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Selected Paper

Three-Dimensional Morphological Chirality Induction in Polythiophene Polymer Deposit Using a Magnetic Field

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Effects of a vertical magnetic field on the three-dimensional morphology of a polythiophene deposit formed by anodic oxidation were examined. At 4 T, a left-handedly twisted polymer deposit is obtained, although the shape is uncurved in a zero field. The twist configuration is right-handed when the field direction is reversed. The mechanism of magnetic field effects is discussed.

Magnetic fields are attractive tools in materials science. Using magnetic fields, we can control various chemical and physical processes and thereby control morphologies and chemical and physical properties of materials.[1] In a previous paper,[2–5] we reported, for the first time, three-dimensional (3D) morphological chirality induction using a magnetic field. Helical and twisted membrane tubes can be formed in a silicate garden reaction through application of a magnetic field. The results are interpreted as the Lorentz force acting on the ions in an outflow from the tube top. Analogous results were reported by Yokoi et al.[6,7] Therefore, it is interesting to examine whether 3D-morphological chirality induction is possible in other reactions.

Regarding electrochemical reactions, two-dimensional chirality induction by magnetic field has been reported. In a two-dimensional electrolysis cell, a polythiophene deposit grows clockwise and spirally in a magnetic field, although it grows radially in a zero field.[8] Analogous magnetic field effects (MFEs) on the electrochemical polymerization of pyrrole have also reported.[9] However, no reports in the relevant literature describe 3D-morphological chirality of a polymer deposit.

As described in this paper, we studied MFEs on anodic oxidation of thiophene as another example of 3D-morphological chirality induction using a magnetic field. We prepared a twisted polythiophene polymer deposit on an anode. The mechanism for 3D-chirality generation is discussed.

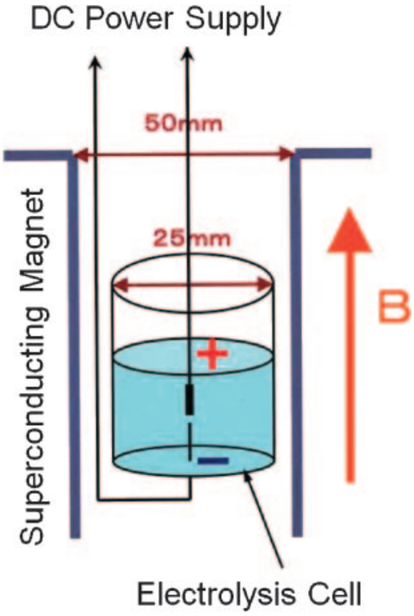

Figure 1. Experimental setup for electrolysis in a strong magnetic field.

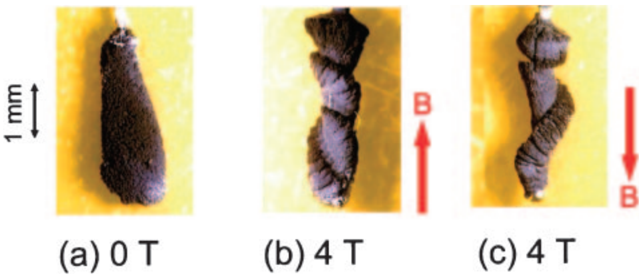

Figure 2. Photos of polythiophene polymer deposit formed on an anode: (a) 0 T, (b) 4 T (up-field), and (c) 4 T (down-field).

Experimental

Thiophene (S grade; Wako Pure Chemical Industries, Ltd.), lithium perchlorate (S grade; Wako Pure Chemical Industries, Ltd.), and acetonitrile (S grade; Wako Pure Chemical Industries, Ltd.) were used as received. Aerated acetonitrile solutions containing thiophene ($0.5\,\mathrm{mol\,dm^{-3}}$) and lithium perchlorate ($0.1\,\mathrm{mol\,dm^{-3}}$) were used for electrolysis.

Figure 1 portrays a schematic diagram of the experimental setup. A glass electrolysis cell (φ, 25 mm; height, 40 mm) was equipped with an anode (Pt; φ, 0.3 mm; length, 5 mm) and a cathode (Pt; φ, 1 mm; length, 10 mm). A cell containing a 10 mL of acetonitrile solution was placed in the bore of a superconducting magnet (HF5-50VT-M2; SHI). The distance between the two electrodes was about 8 mm. Electrolysis was conducted using a potentiostat/galvanostat (HA151; Hokuto Denko Corp.) at room temperature under a galvanostat mode (1 mA, 60 min).

The shape and surface of the polymer deposit on the anode were observed using an optical digital microscope (Keyence Co.) and a scanning electron microscope (JSM-5400; JEOL).

Polythiophene polymer deposits were formed by anodic oxidation on the surface of an anode. To investigate the influence of a magnetic field on the polymer deposit shape, anodic oxidation was conducted in the magnetic field. Figure 2 depicts MFE on the polymer deposit shape. In a zero field, a

