Electrochemical Properties of Polypyrrole-Coated Microelectrode Array and the Fabrication of Polypyrrole-Based Microelectronic Devices*

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Introduction

Conducting polymers have been studied extensively. An interesting property of the conducting polymer is that the conductivity of some polymers, such as polypyrrole, polyaniline, poly(3-methylthiophene) *etc.*, is affected by the voltage applied to them. For polypyrrole, the oxidized state is an electronic conductor and the reduced state is essentially insulating. Using this property, one can fabricate the polymer-based electronic devices. Experimental results of Pickup and Murray[1] showed that "diodes" and "triodes" could be prepared using macroscopic electrodes derivatized with a redox polymer and coated with a porous metal contact. Recently, microelectrode and microelectrode array have received much attention. Several microelectrochemical transistors based on closely spaced microelectrode connected by electroactive materials have been developed by Wrighton's groups[2—9], including those based on platinized poly(3-methylthiophene), a viologen/quinone polymer, ferrocyanide-loaded, protonated poly(4-vinylpyridine), WO_3 and $Ni(OH)_2$. Furthermore, with electrostatic incorporation of the reversible electroactive anionic metal complexes into protonated poly(4-vinylpyridine), microelectrochemical multitransistor devices can be fabricated[10].

We studied the electrochemical properties of polypyrrole-coated microelectrode array in 0.1 mol/L KNO_3 solution and demonstrated the possibility of fabricating microelectronic devices based on the dramatically change in conductivity of polypyrrole as a function of applied voltage. This work is significant for the fabrication of molecules-based microelectronic devices and sensors with various

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functions.

Experimental

1 Preparation of the Microelectrode Array

The fabrication of microelectrode array begins with the design of the array with the aid of computer and the preparation of the masks to be used in the microfabrication procedure. A two-mask process was designed. The first mask was used in a metal lift-off procedure to form the microelectrodes, leads and contact pads. The second mask was used to pattern a photoresist overlayer leaving the microelectrodes and the contact pads exposed. The complete details of fabrication procedure are similar to that previously reported by our group[11].

2 Chemicals and Electrochemical Equipments

Pyrrole (Fluka Chemika) and dimethyl sulphoxide (DMSO) were used after distilling. All other chemicals were of analytical grade and used without further purification.

Most of the electrochemical experiments were carried out with a Model 270 electrochemistry system (EG&G, USA). In some cases, a Model 366 bipotentiostat (EG&G, USA) was used for controlling two microelectrode's potential.

The microelectrode array surface was examined by using X-650 scanning electron microscope (Hitachi, Japan).

3 Experimental Procedures

To carry out electrochemical experiments, a Pt counter microelectrode and a Ag/AgCl reference microelectrode were sealed on either side of microelectrode array to form microelectrochemical cell. Then a *ca.* 30 μL droplet of solution was syringed onto the microcell so as to cover the working microelectrode, reference and counter electrode.

After pretreated by cyclic sweep from 0 V to −2.0 V at 50 mV/s in phosphate buffer (pH 7.0), the microelectrodes array was examined in DMSO solution containing 5×10^{-3} mol/L ferrocene and 0.1 mol/L Bu_4NClO_4 as supporting electrolyte. A well behaved microelectrode showed a sigmoid cyclic voltammogram. Then the microelectrodes were modified by oxidation of pyrrole in 0.1 mol/L KNO_3 solution containing 5×10^{-2} mol/L pyrrole at +0.9 V, and the coverage of polypyrrole was assessed to determine whether polypyrrole coated two or more electrodes to result in a connection between them. All the experiments were carried out at 25℃.

Results and Discussion

1 SEM Characterization of Microelectrode Array

Fig. 1 shows the scanning electron micrograph picture of the microelectrode array. The overall size of this array is 2.0 cm long and 2.0 cm wide. Most im-

