Polypyrrole Fibrils Synthesized on ITO Electrode in the Presence of Polyacrylic Acid

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(Received December 16, 2002; CL-021067)

In the presence of polyacrylic acid (PAA), oriented growth of polypyrrole (Ppy) was achieved on tin-doped indium oxide (ITO) electrode by electropolymerization. The resulting Ppy exhibits unusual fibrillar morphology. The possible mechanism responsible for the formation of Ppy fibrils was discussed.

Conducting polymer fibrils may be very useful in many fields[1,2] involving electroanalysis, electrocatalysis, energy storage, microelectronics, etc. However, the construction of conducting polymer fibrils has been impeded due to the poor processability of conducting polymers. To circumvent this problem, one of the proper strategies is to synthesize conducting polymer fibrils directly in the procedure of processing, rather than after it; therefore, oriented growth of Ppy must be achieved. Several methods, which include electrospinning,[3] using composite electrode,[4] in situ doping polymerization,[5] doped by inorganic acid,[6] and template synthesis method,[7] have been used for preparing conducting polymer fibrils followed the strategy mentioned above. To date, conducting polymer fibrils, including polypyrrole and polyaniline fibrils, are mainly obtained by using a porous membrane as template. Recently, we found a new method to synthesize Ppy fibrils directly on the graphite electrode in the presence of poly(maleic acid-co-vinyl pyrrolidone) (PVP-MA) without using a supporting template.[8] Compared with membrane-templated synthesis, it is easier to prepare Ppy fibrils through direct electrochemical deposition, therefore opening up a new strategy for direct synthesis of conducting polymer fibrils on a variety of electrode materials. In order to prove the reliability of the new strategy, herein, we report the direct synthesis of Ppy fibrils on the ITO electrode in the presence of PAA.

The electropolymerization experiment was conducted in a one-compartment cell using a saturated calomel electrode (SCE) as the reference electrode, a platinum coil as the counter electrode, and a piece of ITO (active area = 0.5 cm^2) as the working electrode. The experiment was performed on TD 73000 Electrochemical System controlled by a computer. The solution used in the experiments contained 0.075 M $LiClO_4$, 0.15 M pyrrole, 0.2 M phosphate buffer solution (pH = 6.86) and 0.4 wt% PAA. The Ppy fibrils can be electrogenerated on the ITO electrode by potential step experiment.

The morphology of Ppy prepared by this method was examined under a scanning electron microscope (SEM) (Philip XL30). As Figure 1A shows, as-obtained Ppy clearly exhibits unusual fibrillar morphology. The diameters of the fibrils are about 90 nm.

Like PVP-MA, there are many carboxyl groups along the molecular chains of the PAA. When PAA is dissolved in water, pyrrole molecules will be attracted onto the surface of these carboxyl groups by forming hydrogen bond. Therefore, when electropolymerization was initiated, the adsorbed pyrrole monomer will polymerize along the chain of PAA, thus the oriented growth of Ppy was achieved. Then the formed oligomers will precipitate out from solution and deposit onto the ITO electrode to form the nucleation sites to grow extended Ppy fibrils. Figure 2 is a schematics diagram describing the oriented growth of Ppy fibrils.

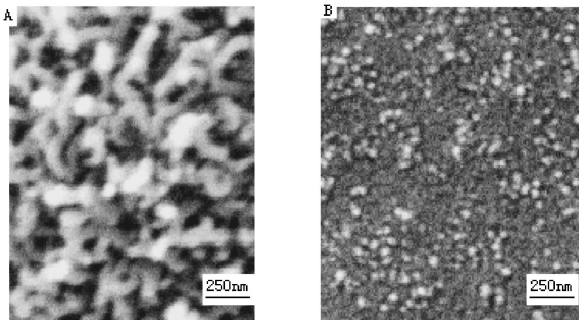

Figure 1. SEM images of Ppy synthesized at different times. 0.80 V vs SCE, 0.075 M $LiClO_4$, 0.15 M pyrrole, 0.2 M phosphate buffer solution (pH = 6.86) and 0.4 wt% PAA; (A) 60 s; (B) 5 s.

To confirm the possible mechanism mentioned above, we examined a sample after a short time of electropolymerization (5 s). At this stage the polymer deposited onto the ITO surface as small particles about 30 nm in diameters (Figure 1B). This may be in accordance with the nucleation stage and accordingly the particles may be the nucleation sites. If the electrochemical deposition was extended for 60 s, much longer fibrils were observed (Figure 1A).

Figure 3 shows the FTIR spectra of the Ppy formed with and without PAA under the same condition. According to Martin et al.,[9] based on a study by Zerbi et al.,[10,11] as the conjugation length is increased, the peak intensity of the asymmetric ring stretching mode will decrease relative to the peak intensity of the symmetric mode. Therefore the ratio of the integrated absorption intensities at 1537 cm^{-1} (corresponds to the asym-

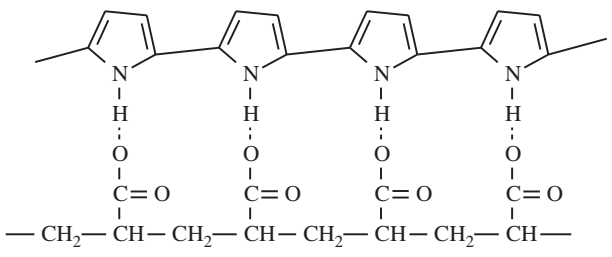

Figure 2. Schematic diagram describing the oriented growth of PPy.

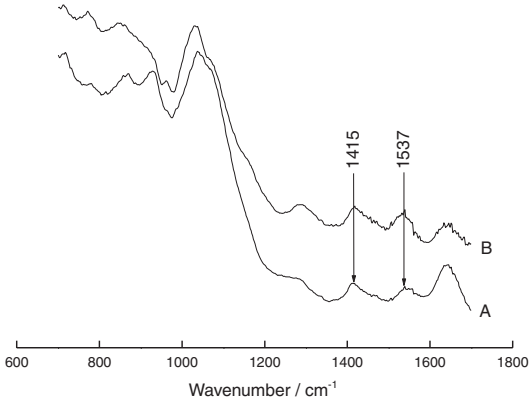

Figure 3. FTIR spectra of Ppy (A) formed with PAA (Ppy fibrils) and (B) without PAA (bulk Ppy) under the same condition.

metric ring stretching mode) and 1415 cm^{-1} (corresponds to the symmetric mode) (A_{1537}/A_{1415}) for the Ppy sample is used as a measure of the conjugation length and thus the conductivity. From Figure 3, the value of A_{1537}/A_{1415} of Ppy fibrils is 0.48, which is lower than that of the bulk Ppy (0.92). These mean that as-obtained Ppy fibrils have enhanced conjugation length and thus the conductivity. The room temperature conductivity of the Ppy fibrils is about 80 S/cm, which is much higher than that of the bulk Ppy ($\approx$30 S/cm).

In summary, the Ppy fibrils have been synthesized directly on ITO electrode in the presence of PAA. We propose that Ppy fibrils are resulted from the oriented growth of Ppy along the molecular chain of PAA. The resulting Ppy fibrils have enhanced conjugation length and the conductivity. This is a novel approach for synthesizing Ppy fibrils and we believe it will have great potential for preparing other conducting polymer fibrils as well.

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Published on the web (Advance View) May 20, 2003; DOI 10.1246/cl.2003.528