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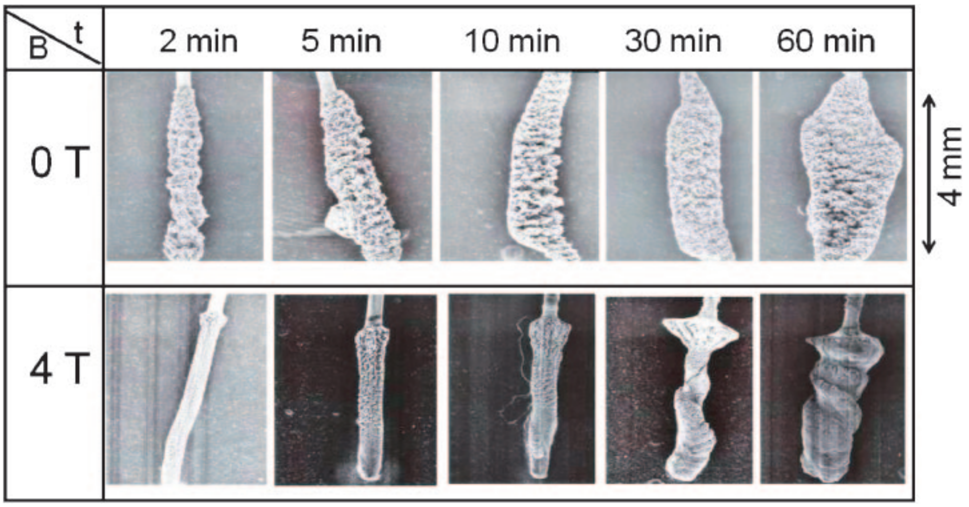

Figure 3. SEM images of polythiophene polymer deposit in the absence and presence of a 4 T field as a function of reaction time (*t*).

deposit with an uncurved surface was obtained (a). A left-handedly twisted deposit was formed in the presence of a vertical 4 T field (b). The pitch of the deposit was slightly less in a higher magnetic field: changing it from 1 to 4 T changed the pitch from about 1.5 mm to about 1 mm. A right-handed twisted deposit was obtained when the field direction was reversed (c).

In this reaction, the solution included a nonelectrolyte (acetonitrile and thiophene) and an electrolyte (lithium cation and perchlorate anion). During electrolysis, anions moved to the anode and cations moved oppositely because of the electric force. Because of collision, the force acting on ions was transferred to the solvent and the solute molecules surrounding them. Consequently, the acetonitrile solution containing thiophene was transported to the anode, where thiophene oxidation occurred.

In a magnetic field, the Lorentz force $\boldsymbol{F}_\mathrm{L}$, which is given by the following equation, affects the motion of ions in solution.

$$\boldsymbol{F}_\mathrm{L} = q\boldsymbol{v} \times \boldsymbol{B}/\mu_0 \tag{1}$$

In that equation, q is the ion charge, $\boldsymbol{v}$ signifies the velocity of the ion, $\boldsymbol{B}$ is the magnetic flux density, and μ_0 is the magnetic permeability of vacuum. The Lorentz force acting on ions is transferred to the solvent and solute molecules surrounding them, resulting in convection of the solution (magnetohydrodynamic (MHD) convection), which is the cause of the chemical reaction yield and morphology changes of the deposit on the anode. The observation that the deposit pitch decreases concomitantly with increasing magnetic field is explainable qualitatively by the MHD convection, as discussed in an earlier report.[2] According to eq 1, the direction of MHD convection depends on the magnetic field direction. Therefore, eq 1 explains the observation that reversal of the field direction changes the chirality of the twisted polymer deposit from a left-handed to right-handed configuration. Indeed, in situ observation of the solution motion in a magnetic field confirms that the solution undergoes MHD circular convection to the left-handed configuration with a speed of 10–15 $\mathrm{mm\,s^{-1}}$ during oxidation when an upward magnetic field of 4 T is applied. The deposit is twisted along the direction of MHD convection.

However, the above-described argument does not explain why the MHD convection induces twisted growth of the polymer deposit on the anode: the twisted deposit cannot be formed if the solution around the anode moves uniformly. To clarify the mechanism of 3D-morphological chirality induction, additional experiments were conducted.

Figure 3 portrays SEM images of the deposit surface obtained at several reaction times. After growth in a zero field, the deposit has a bulky and uncurved surface; its morphology does not differ markedly according to the reaction time. After short reaction times (2, 5, and 10 min) in a magnetic field, the deposit displayed a fine and dense surface that is not twisted. After long reaction times (30 and 60 min) the surface was twisted, indicating that a twist formation is not inherent in the magnetic field effect. Instead, it is acquired during a long reaction time. Results show that the pitch of the twist deposit is influenced considerably by experimental conditions such as the solution volume and electrolysis cell size, suggesting that a twisted surface can be formed as a result of non-uniform motion of the solution moving around the anode. We tentatively propose the following mechanism for twisted deposit growth. Upon anodic oxidation in magnetic field, MHD convection of the solution occurs. The convection around the anode is not uniform. The solution near the surface moves somewhat rapidly because it has an open surface. The inner bulk solution moves somewhat slowly because it is impeded by the bulk solution, whose motion is affected by frictional force from the cell wall. Influence of the non-uniform flow might be negligibly small when the thickness of the deposit is small. During growth, the effect might become substantial because of the deposit surface impedance.

The present mechanism of 3D-morphological chirality generation differs slightly from that of a silicate garden reaction, in which chirality induction is considerable because the magnetic field affects the outflow from the tube top directly at the growth point of the tube. In the present case, chirality induction is not great: 3D-morphological chirality is not induced solely by MHD convection. To induce a twisted shape, inhomogeneous convection might be necessary near the anode. The present result suggests the potential application of a magnetic field for 3D-morphological chirality induction of functional materials formed by electrochemical reaction, although further study is necessary to clarify the mechanism in detail.

So far we have focused our attention on the morphological effect of magnetic fields. However, it is most probable from Figure 3 that not only the morphology but also the physical properties of the deposit could be dependent on both magnetic field and reaction time, as reported in two-dimensional polythiophene deposits.[8]

In conclusion, MFEs on the 3D-morphology of polythiophene polymer deposit prepared by anode oxidation were studied. Through application of a vertical 4 T field, the deposit surface becomes left-handedly twisted, although it is not curved in a zero field. The twist has a right-handed configuration when the field direction is reversed, suggesting that inhomogeneous MHD convection around the anode causes the twist.

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