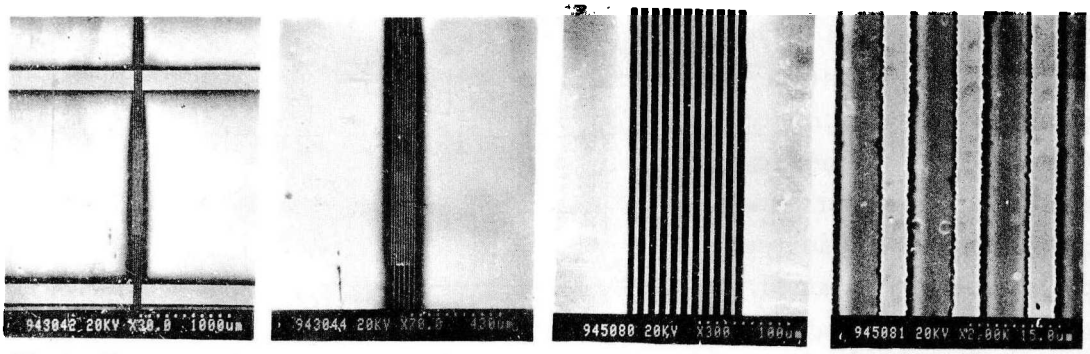

Fig. 1 Scanning electron micrographs of a fabricated microelectrode array.
The brighter areas in the micrographs are the Au wires.

portantly, the Au microelectrode array consists of ten microband electrodes, each of them is 4.0 μm wide with a gap of 8.0 μm and 1.0 mm long. Prior to use, the array is tested to make sure that each microband gold electrode is not short-circuit with the adjacent microelectrode.

2 Electrochemical Characterization of Microelectrode Array

Fig. 2 shows the cyclic voltammograms of ten microelectrodes in DMSO solution containing 5×10^{-3} mol/L ferrocene. Because the nonlinear diffusion of microband electrode results in rapid attainment of quasi-steady-state currents, the cyclic voltammograms at a 50 mV/s sweep rate are of sigmoid shape and the current is limited by diffusion of the ferrocene redox couple. This is the behavior expected for electrodes having a sufficiently small dimension[12]. The nearly zero initial currents, the magnitude of the limited currents and the similarity of response from each of the electrodes are important aspects. The characteristics represented by Fig. 2 indicate that the microelectrode array as a working electrode is usable.

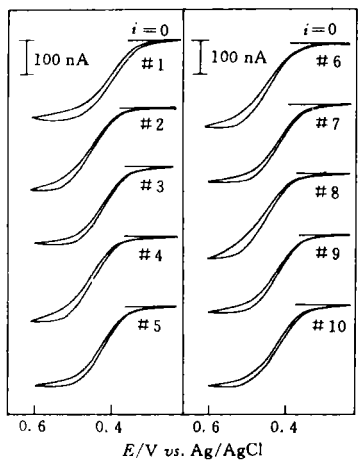

Fig. 2 Cyclic voltammograms for an array of ten microelectrodes in a 0.1 mol/L Bu_4NClO_4 DMSO solution containing 5×10^{-3} mol/L ferrocene.
Scan rate: 50 mV/s.

3 Electrochemical Characterization of Microelectrodes Modified with Polypyrrole

Au microelectrode array can be modified with polypyrrole by means of electrochemical oxidation of pyrrole[13]. It is possible to modify the electrode in a controllable fashion and to leave some microelectrodes "naked", some with a small amount of polypyrrole, and some with sufficient polypyrrole to connect two or more adja-

cent microelectrodes. Figure 3 shows the typical cyclic voltammograms of a polypyrrole modified microelectrode array. Some of the microelectrodes (see Fig. 3 A) are not functionalized with polypyrrole, as a consequence, no redox peaks of polypyrrole are obtained. Some of the microelectrodes (Fig. 3 B) show the cyclic voltammetric characteristic of polypyrrole. The shape of cyclic voltammogram is nearly the same as that in our previous report at a gold ultramicroelectrode[13]. In this case, the amounts of the polypyrrole deposited on the microelectrode are not enough to connect electrode B with other adjacent electrode. In the extreme case, the amounts of deposited polypyrrole are sufficient electrically to connect the adjacent microelectrodes (Fig. 3 C and D), then the cyclic voltammograms of them are the same. When all microelectrodes connected with polypyrrole are externally connected, the cyclic voltammogram is the same as that when only one of the microelectrodes is driven as the electrode. Fig. 4 illustrates this situation. The fact that C alone, D alone, and C+D driven together give the same response shows that the electrodes C and D are connected by the polypyrrole. If electrodes were not connected, C and D driven together would give the sum of C alone and D alone.

