leading to the formation of a novel morphological structure of conductive polymer films, which will be communicated here.

2. Experimental

Electrochemical polymerization was performed under potentiostatic condition by applying a constant potential of 2.0 V versus SCE from an aqueous solution of 0.1 M $NaNO_3$ containing 0.5 M pyrrole. The solution pH was adjusted to 12 by adding NaOH. The electropolymerization process was performed at certain times controlling the amount of polymer electrodeposited on the substrate surface. The data reported here correspond to the typical synthesis by applying the quoted potential for 600 s.

The working electrode was prepared from a pure aluminum wire (0.5 mm in diameter). The electrode was carefully polished before electrochemical experiments. All electrochemical experiments were performed using a Princeton Applied Research potentiostat/galvanostat model 173 (PAR 173) equipped with a model 175 universal programmer in conjunction with CorrView software. FT-IR measurements were carried out using a Bruker

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spectrometer. Scanning electron microscopic (SEM) investigations were performed using a Cambridge Steroscan 360.

3. Results and discussion

Fig. 1 shows morphological structure of polypyrrole film electrosynthesized under potentiostatic condition by applying a constant potential of 2.0 V (versus SCE) on the aluminum substrate. The general view of the whole electrode (Fig. 1a) indicates formation of conventional polypyrrole film on the substrate electrode and a novel structure generated on the lateral layer of the polymer film. Polypyrrole macro-tubes are formed on the preliminary polypyrrole film (i.e. a thin film of the polymer electrodeposited directly onto the substrate surface), which
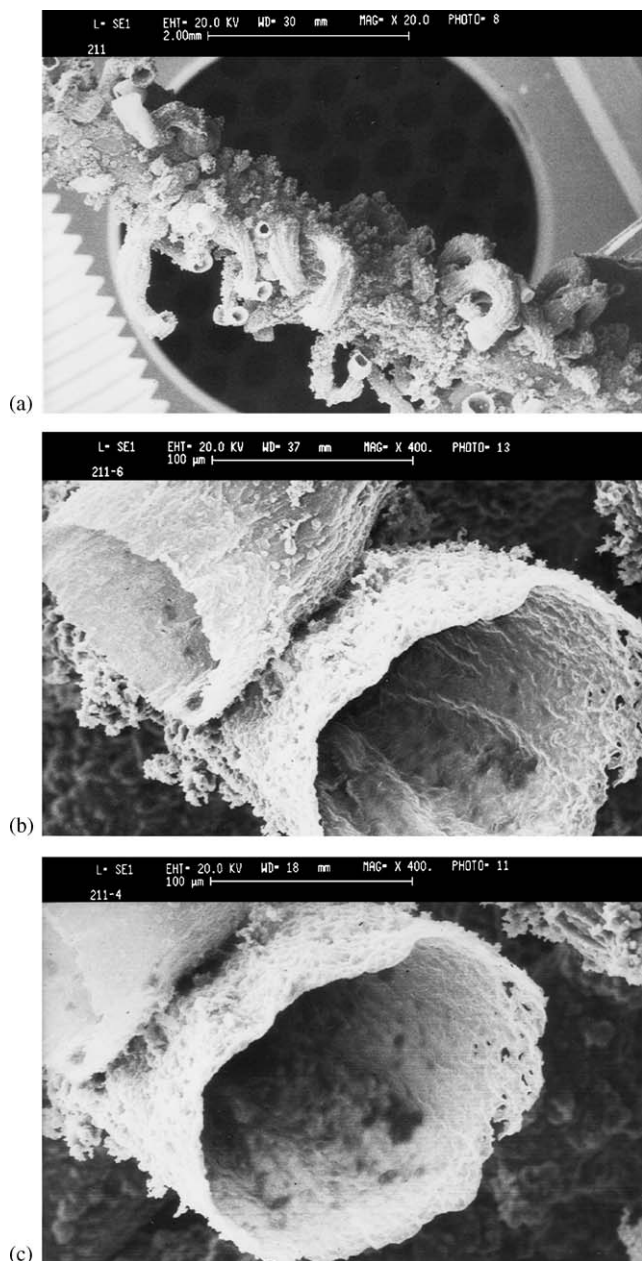

(a)

(b)

(c)

Fig. 1. SEM images of the polypyrrole macro-tubes electrosynthesized on aluminum substrate: (a) the whole electrode and (b and c) individual macro-tubes.

are appeared across the electrode surface (Fig. 1a). Since these polypyrrole macro-tubes are lengthy, they have wrapped around the electrode. These large tubes named macro-tubes are truly wide (Fig. 1b and c), ranging from 100 to 200 μm in diameter. Contrary to this wideness, the lateral walls of these macro-tubes are relatively thin (e.g., 5–10 μm). However, as will be discussed below, these thin walls have excellent stability avoiding breakdown.

