

Rapid Communication

NOVEL POLYPYRROLE MICROSTRUCTURES GENERATED BY DIRECT ELECTROCHEMICAL OXIDATION OF PYRROLE ON *p*-TYPE SILICON SUBSTRATE*

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Abstract Polypyrrole microstructures with morphology like bowls, cups, goblets and bottles have been electrochemically generated by direct oxidation of pyrrole on *p*-silicon substrate in the aqueous solution of camphorsulfonic acid. The well-ordered microstructures can stand upright on the working electrode surface and their morphological features can be easily controlled by changing the electrochemical polymerization conditions. The growing process of microstructures was studied by scanning electron microscopy. The microstructures made of polypyrrole films in doped state were characterized by Raman and Infrared spectra.

Keywords Polypyrrole, *p*-Type silicon, Composite materials, Microstructures

INTRODUCTION

Conjugated polymers have attracted enormous attention since the discovery of an appreciable conductance in these materials and have been extensively explored as alternatives to metals or inorganic semiconductors in fabrication of microelectronic, optoelectronic, and microelectromechanical devices^[1–12]. Among the intrinsically conducting polymers, polypyrrole (PPy) is prominent with various interesting properties such as high conductivity, good thermal and environmental stability, and biocompatibility^[13]. On the other hand, microstructured polypyrrole is useful for fabricating microdevices including reactors, actuators and sensors^[14–17]. In our previous papers, we reported the electrochemical growth of polypyrrole microcontainers by direct oxidation of pyrrole in an aqueous solution of β -naphthalenesulfonic acid on a stainless steel sheet^[18, 19].

In this paper, we report a novel electrochemical route to prepare well-aligned three-dimensional polypyrrole (PPy) microstructures on *p*-silicon substrate. This developed into a novel, convenient and effective method for fabrication of composite materials of inorganic/organic semiconductors. In addition, the PPy films with microstructures may have potential applications in fabrication of high-quality microelectronics such as capacitors and sensors.

EXPERIMENTAL

(+)- and (–)-camphorsulfonic acid (Fluka, Japan) was used as received and pyrrole (Chinese Army Medical Institute, Beijing, China) was distilled before use. The growth of polypyrrole (PPy) microstructures was carried out at room temperature in a one-compartment cell by the use of a Model 283 potentiostat-galvanostat (EG&G

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Princeton Applied Research) under computer control. The working and counter electrodes were a *p*-silicon wafer ($10^{-3} \Omega \text{ cm}$) and a stainless steel sheet (AISI 321), respectively. They have a surface area of 0.5 cm^2 each and are placed 0.5 cm apart. All potentials were referred to a saturated calomel electrode (SCE). The solutions were deaerated by a dry nitrogen stream and maintained at a slight overpressure during the experiments. The typical electrolyte was the aqueous solution of 0.5 mol/L pyrrole and 0.7 mol/L (+) or (–)-camphorsulfonic acid.

Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 633 nm laser beam. The infrared spectra were obtained using a Spectrum GX FT-infrared spectrometer of Perkin-Elmer Company with KBr pellets. The morphology of the microstructures was studied by the use of a KYKY2800 scanning electron microscope (Beijing Scientific Instrument Company, Beijing, China) after sputter-coating the samples with gold.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the typical scanning electron microscopic (SEM) images of PPy microstructures prepared by electrolysis of 0.5 mol/L pyrrole in 0.7 mol/L (+)-camphorsulfonic acid ((+)-CSA) aqueous solution. It is clear from this figure that the microstructures stand upright on the electrode surface and align fairly well. The microbowls (Fig. 1a), microcups (Fig. 1b, c) and microtubules (Fig. 1d) were formed by electrolysis at constant potentials of 0.8, 0.9, 1.0, and 1.2 V for 300 s each, respectively. With the increase of applied potential from 0.8 to 0.9 V, the height of the bowls increased from *ca.* 50 μm to *ca.* 100 μm while their calibre changed only a little. When a constant potential of 1.0 V was applied, the “bowls” turned into “cups”, and their height increased to over 200 μm . The wall of the microbowls and microcups is semitransparent, and their outside and inner side surfaces are quite smooth. Microtubules about 500 μm long were obtained at 1.2 V as shown in Fig. 1(d). It is obvious that the height of the microstructures can be controlled by changing the value of the applied potential.

