

Electrochemical synthesis of novel polypyrrole microstructures†

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Polypyrrole microstructures with unusual morphologies have been synthesized by direct electrochemical oxidation of pyrrole in β -naphthalenesulfonic acid aqueous solution.

Nano- and micro-structured materials such as carbon nanotubes, fullerenes and micro- and nano-tubules of conducting polymers have come up with many surprises in recent years.^{1–5} They show wide potential applications in microelectronics, sensors, catalysis, optics and biomedical science, *etc.* Growing microcontainers is also important for nano- and picoliter chemistry.⁶ Furthermore, the chemical composition and the geometrical structures control the properties of solid surfaces. For example, the super-hydrophobic property of the lotus leaf is mainly due to its surface microstructures.⁷ Here, we describe the spectacular growth of polypyrrole microstructures with unusual morphologies like dishware such as bowls and cups.

The remarkable growth of polypyrrole (PPy) microstructures was carried out at room temperature in a one compartment cell with the use of a Model 283 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The working and counter electrodes were two stainless steel sheets (AISI 321) with surface area of 0.5 cm² each and placed 0.5 cm apart. All potentials were referred to a saturated calomel electrode (SCE). The solutions were deaerated by dry nitrogen stream and maintained at a light overpressure during the experiments. The typical electrolyte was an aqueous solution of 0.53 M pyrrole and 0.57 M β -naphthalenesulfonic acid (β -NSA).

Fig. 1 shows the typical scanning electron microscopic images of the polypyrrole microstructures generated by electrolysis of 0.53 M pyrrole in 0.57 M β -naphthalenesulfonic acid (β -NSA) aqueous solution (A–H). The results showed good reproducibility. It is clear from this figure that the microstructures are stood upright on the electrode surface. They have fairly good uniformity and align in a high density of about 2000–8000 units cm⁻². The micro-bowls are formed by cyclic voltammetric scanning in the potential scale of 0–1.2 V at 20 mV s⁻¹ for 1 cycle (Fig. 1A). The two surfaces of the bowl wall were smooth. The height of the bowls was in the range of 45–50 μ m and the calibre was in the scale of 80–90 μ m. After potential scanning for 3 cycles, the ‘bowls’ (Fig. 1A) changed into ‘cups’ (Fig. 1B). The cups were higher (80–90 μ m) than the bowls shown in Fig. 1A, while the calibres of both the bowls and cups were almost the same. Furthermore, the outside surface of the cup wall was rough, indicating that it was made of relatively thick polypyrrole film. The shape and size of the microstructures depend strongly on the value of applied potential, which can be observed clearly in Fig. 1C, D and E. Micro-bowls were formed at relatively low constant potentials (\sim 1.0 V, Fig. 1C). They are short and have wide mouths (\sim 100 μ m in height and 150–160 μ m in calibre). Micro-cups were produced at relatively high potentials (Fig. 1D and E; 1.2 and 1.4 V, respectively) and their mouths became smaller and smaller by increasing applied potential (\sim 100 μ m in Fig. 1D and \sim 90 μ m

in Fig. 1E). The diameter and the calibre of the cups also can be modulated by the value of applied potential. This is reflected clearly in Fig. 1F. The ‘goblets’ have thin root parts (80–90 μ m, grown at 1.4 V for 40 s) and wide middle parts (130–140 μ m, grown at 0.75 V for 120 s) and small mouths (80–90 μ m, grown at 1.4 V for 60 s). The effect of current density on the microstructures is similar to that of applied potential. The onion-like bottles shown in Fig. 1G and H can be prepared by electrolysis at 1.2 V for 60 s and successively at a constant current density of 0.36 mA cm⁻² for 300 s. As a result, the morphology of the polypyrrole microstructures can be easily controlled by changing the electrolysis conditions.

The microscopic Raman spectra (the laser spots focused on the wall, bottom, inner and outside surfaces give spectra with similar features) and transmission infrared spectra (with KBr

