

Controlled syntheses of conducting polymer micro- and nano-structures for potential applications

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Abstract

The development of nanostructured polymers has opened up novel fundamental and applied frontiers, which has attracted tremendous interest in recent years. We have recently developed techniques for the micro-lithographic formation of conducting polymer patterns on the micrometer scale and for coating conducting polymers on individual aligned carbon nanotubes. The micro- and nano-fabrication facilitates the use of conducting polymers for various applications ranging from multicolor polymer light-emitting displays to biosensors. More recently, we have demonstrated the controlled syntheses of conducting polymer microcontainers through electrochemical generation of surfactant (i.e. β -naphthalenesulfonic acid, β -NSA)-stabilized H_2 gas bubbles on the working electrode, followed by electrochemical polymerization of pyrrole around the wall of the “soap bubble” template. By pre-patterning the working electrode surface with non-conducting polymers through micro-contact printing (μ CP) or plasma patterning, we have also produced conducting polymer microcontainers in a patterned fashion. Furthermore, potential applications of the patterned and non-patterned conducting polymer microcontainers have been demonstrated, for example, by immobilizing glucose oxidase (GOX) onto the conducting polymer microcontainers for glucose sensing. This paper provides a brief summary of our work on micro- and nano- fabrication of conducting polymer for various potential applications.

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1. Introduction

Conducting polymers have attracted a great deal of interests during the past three decades or so. With recent development in nanoscience and nanotechnology, conducting polymer micro-/nano-structures received an ever increasing attention [1]. For instance, various methods, including template syntheses [2], scanning probe electrochemical polymerization [3], and electrospinning [4], have been devised to prepare micro- or nano-tubes and nanofibers of conducting polymers.

In this context, we have previously demonstrated the electrochemical generation of conducting polymer patterns onto conducting surfaces pre-patterned with certain non-conducting plasma polymers [5]. We have also synthesized aligned co-axial nanowires of carbon nanotubes sheathed with conducting poly-

mers by electrochemically polymerizing a concentric layer of appropriate conducting polymers onto individual aligned carbon nanotubes [6].

Based on the above work, we, along with others [7], have recently developed a simple, but effective, method for preparing conducting polymer microcontainers by electrochemical polymerization of appropriate monomers using soap bubbles as a soft template [8]. The conducting polymer microcontainers thus produced have been demonstrated to display unusual morphologies and possess a large surface area of potential applications. By pre-patterning the working electrode surface with non-conducting polymers through μ CP and plasma patterning, region-specific electrodeposition of conducting polymer microcontainers can be readily achieved. We summarize here our recent work on the growth of polypyrrole microcontainers in a patterned and non-patterned fashion. We will also demonstrate the potential applications of the patterned and non-patterned conducting polymer microcontainers, for example, for sensing applications.

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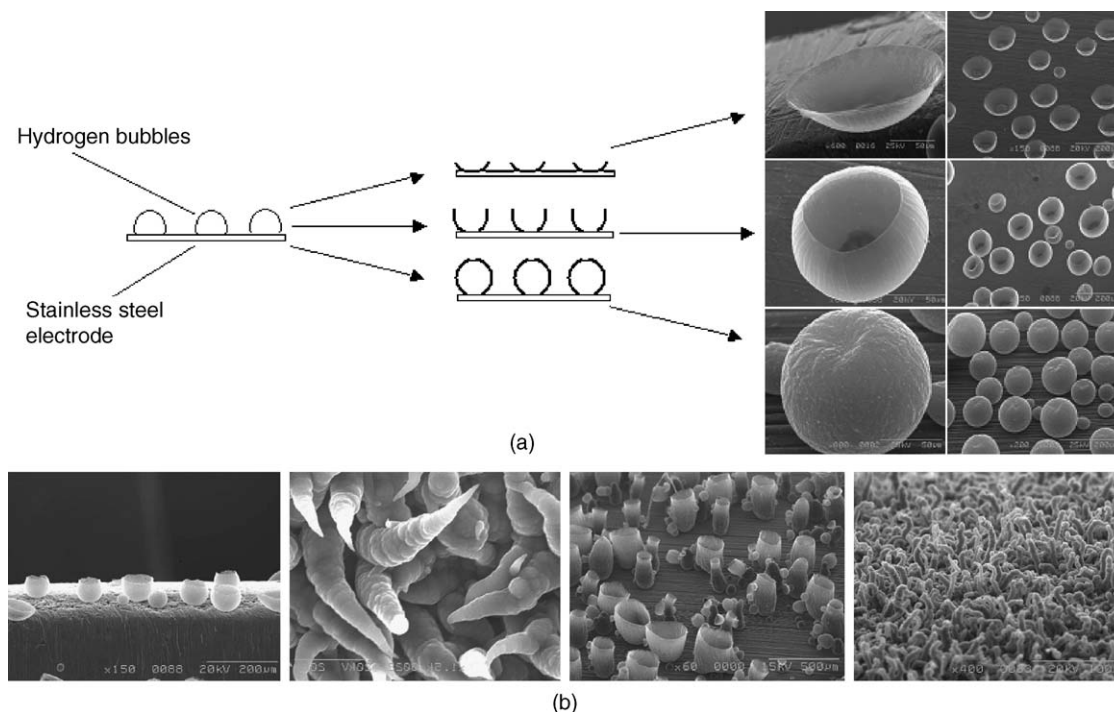