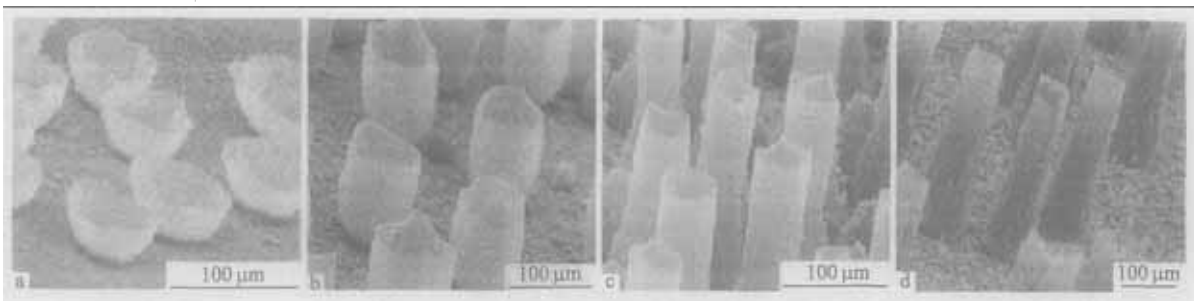


Fig. 1 SEM images of PPy microstructures obtained by electrolysis of 0.5 mol/L Py in an aqueous solution of 0.7 mol/L (+)-CSA at different applied potentials for 300 s each, (a) 0.8 V; (b) 0.9 V; (c) 1.0 V; (d) 1.2 V

The morphology of the microstructures also depends on the concentration of (+)-CSA. As the concentration of (+)-CSA decreased from 0.7 mol/L to 0.6 mol/L, the morphology of the microstructure grown at 1.2 V for 300 s changed from microtubules (Fig. 1d) to microbottles (Fig. 2a), with the density of microstructures decreased. When the concentration of (+)-CSA was lower than 0.5 mol/L, the number of the microstructures was fairly few (Fig. 2b). Thus low concentration of (+)-CSA leads low electrolysis rate of pyrrole and unfavourable to the microstructures growth.

Polypyrrole microstructures also can be generated and controlled by the cyclic voltammetric (CV) scanning technique. Figures 3(a)–(d) illustrate the SEM images of microstructures grown in the aqueous medium of 0.5 mol/L pyrrole and 0.7 mol/L (+)-CSA by CV scanning in the potential-range of 0–1.2 V at 20 mV/s for different cycles. Potential scanning for 1 cycle generated micro-bowls of *ca.* 80 μm in caliber and *ca.* 100 μm in height (Fig. 3a). The walls of the micro-bowls are smooth and thin. As the potential cyclic number increased to 2, the microstructures grew higher (*ca.* 200 μm) and their walls became rougher and thicker (Fig. 3b). Furthermore,

a line appeared between the two parts formed between the adjacent cyclic scans. Further experiments confirmed (as shown in Figs. 3c and 3d) that the microstructures were grown from bottom to top and that the number of annular parts in a single microstructure was consistent with that of CV cycles. In addition, the potential scan rate also can affect the morphology of the microstructures. As shown in Figs. 3(e) and 3(f), the micro-bowls obtained at the scan rate of 50 mV/s for 4 cycles (Fig. 3e) are larger than those prepared at the scan rate of 100 mV/s (Fig. 3f). In contrast to Fig. 3(c), there was no adjacent line formed on the bowls. This is mainly because a high potential scan rate results in a high PPy growth rate and a short time interval between two neighboring cycles.

