Electropolymerization of Two-Dimensional Polypyrrole with Fractal Patterns under a Mica

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With the needle-circle electrode configuration, two-dimensional(2-D) Polypyrrole(PPy) with a fractal pattern was electropolymerized under a mica which was set on the electrolyte solution surface. The mica serves as a sample of the induction substrate to support the growth of PPy. The results provide a new way to obtain 2-D PPy and have prospect in research and practice.

To obtain 2-D electric metal deposits with fractal patterns, researchers have applied some kinds of methods.[1-4] The usually used method is to use two glass plates separated by a thin counter electrode ring and samples of products were prepared and observed in this thin-layer electrochemical cell.[2,3] 2-D PPy with a fractal pattern was first polymerized via this system by J.H. Kaufman *et.al.*[5] With the needle-circle electrode configuration in electrolyte solution of acetonitrile containing electrolytic ions and monomer (Figure 1), M. Fujii *et al.* had achieved the same purpose, and a numble of fractal patterns of the PPy have been prepared and investigated by them through this installation.[6-9] However, the 2-D PPy they got grew with branching on the cell bottom. If the anode needle is set in the middle of the solution, PPy would first grow into the solution with 3-D mode; When some points of the PPy touch the cell bottom, which may be due to the difference between the specific weight of the polymer and that of the solvent they proposed, the polymer would then spread with 2-D growth pattern on bottom.[6,7]

To examine the observation they reported, we set a mica substrate bore a hole that could be only passed by the needle tip on the solution surface to perform the same reaction. In our experiments, a stainless needle (<0.02 mm in diameter) and a ring

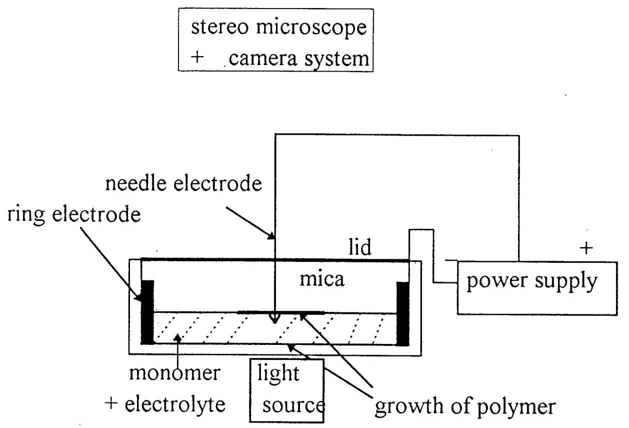


Figure 1. Experimental Configuration. The lid is used to prevent the volatilization of the solvent.

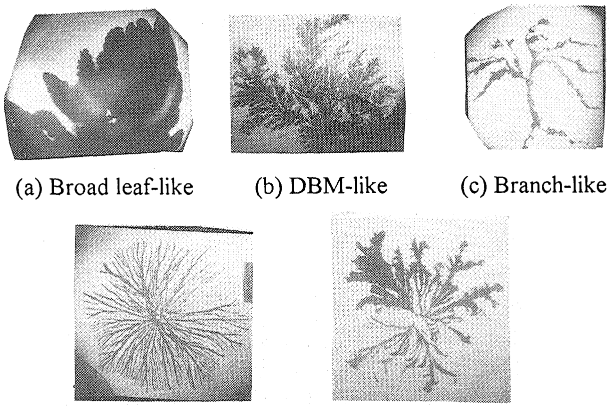
electrode (8.5 cm in diameter, height of 1 cm, thickness of 0.2 mm) were set concentricaly in a cell as an anode and a cathode respectively. Electrolyte solution of acetonitrile containing sodium *p*-toluenesulfonate and pyrrole monomer was poured into the cell. The various concentration of monomer from 0.05 to 0.5 M and electrolyte salt from 0.05 to 1 mM. The applied voltage was varied between 5V and 20V. The needle tip should be controlled to be as parallel the low part of the mica as possible.

When we discharged different voltages to the solution varying in concentration, 2-D PPy with fractal patterns sticking under the mica was successfully got. Four typical morphologies were shown in Figure 2(a-d). The patterns we displayed are very similar to those electrodeposits, especially the pattern of Figure 2(b) that is Dense-Branch Morphology (DBM) has never been reported in organic polymers before, and this pattern has received researchers' attention in morphology transition in electrochemical deposition.[10] In this case, the PPy didn't fall down into the solution as expected if only the weight factor is in function.

We think that it may be ascribed to the wetting-effect of the mica to the monomer and electrolytic ions, which cause the higher local solution concentration near the low part surface of the mica. Meanwhile, the induction of the mica to the PPy may also make the product stick under it. However, we also found that if the applied voltage was not high enough (under 7V), and the concentration of monomer is no more than 0.5 M, some parts of PPy would grow into the solution in 3-D pattern. Under lower voltage such as 5 V, in this condition we can get 2-D PPy on the cell bottom, PPy can not grow under the mica with 2-D pattern anymore. Electric field and substrate, especially the substrate, have played an important role on the PPy growth, for no matter how high the voltage is, PPy with 2-D pattern will never grow on the surface or in the middle of the solution. So, together with the weight, substrate serves as a support should be also taken into the consideration.

Another relative experiment we engaged is to put a mica on the cell bottom surface and made the needle tip close it to polymerize pyrrlole monomers. Under the same reaction solution and voltage as those of Figure 2(d), PPy formed is leaf or twig-like pattern, which is thicker and obviously in different pattern from dense radial-like pattern that we could get easily under a mica. The pattern is shown in Figure 2(e). In other same conditions but the different placement of the mica and the needle tip, the different morphologies have been observed also.

In summary, we have devised a new installation using a mica on the solution surface to induce the growth of the 2-D PPy. This work leaves an important question unanswered. What is the growth mechanism of 2-D PPy with various morphologies under the mica, which is apparently having different progression from



(a) Broad leaf-like (b) DBM-like (c) Branch-like

(d) Dense radial -like (e) Twig-like

Figure 2. Morphologies of PPy (a), (b), (c), (d) under a mica. (e) on a mica. (d) and (e) have the same reaction conditions. Polymerization conditions: (a) monomer of 0.15 M / electrolyte of o.5 mM / voltage of 13 V; (b) 0.08 M / 0.25 mM / 12V; (c) 0.3 M / 1mM / 8 V; (d) 0.3 M / 1mM / 18V.

those growing on the mica? The explanation in our paper is only tentative and deserved more study.

So far, great progress has been achieved in understanding the patterns of those electric metal deposits. But in these conjugated polymers with fractal patterns, the work is still preliminary. Recently, the use of fractal pattern of the conjugated polymers as the model of neural network patterns has received much attention.[11,12] For the products we got are intact when the reaction is over, to inspect the physical and electric properties of these semi-conductor materials with various patterns is very convenient. On the contrary, the metal deposits formed in the end at any configuration can't be disposed like those organic polymers. The application prospect is broadly.

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