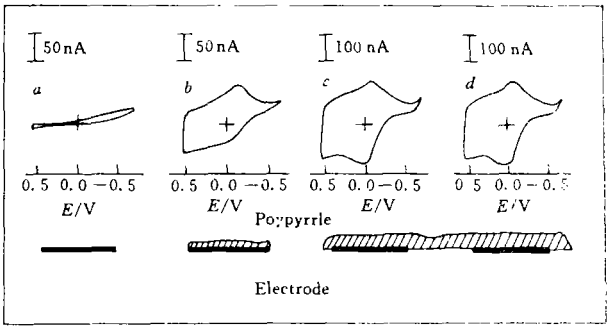

Fig. 3 Typical cyclic voltammograms for microelectrode array modified with polypyrrole in 0.1 mol/L KNO_3.

Scan rate: 50 mV/s. A: "naked"; B: Slightly coating; C and D: Heavily coating.

The deposited polypyrrole on the microelectrodes can also be observed by scanning electron microscopy. Fig. 5 shows that one electrode in array has a little of polypyrrole on

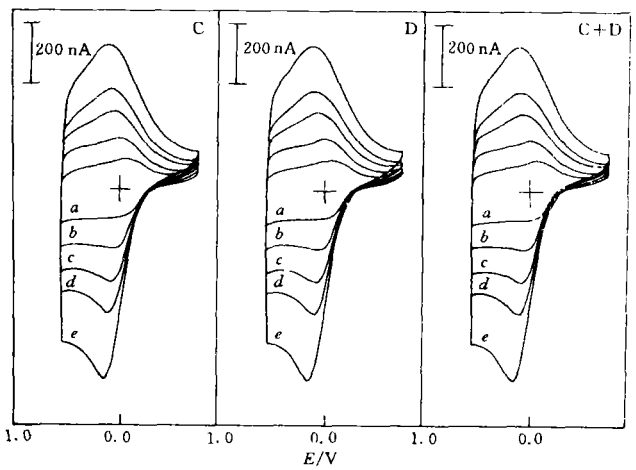

Fig. 4 Scan rate dependence of the cyclic voltammograms in 0.1 mol/L KNO_3 aqueous for two adjacent Au microelectrode coated with polypyrrole.

Scan rate(mV/s): *a*, 50; *b*, 100; *c*, 150; *d*, 200; *e*, 300.

it and can not be connected with other electrodes. The other three microelectrodes in the same array have a sufficient amount of polypyrrole to connect them.

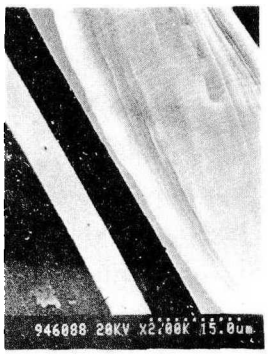

Fig. 5 Scanning electron micrograph of one microelectrode in an array lightly coated with polypyrrole (left) and three microelectrodes in the same array heavily coated with polypyrrole (right).

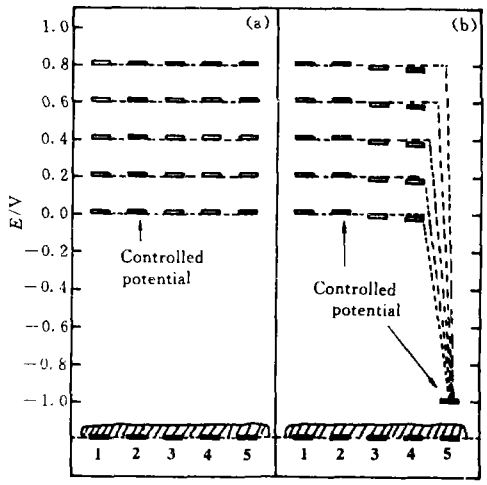

Fig. 6 The spatial potential distribution of five electrodes connected by polypyrrole (a) when electrode is under active potential control where the polypyrrole is expected to be conducting, and (b) when one electrode potential is controlled (a) but the other is controlled at −1.0 V (b). The (a) and (b) are measured in 0.1 mol/L KNO_3.

4 Conductivity of Polypyrrole on Microelectrode Array

For polypyrrole, the oxidized state is electronic conductor and the reduced state is essentially insulator. The conductivity varies by a factor of more than 10^5 depending on the redox state of the polymer[14]. The consequence of the extreme difference in conductivity with redox state is that the potential drop can occur across a very small fraction of the length of the connecting polymer when one microelectrode is held at a potential where the polymer is reduced and the other is held at a potential where the polymer is oxidized. We carried out experiments to show that the conductivity properties of polypyrrole as a function of potential can be measured using heavily coated microelectrode array.