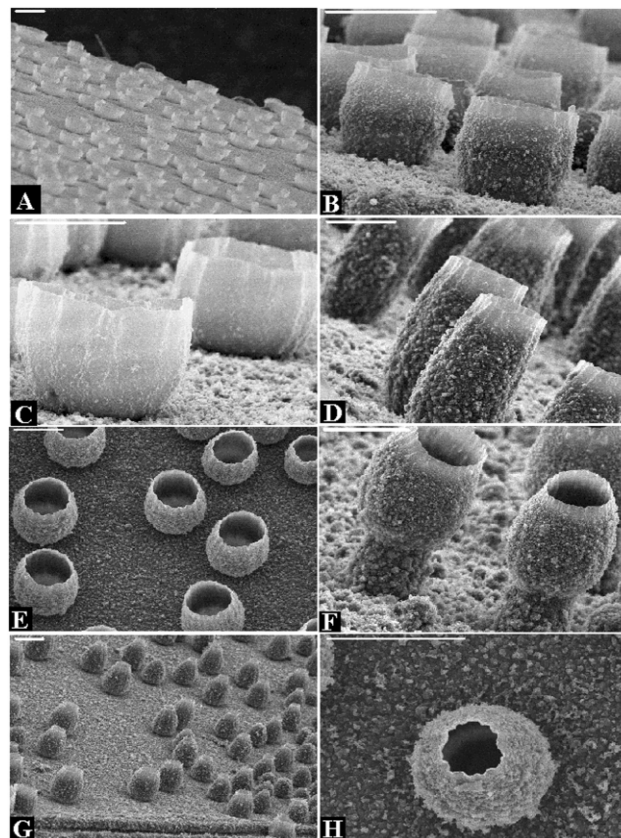


Fig. 1 Scanning electron micrographs of polypyrrole microstructures. A and B were prepared by cyclic voltammetric scanning in the potential scale of 0–1.2 V for 1 and 3 cycles (potential scan rate: 20 mV s⁻¹), respectively; C, D and E were obtained at 1.0 V (120 s), 1.2 V (120 s) and 1.4 V (60 s), respectively; the ‘goblet’ F were formed by electrolysis at a constant potential of 1.4 V for 40 s and successively 0.75 V for 120 s and then 1.4 V for 60 s; The onion-like bottles G and H were produced at a constant potential of 1.2 V for 60 s and subsequently at a constant current density of 0.36 mA cm⁻² for 300 s. From A to H, the typical electrolyte was the aqueous solution containing 0.53 M pyrrole and 0.57 M β -naphthalenesulfonic acid (β -NSA). Scale bars: 100 μ m.

† Electronic supplementary information (ESI) available: Fig. S1: transmittance IR and Raman spectrum of a PPy film generated at 1.2 V. See <http://www.rsc.org/suppdata/cc/b2/b209245j/>

pellets) of the microstructures prepared in the aqueous electrolyte of β -NSA demonstrated that the microstructures were made of polypyrrole films in doped (conductive) state. The infrared spectra showed very weak absorption in the region around 1700 cm^{-1} , indicating that the polymer was only slightly over-oxidised during the polymerization process.

What induces the unusual growth of polypyrrole microstructures on the electrode surface? An explanation for this is a 'soap bubble' or 'gas bubble' template growth mechanism.⁸ Careful observation during the electrochemical synthesis of these microstructures shows that small gas bubbles are released from the electrode surface. Furthermore, the polarization curve of a pristine stainless steel (SS) electrode in $0.57\text{ M } \beta$ -NSA aqueous solution showed a weak passivation wave of the electrode at *ca.* 1.0 V , and a strong anodic current wall of water decomposition (Fig. 2A). The onset oxidation potential of water is read to be 1.25 V (*vs.* SCE), which is very close to the reported value (1.23 V , *vs.* SCE).⁹ In comparison, the onset oxidation potential of the electrolyte at a polypyrrole film with a microcups coated SS electrode was found to be at only *ca.* 0.8 V (Fig. 2C), which implied that the polypyrrole film could catalyze the decomposition of water. The oxidation wave of PPy and the passivation wave of the electrode are too weak to be observed clearly from this curve. To confirm the catalytic effect of the polypyrrole film, a platinum (Pt) sheet was used as working electrode to replace the SS electrode. The decomposition potential of $0.57\text{ M } \beta$ -NSA aqueous solution at the pristine Pt electrode is at *ca.* 1.23 V (Fig. 2B) in accordance with the value reported.⁹ However, the oxidation potential of water at a polypyrrole film coated Pt electrode, was also found at only *ca.*

0.8 V (Fig. 2D), which is in good agreement with that shown in Fig. 2C. Li and Qian also reported that oxygen gas could be generated by electrolysis of acidic water ($\text{pH} = 3$) on a PPy coated Pt electrode in a fairly low potential region ($0.8\text{--}1.1\text{ V vs. SCE}$).¹⁰ On the other hand, cyclic voltammetric studies demonstrated that the oxidation wave of polypyrrole film in a $0.57\text{ M } \beta$ -NSA aqueous solution was at *ca.* 0.5 V . This result confirms that the oxidation waves (at *ca.* 0.8 V) in Fig. 2C and D are not caused by the oxidation of polypyrrole. Accordingly, it is reasonable to conclude that the bubbles were produced by the decomposition of water. The gas bubbles and the aqueous solution containing the monomer and β -NSA (a typical surfactant) lead to the formation of 'soap bubbles'. The growth of polypyrrole around these bubbles results in the microstructures described above. The 'soap bubble' size and generation rate and the growth rate of polypyrrole film depend strongly on the experimental conditions. Thus, changing the electrolysis conditions can modulate the shape, size and calibre of the polypyrrole microstructures. No microstructures were generated at potentials lower than 0.8 V and the microstructures were grown on PPy films (not in contact with the metallic electrode directly). These observations also supported the mechanism described above.

We have shown that the electrochemical polymerization of pyrrole in an aqueous medium can generate polypyrrole structures with very unusual morphology, which have potential applications in microreactors, microencapsulations, micro-sensors, and so on. For example, the microstructures may be used as a biological microencapsulation substance.¹¹ Furthermore, the technique described here can be extended to synthesize other materials with similar microstructures by changing monomers and surfactants.

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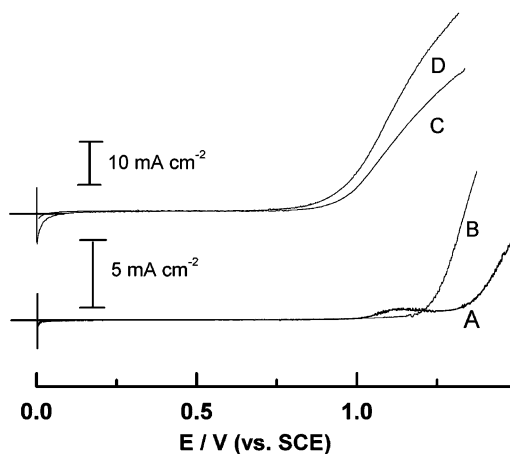


Fig. 2 Anodic polarization curves of $0.57\text{ M } \beta$ -NSA aqueous electrolyte at pristine SS (A), Pt (B) electrode or a polypyrrole film with microstructures (1.0 C cm^{-2}) coated SS (C), Pt (D) electrode at a potential scan rate of 20 mV s^{-1} .

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