As can be judged from the results obtained from scanning electron microscopic investigations, formation of such macro-tubes corresponds to secondary electropolymerization process occurring on the preliminary polypyrrole film electrodeposited in the course of first moments of electropolymerization. This means that the formation of such macro-tubes has not been initiated from the polymer formation on the substrate surface, but on the polymer initially electrodeposited onto the aluminum substrate. In other words, the aluminum substrate results in the formation of an apparently conventional film of the polymer, which acts as the backbone for the formation of such macro-tubes in the course of the electropolymerization progress. Although, it is evident that the generation of such polypyrrole macro-tubes is due to the structure of the preliminary polypyrrole, it is not the only controllable parameter to obtain the macro-tubes. In fact, the main feature of the present work leading to synthesis of such special-shaped macro-tubes is applying a relatively high constant potential, which is not usually common for synthesis of this class of conductive polymers (since they can be easily electrosynthesized at lower potentials).

By looking at preliminary polypyrrole film existing beneath the polypyrrole macro-tubes (e.g., from an electrode such as that illustrated in Fig. 1a), it is possible to judge about its morphological structure. Fig. 2 indicates that morphological structure of the preliminary polypyrrole film is completely conventional. For instance, the SEM illustrated in Fig. 2a is exactly similar to that reported in Ref. [10]. Saidman and Quinzani [10] synthesized polypyrrole at potential of 0.9 V (versus SCE). At this potential, the preliminary polypyrrole forms as well as the present work, but formation of macro-tubes is improbable. This is due to the fact that electropolymerization at lower potential is more difficult. Whereas, in the present case, high applied potential strengthen the electropolymerization leading to the occurrence of an additional process generating the macro-tubes.

This leads us to a conclusion that although the preliminary polymer film formed at high or low applied potentials are apparently the same, but their properties are significantly different, as that prepared under a low potential (as reported in the literature) is not capable of being the backbone for the formation of the above-mentioned macro-tubes. In other words, the preliminary polymer film plays an important role in the formation of such macro-tubes, though revealing the exact mechanism needs further investigations from fundamental points of view. It should be emphasized that the formation of the preliminary polymer and such macro-tubes are just two stages of an electropolymerization process, and cannot be distincted. This means that the mechanism of nucleation and growth of the polymer just beginnings on the substrate surface, but initially it leads to the formation of an apparently conventional film, and subsequently the macro-tubes.

(a)

(b)
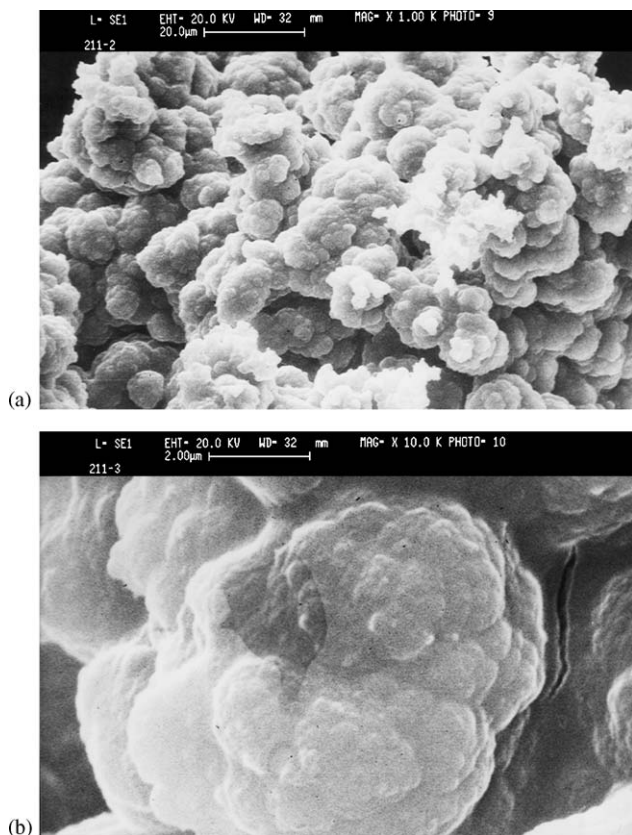
Fig. 2. (a and b) SEM images of the preliminary polypyrrole layer (the layer beneath the macro-tubes).