Fig. 6 summarizes the spatial potential distribution across the polypyrrole coated microelectrode array where five electrodes are connected with polypyrrole. Fig. 6a shows that only one of the microelectrodes (electrode 2) is controlled at the positive potential region, all of the others are at the same potential as would be expected because there is an electrical connection between them.

When the potential of one of five electrodes (electrode **5**) is set at a negative potential, −1.0 V, and another one (electrode **2**) at a variable positive potential, we can measure the potential of the microelectrodes which are not under potential control. As shown in Fig. **6**b, the potentials of all the electrodes except electrode **5** are closely equal to the positive potential at electrode **2**. A small potential drop occurs over the electrodes **3** and **4**, but an important fact is that nealy all (up to 1.8 V) the potential drop occurs across a narrow region (between electrodes **4** and **5**, in about 8.0 μm region). This is due to the different redox states of polypyrrole on the adjacent electrodes.

5 Characteristics of Polypyrrole-based Microelectronic Devices

Paul[9] *et al.* showed that polyaniline-coated microelectrode array had diode-like characteristic in aqueous solution. We used the configuration represented in Fig. 7 to exame the diode-like characteristic of polypyrrole-coated microelectrode array in 0.1 mol/L KNO_3 solution.

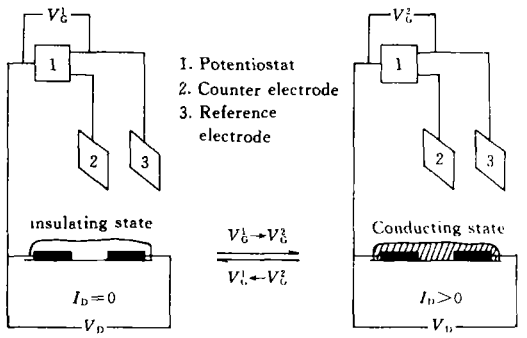

Fig. 7 Configuration of polypyrrole-based microelectronic device.

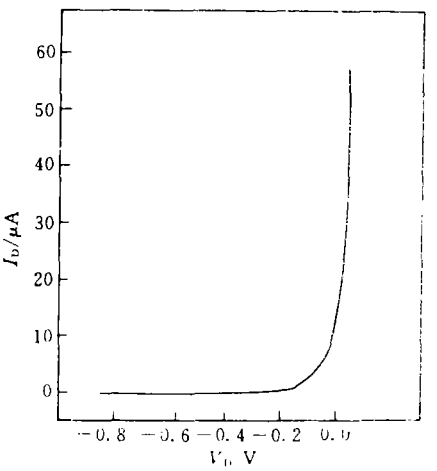

Fig. 8 Diode-like I_D—V_D curve when V_G at a potential −0.1 V.

The operation of a microelectrochemical transistor based on conductivity of polypyrrole is represented in Fig. 7. The extent of oxidation (*i.e.*, the extent of conductivity) is controlled by the gate potential, V_G. The potential difference between the microelectrodes is the drain voltage, V_D. The current is termed as the drain current, I_D. When V_G equals to V_G^1, polypyrrole is reduced, and there is no current flowing in the drain circuit, $I_D=0$. When polypyrrole is oxidized by changing V_G from V_G^1 to V_G^2, the polypyrrole is conducting, there is a current in the drain circuit, $I_D>0$. When V_G is at V_G^1 value where polypyrrole is insulting, the I_D—V_D curve of diode-like can be obtained (see Fig. 8). The onset current corresponds closely to the position where the V_D results in the conversion of the polypyrrole from its insulating state to its conducting state, as would be expect-

ed.

The device represented by Fig. 7 has some features in common with a solid state transistor, but there are also some differences between them. The solid state device, for example p—n junction with two terminals, can be operated in high frequency, while the characteristic of chemical-based device stems from electrochemical reaction at a particular potential. So the "on-off" time for the chemical-based device depends on the reversion rate of the polypyrrole from the oxidized state to the reduced state.

The molecules-based transistor can be made up into a microsensor, which can be used in clinical chemistry, environment monitoring, process control, automobile emission control and biological system[15] *etc.* In comparison with other sensors, it has advantages in small size and low output impedence, which make it ideal for in vivo monitoring or analysis of small sample volume.

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