Fig. 1. (a) Schematic representation of the growth process of polypyrrole microcontainers and (b) some of the special micro-/nano-structures of conducting polymers prepared by the “soap bubble” template technique.

2. Experimental

Pyrrole (99%) and 2-naphthalenesulfonic acid sodium salt (β -NSA, 99%) were purchased from Acros. 5-((5-Aminopentyl) thioureidyl) fluorescein, dihydrobromide salt (fluorescein cadaverine, Fc) was purchased from Sigma. Electrochemical polymerization was performed on a Model CHI 604 electrochemical analyzer (HCH Instruments Inc.) using two stainless steel sheets (length: 1.0 cm; widths: 0.5 cm; thickness: 0.6 mm) as the working and counter electrodes against an Ag/AgCl reference electrode. An aqueous solution of 0.5 M pyrrole and 0.4 M NSA was used; the latter was used both as the surfactant and electrolyte. Prior to the electropolymerization, the electrolyte solution was degassed by a pure nitrogen flow for 15 min and maintained under a small overpressure throughout the electrochemical process. Cyclic voltammetric scanning(s)

were performed to generate H_2 bubbles on the working electrode surface by scanning potential from -1.0 to -1.6 V for the first cycle, followed by changing the potential window to the range of $+0.5$ to $+1.1$ V for next three cycles for electrochemical polymerization of pyrrole around the “soap bubble”. While scanning electron microscopic images of the resulting microcontainers were taken on a HITACHI S-2150 SEM, photoluminescence emissions were recorded on a LS 55 Luminescence Spectrometer (PerkinElmer, Inc.).

3. Results and discussion

3.1. Syntheses of polypyrrole microcontainer

Fig. 1a shows schematically the formation of various spherical conducting polymer microcontainers, depending on how

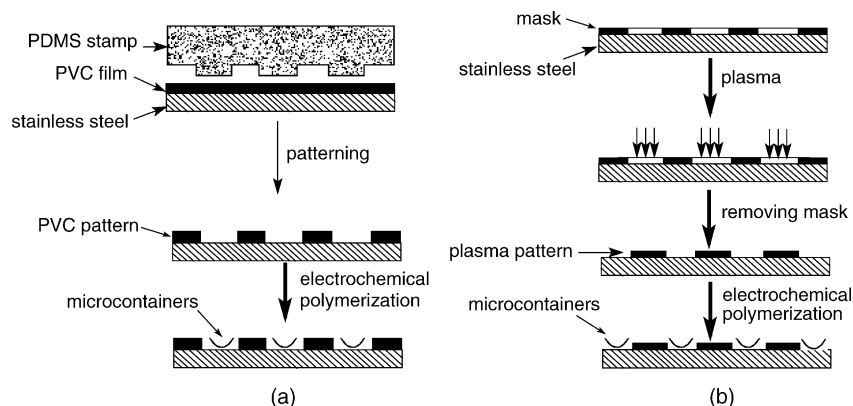


Fig. 2. Schematic illustration of the procedures for fabricating patterns of polypyrrole microcontainers by (a) μ CP and (b) plasma patterning.

long the “soap bubble” template could keep its structural completeness during the electropolymerization process. Also shown in Fig. 1 are some of the conducting polymer micro-/nano-structures prepared with the “soap bubble” template of special structures (Fig. 1b).