Fig. 3. FT-IR spectrum of the polypyrrole macro-tubes cut from the polypyrrole layer directly growth on aluminum substrate.

Although, the lateral layer (containing the macro-tubes) formed on the electrode surface has a good stability, it is possible to cut the lateral layer because of its large thickness. This provides an excellent opportunity for the synthesis of powders of such polypyrrole macro-tubes. In other words, electrochemical polymerization of such macro-tubes is not restricted to the preparation of films attached to electrode surfaces. Of course, this can be utilized for the preparation of milligrams of the polymer (depending on the electrode size), as the thick films of ca. few millimeters can be easily cut, and even upon further progress of the electropolymerization, the depositing film can be simultaneously falls from the electrode surface, to be precipitated at the bottom of the electrochemical cell.

To inspect the chemical structure of the polypyrrole macro-tubes synthesized, FT-IR technique was used as a reliable method in this context. To assure that the results correspond to the secondary layer (the polypyrrole macro-tubes) not the preliminary layer (the conventional polypyrrole film electrodeposited directly on the substrate surface), the lateral layer was cut for FT-IR measurements. Fig. 3 depicts a typical FT-IR spectrum of the polypyrrole macro-tubes. It is obvious that it is characteristic of a conventional polypyrrole. Indeed, there is no difference in chemical structure of the preliminary and secondary layers, but significant differences in morphological structure. In other words, the additional electropolymerization process leading to the formation of polypyrrole macro-tubes just controls the polypyrrole morphology.
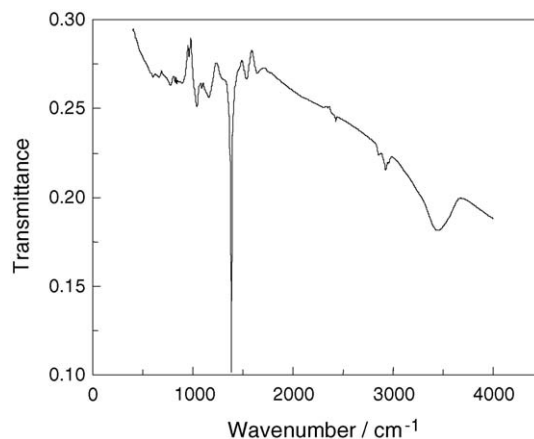
On the other hand, the FT-IR spectrum is similar to that reported for the preliminary polypyrrole layer synthesized in the same experimental condition but at potential of 0.9 V (versus SCE) [10]. The spectrum indicates a sharp peak at 1357 cm^{-1} corresponding to the nitrate dopant [11]. This shows that even anion doping of the polypyrrole macro-tubes is similar to that of conventional polypyrrole film electrodeposited on the substrate electrode.

Since the electrochemical polymerization was performed under potentiostatic condition, corresponding chronoamperometric measurements can reveal the process associated with the formation of the polypyrrole macro-tubes. A typical chronoamperogram of the system under investigation is illustrated in Fig. 4a. For electrochemical investigations, the polymerization process was performed in two steps: first 100 s and then additional 500 s. By this strategy, it is possible to inspect chronoamperometric response of the system under investigation in the course of the formation of polypyrrole macro-tubes, since the preliminary layer is completely formed in the first step (i.e. first 100 s).

It is obvious that the curve of the current changes has pulsed-shape indicating the formation of this novel morphological structure. It is believed that the backbones of the macro-tube are formed when the current has a sudden rise in each pulse, and the macro-tubes grow when the current is approximately constant. Interestingly, the pulse heights are approximately the same, which indicates that the process of formation of the macro-tube backbones is independent of the progress of film growth. Whereas, the steady state parts of the pulses are significantly longer when more time is passed. This is in good agreement with the morphological analysis, since longer macro-tubes are found for thicker films (longer electropolymerization).