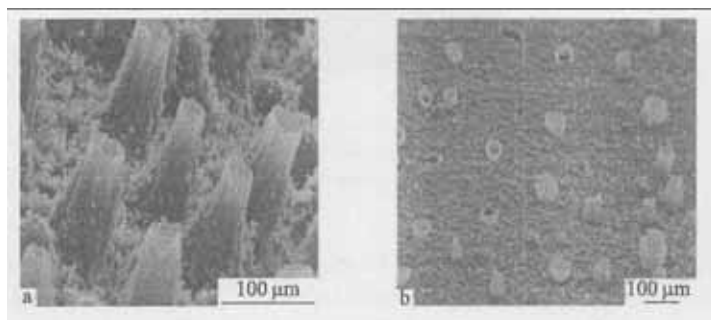


Fig. 2 SEM images of PPy microstructures obtained at a constant applied potential of 1.2 V by electrolysis of 0.5 mol/L Py in aqueous media with different (+)-CSA concentrations for 300 s each, (a) 0.6 mol/L; (b) 0.5 mol/L

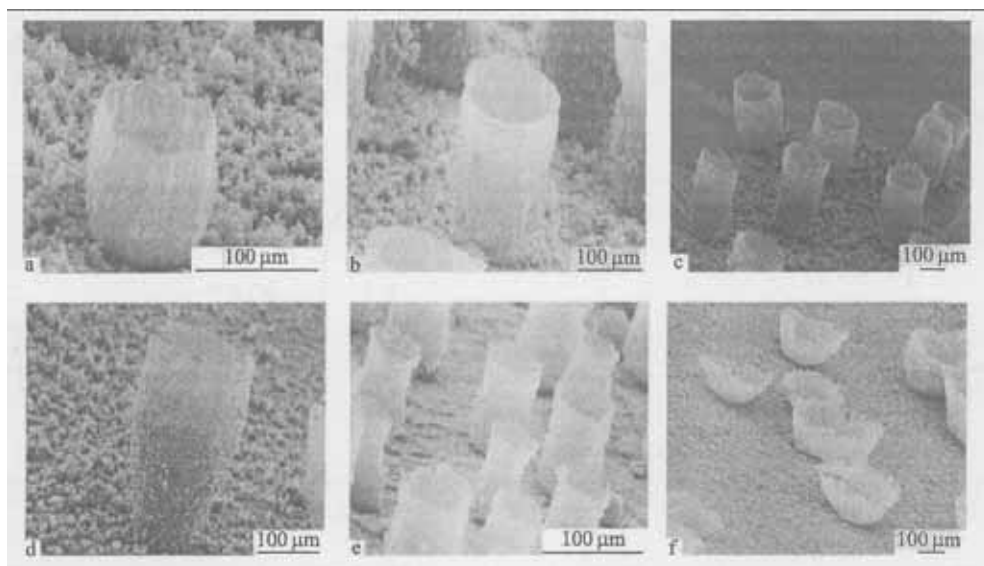


Fig. 3 SEM images of the microstructures generated by voltammetric scanning in the potential range of 0 to 1.2 V at a scan rate of 20 mV/s for different cycles (a: 1; b: 2; c: 4; d: 6) or at different scan rates (e: 50 mV/s; f: 150 mV/s) for 2 cycles

The electrolyte is an aqueous solution of 0.5 mol/L pyrrole and 0.7 mol/L (+)-camphorsulfonic acid.

By modulating the electrochemical conditions, the microcontainers with different height, calibre, and shape can be obtained. As a result, the morphology of the polypyrrole microstructures can be controlled simply by changing the electrolysis conditions. A typical example is the potential control growth of the “goblets” (Fig. 4). The “goblets” were obtained by electrolysis at 1.2 V for 60 s and successively at 1.0 V for 120 s.