Fig. 2a and b schematically show the steps for the patterning processes by the μ CP and plasma method, respectively. Prior to the patterning, all of the stainless steel electrodes were cleaned by an aqueous solution of HNO_3 (1:1 v/v, HO_2/HNO_3) under ultrasonication for 30 min, followed by thoroughly washing with distilled water and acetone. For the μ CP patterning (Fig. 2a), a drop of the polyvinyl chloride (PVC) solution in chloroform was spread out on a clean stainless steel electrode and region specifically confined with a poly(dimethylsiloxane) (PDMS) stamp by pressing. After drying at room temperature for about 1 min, polymer patterns were observed upon removal of the PDMS stamp. The PVC patterns on the stainless steel surface thus produced then act as a physical mask for patterned growth of the polypyrrole microcontainers. Alternatively, non-conducting plasma polymer patterns can be produced on the stainless steel electrode surface by plasma polymerization of an appropriate monomer (e.g. *n*-hexane at 150 kHz and 0.3 Torr for 2 min) through a mask (Fig. 2b). These electrodes with pre-patterned non-conducting polymer thin films either by the μ CP or plasma method were then used for region-specific electrodeposition of the polypyrrole microcontainers.

Fig. 3a shows a typical SEM micrograph of the microcontainer patterns generated on a stainless steel electrode by the μ CP method. The darker regions with relatively thick strips seen in Fig. 3a indicate the presence of the patterned PVC coating and the polypyrrole microcontainers are well registered within the PVC-free regions. Fig. 3b reproduces a SEM image for similar patterned polypyrrole microcontainers produced by the plasma patterning technique. As can be seen in Fig. 3, polypyrrole microcontainers can be region-specifically electrodeposited onto electrodes pre-patterned with non-conducting polymers generated from different patterning methods. The patterned conducting polymer microcontainers thus prepared may find applications in certain sensing and optoelectronic devices.

3.2. Polypyrrole microcontainers for glucose sensing

The above-mentioned conducting polymer microcontainers with a large surface are also good candidates for sensing applications. We found that the response current for the polypyrrole

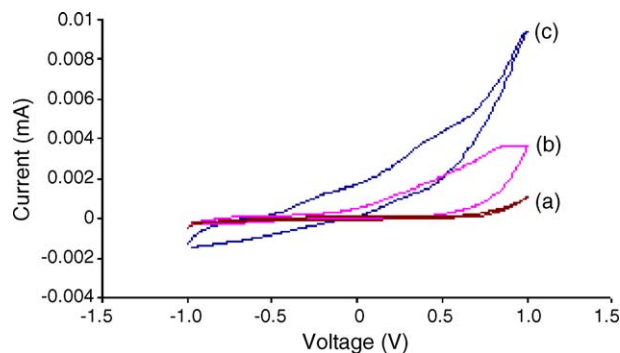
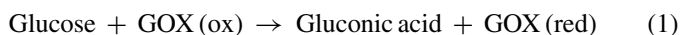


Fig. 4. Electrochemical responses of the (a) stainless steel electrode, (b) polypyrrole film and (c) polypyrrole microcontainers in a pH 7.0 phosphate buffer at scan rate 100 mV/s.

microcontainer is roughly double than that of the corresponding polypyrrole film (Fig. 4).

Since the sensing of glucose involves electrochemical detection of H_2O_2 generated from the oxidation of glucose by glucose oxidase (GOX, Reactions (1) and (2)) [9], this electrochemical process was investigated as an example for demonstrating the bio-sensing capabilities of the polypyrrole microcontainers.



To demonstrate that these conducting microcontainers can be used for sensing glucose, we tested the response of the polypyrrole microcontainer electrode to different H_2O_2 concentrations (Fig. 5).

The above results obtained from the measurements of pure H_2O_2 prompted us to carry out the sensing measurements for glucose using the GOX-immobilized polypyrrole microcontainers. As can be seen from Fig. 6a, the CVs are quite responsive to glucose in the concentration range of 0.001–0.02 M, and then saturated with higher glucose concentrations. The redox peak current at the oxidative potential of H_2O_2 from the GOX-immobilized polypyrrole microcontainers for glucose sensing was found to increase with increasing glucose concentrations (Fig. 6b), indicating that these conducting polymer microcontainers are promising materials for sensing applications.