To inspect the possibility of the formation of the polypyrrole macro-tubes at the first movements of the experiment, the chronoamperogram was enlarged (Fig. 4b). It can be observed that pulsed-shape increase of the current starts at the beginning of the experiment. This shows that when the preliminary layer of the polypyrrole is available, the polypyrrole macro-tubes begin to grow at the first moments of experiment. The chronoam-
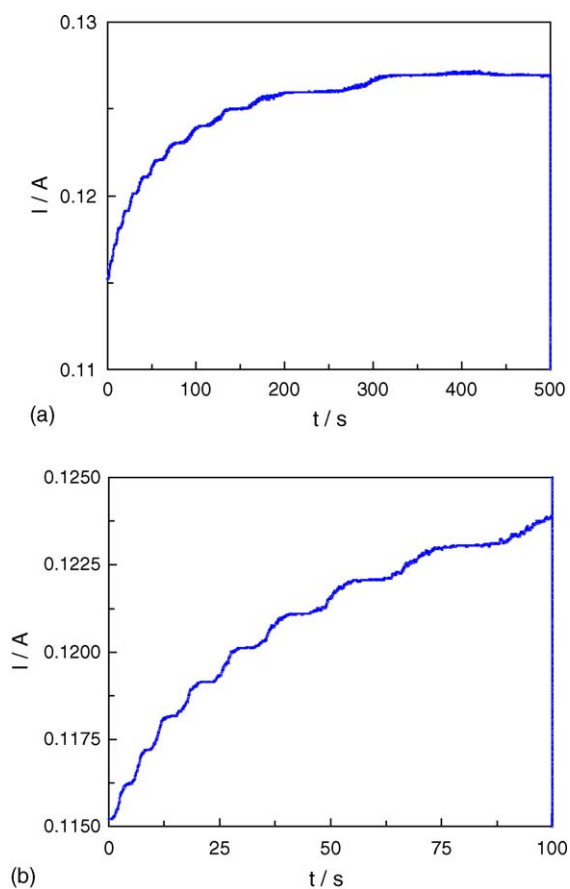
Fig. 4. (a and b) Chronoamperogram of pyrrole electropolymerization on aluminum electrode by applying a constant potential of 2.0 V (vs. SCE). Before this experiment, electropolymerization was subject of 100 s electropolymerization at the same experimental condition to assure about the formation of the preliminary polypyrrole layer.

perogram of the polypyrrole on bare aluminum substrate (the first 100 s) is similar to that illustrated in Fig. 4b (i.e. the second 100 s of the polymerization), but pulsed-shape peaks are absent (not shown). This means that at the first moments of the polymerization process, polypyrrole film grows on the base aluminum substrate, and the in subsequent stage the polypyrrole macro-tubes form on the polypyrrole film. When starting with a 600 s chronoamperogram for a bare aluminum electrode (note that Fig. 4a is a 500 s chronoamperogram for a polypyrrole-coated electrode), after preliminary stage corresponding to the growth of preliminary polypyrrole layer, some pulsed-shape peaks appear.

The morphological structure of the preliminary layer is not highly sensitive to experimental conditions, as electropolymerization of pyrrole on aluminum substrate at different applied potentials and electrolyte solutions leads to similar morphologies [3,10] (like that obtained in the present case as illustrated in Fig. 2). The different influence of the experimental condition utilized in the present work appears during long electropolymerization when a sufficient time is passed and secondary layer begins to grow on the preliminary polypyrrole layer. At low potentials employed in the literature, only particle sizes increase upon the polymerization progress [10].

More recently, Fujikawa et al. [12] have reported an interesting synthesis of nano-structured polypyrrole. They have synthesized polypyrrole donuts by a similar electrochemical process. Although their work is significantly different from the present work, however, there are some similar features deserve further comparison and discussion. The polypyrrole donuts reported in Ref. [12] are nano-objects and about three orders of magnitude smaller than the macro-tubes reported here. The similarity of these two works is the preliminary formation of annular backbones. In the case of nano-donuts [12], upon further polymerization the annular backbones grow horizontally to form donuts (this process needs particular control to avoid change of the donut shape to conventional particles). Whereas, in the present case, the large annular backbones grow vertically to form long macro-tubes, and this process does not need any control.

However, the chronoamperometric measurements performed in Ref. [12] regarding the formation and growth of annular backbone is similar to the case reported here. Fujikawa et al. [12] showed that the formation of the annular backbones occurs at the chronoamperometric peaks and their further growth occurs at the steady state parts of the chronoamperogram. This is exactly what detected in our experiments. In fact, similar morphological structure of conductive polymer is of particular interest, and considerable attention has been paid to this issue [12–18].