Whether (+)- or (-)-camphorsulfonic acid were used, as long as the electrolysis condition was the same, the microstructures with similar morphological features were observed. In conclusion, the morphology of PPy microstructures depends only on electrolysis conditions. Thus, the shape and size of the microstructures can be

simply controlled by changing the electrochemical conditions.

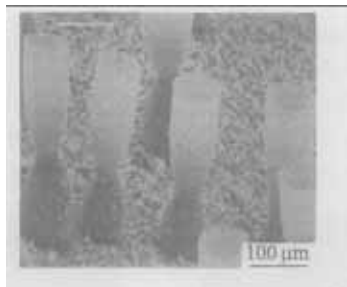


Fig. 4 SEM image of the microstructures formed by electrolysis at 1.2 V for 60 s and successively at 1.0 V for 120 s in an aqueous solution of 0.5 mol/L pyrrole and 0.7 mol/L (+)-CSA

Raman and Infrared Characterization

The 633 nm excited microscopic Raman spectra (the laser spots focused on the inside and outside surfaces of the walls gave spectra with similar features) of the microstructures (Fig. 5) showed strong bands at *ca.* 1375 and 1085 cm^{-1} which were attributed to the ring stretching and the N—H in-plane deformation of the oxidized (doped) species, respectively^[20]. The Raman band at *ca.* 1600 cm^{-1} represents the backbone stretching mode of C=C bonds. The FT-infrared spectra of the microstructures (Fig. 6) are similar to those of PPy obtained by other methods^[21]. Two bands at 1035 cm^{-1} and 1735 cm^{-1} are attributed to the $-\text{SO}_3^-$ group and carbonyl group of the camphorsulfonic acid. The strong bands near 2800 and 2900 cm^{-1} are assigned to the CH_3 and CH_2 groups of camphorsulfonic acid. These results indicate that the PPy microstructures were doped by chiral (+)- or (–)-camphorsulfonic acid.

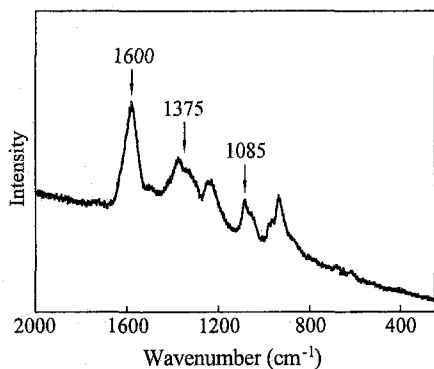


Fig. 5 Raman spectrum of the microstructures obtained by constant applied potential 1.0 V in aqueous solution of 0.5 mol/L pyrrole and 0.7 mol/L (+)-CSA

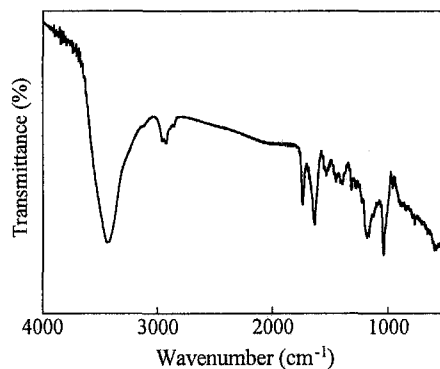


Fig. 6 Infrared spectrum of the microstructures obtained by constant applied potential 1.0 V in aqueous solution of 0.5 mol/L pyrrole and 0.7 mol/L (+)-CSA

CONCLUSIONS

Polypyrrole microstructures with very unusual morphology can be generated by electropolymerization of pyrrole on a *p*-silicon substrate with resistance of $10^{-3} \Omega \text{ cm}$ in an aqueous solution of camphorsulfonic acid. The shape and size of the microstructures can be modulated electrochemically and the microstructures are made of PPy in the doped state. In addition, the technology by developed in this work provides a novel, convenient and effective method for fabrication composite materials from inorganic/organic semiconductors, and can be extended to synthesize other materials with similar microstructures by changing monomers and surfactants.

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