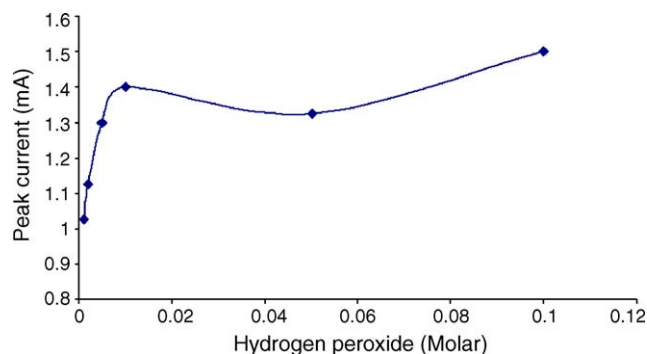


Fig. 5. The dependence of the H_2O_2 redox peak current on the concentration of H_2O_2 .

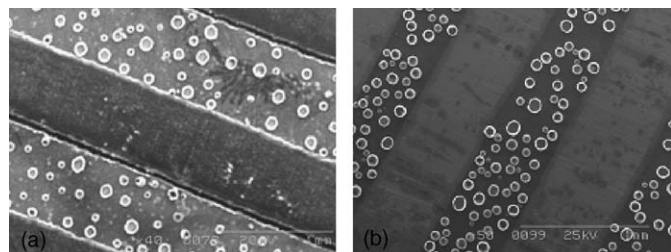


Fig. 3. SEM images of polypyrrole microcontainers patterns obtained by (a) μ CP and (b) plasma patterning method.

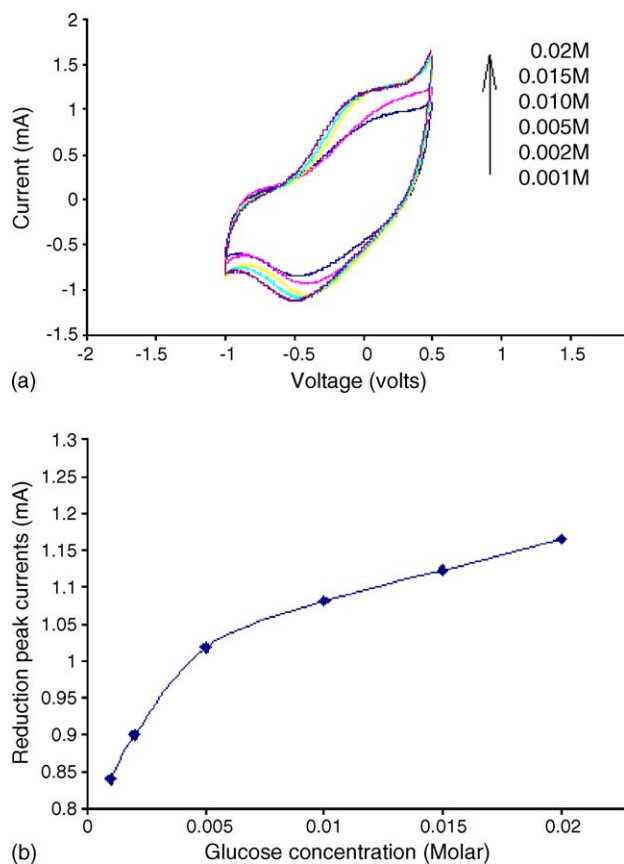


Fig. 6. (a) The cyclic voltammetric (CV) spectrum of the microcontainer electrode in response to the change in concentration of glucose and (b) the dependence of the peak current on the glucose concentration.

4. Conclusion

We have demonstrated that conducting polymer microcontainers can be prepared by electrochemical polymerization of appropriate monomers using soap bubbles as a soft template. The process involves the generation of H_2 gas around the counter

electrode at a negative potential, followed by self-assembling the soap bubbles on the working electrode and electrochemical polymerization of pyrrole along the wall of the soap bubbles at a positive potential. By pre-patterning the working electrode surface with non-conducting polymers through μ CP and plasma patterning, region-specific electrodeposition of conducting polymer microcontainers can be readily achieved. Owing to their large surface area and good electrochemical activity, these conducting polymer microcontainers have been demonstrated to be used for sensing applications. Therefore, the patterned and non-patterned conducting polymer microcontainers thus prepared are very attractive for a wide range of potential applications, ranging from as sensors to controlled release of drugs.

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