Of course, the present work is significantly different from those previously reported, as these are ideal tubes with constant diameter. Whereas, the micro-containers tend to form closed tubes by further polymerization [14]. This can be another advantage of the present work, as there is no need for controlling the polymerization progress to obtain the structure under investigation, but the special structure of micro-containers will just be formed at a certain degree of electropolymerization. Although, a comparison with Ref. [12] was made to propose a possible mechanism for the system under consideration, but it should be emphasized that the main motivation for the formation of such structures is different. It has been claimed that the gas bubbling is responsible for the formation of micro-containers [14], but it cannot be the case for the system under investigation, as the tube is very long. In fact, the mechanism of the formation of such macro-tubes is so complicated.

According to the results reported and discussed above, possible conditions and mechanism of the formation of the polypyrrole macro-tubes were understood. Since this novel morphological structure is of particular interest for applied purposes, it is necessary to investigate the microscopic structure of such macro-tubes. Although it seems that such macro-tubes are unstable and falls from the electrode (as stated above for extremely thick films), the polypyrrole macro-tubes had good mechanical stability upon conventional handling, as no mechanical destruction of the macro-tubes was observed. Although, general view of the macro-tubes (Fig. 1) apparently suggests that the tube walls are very porous and fragile, closer look at the tube walls indicates a stable and dense structure. Fig. 5 illustrates different places of a polypyrrole macro-tube. It is observable that though there are some holes within the tube walls (mainly on the head of the tube), the polymer structure is significantly dense.
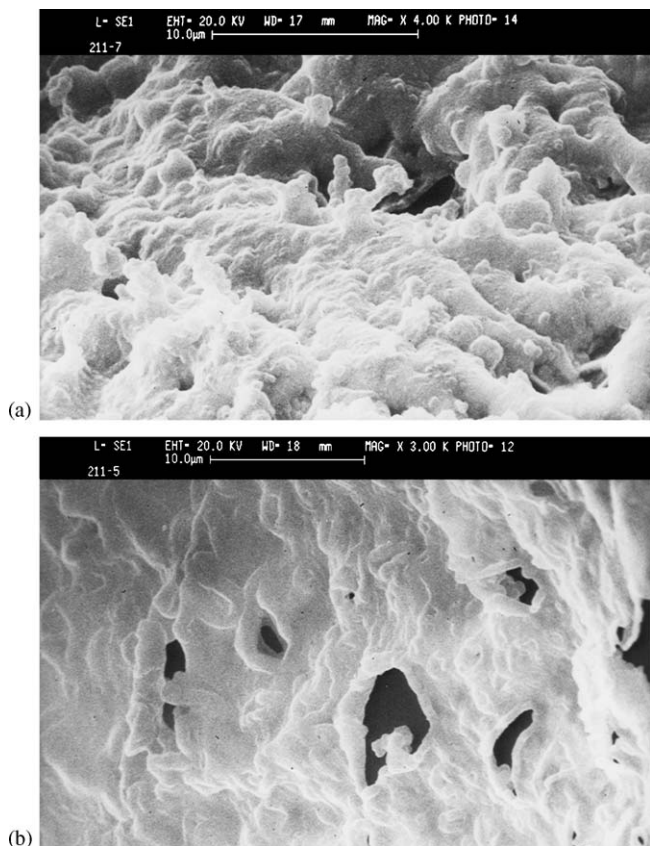
Fig. 5. SEM images of the polypyrrole macro-tubes taken from: (a) middle and (b) head of a macro-tube.

The results reported provide an opportunity for the preparation of macro-tubes of conductive polymers by means of a simple approach. This method is of double interest, since can be used for the preparation of both film and bulk. For thinner films, it is possible to attach such macro-tubes on the polymer-coated aluminum substrate. In fact, aluminum is known as an excellent substrate for the deposition of various electroactive films [19–21], not only for conductive polymers. On the other hand, it is possible to synthesize bulk of polymer macro-tubes by preceding the polymerization process to form extremely thick films. Since the size of these macro-tubes is very large, it is truly easy to handle individual macro-tubes for specified applications. For instance, individual polymer macro-tube can be used for the construction of numerous microdevices employing organic electronic materials.

4. Conclusion

The present work proposed a simple method for the fabrication of a novel morphological structure of conductive polymers, which may be of particular interest for applied performances. In fact, it was demonstrated that not only aluminum is an excellent substrate for the deposition of stable conductive polymer films, but also it can be used to control morphology of conductive polymer films. In spite of the general similarity, this structure is different from that of micro-containers recently reported in the literature, as the tube diameter is approximately constant across the tube. This special morphological structure is formed on the polymer backbone directly formed on the aluminum substrate. In other words, not only the polymer growth but also the initial formation of the polymer on the substrate electrode are both responsible for the formation of this special structure.

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