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Linear arrangements of polypyrrole microcontainers

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Received (in Cambridge, UK) 14th January 2004, Accepted 2nd March 2004
First published as an Advance Article on the web 18th March 2004

Linear arranged polypyrrole microcontainers have been assembled into one or two lines on patterned silicon microelectrodes with line widths of 50 and 200 μm, respectively.

Extensive work has been devoted to the synthesis of nano- and micro-structured materials such as carbon nanotubes, fullerenes, micro- and nano-particles, wires, tubes and spheres of metals, semiconductors, oxides and polymers.[1–3] The unique properties of these materials provide potential applications in microelectronics, sensors, catalysis, optics and biomedical science, *etc.* Growing micro-containers is also important for nano- and pico-liter chemistry.[4] Recently, we electrochemically generated polypyrrole (PPy) micro-containers with morphologies like bowls, cups and bottles by using self-assembled micro-sized gas bubbles onto the working electrode surface as the templates.[5] However, the micro-containers were randomly located on the electrode surface, which obstructed their applications. Patterned conducting polymer microstructures are important for fabricating integrated circuits, flexible organic transistors and biochips.[6] Traditionally, the construction of patterned conducting polymer structures is achieved through photolithography, electron-beam writing, screen printing or ink-jet printing.[7] Here, we report linear arrangement of PPy micro-containers by self-assembling the gas bubbles acting as templates on a silicon electrode surface patterned by photolithography (Fig. 1). It was found that the capillary interactions between gas bubbles and the polymer photoresist walls led the micro-containers to be arranged linearly.

Fig. 2 shows the typical scanning electron microscope (SEM) images of the polypyrrole micro-containers generated by electrolysis of 0.5 M Py in 0.7 M aqueous solution of (+)-camphorsulfonic acid ((+)-CSA) at a constant applied potential of 1.0 V for 100 s. The results showed good reproducibility. It is clear from this figure that the micro-containers are stood upright on the electrode surface. They have fairly good uniformity and align linearly along the clean silicon electrode in a density of 100–120 units cm^{-1}. The micro-containers have morphologies like bowls with mouth diameters of about 100 μm. The containers with morphologies like cups, bottles and hollow spheres also have been generated by changing the electrolysis conditions as shown in Fig. 3. On the surface of the silicon electrode with width of 50 μm, all the micro-containers grew along the electrode line (Fig. 2A, B).

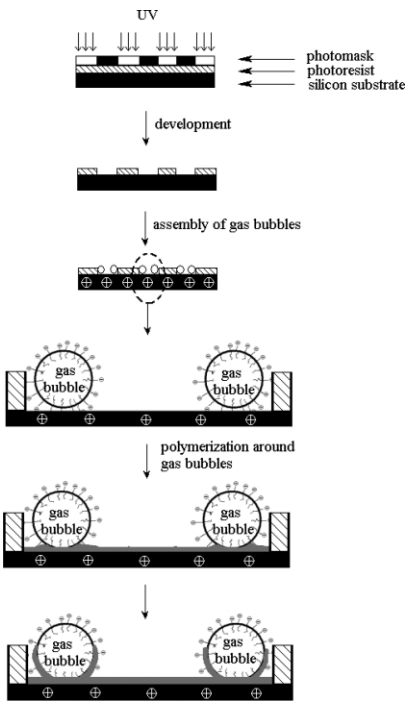


Fig. 1 Scheme of generating linearly arranged PPy micro-containers.

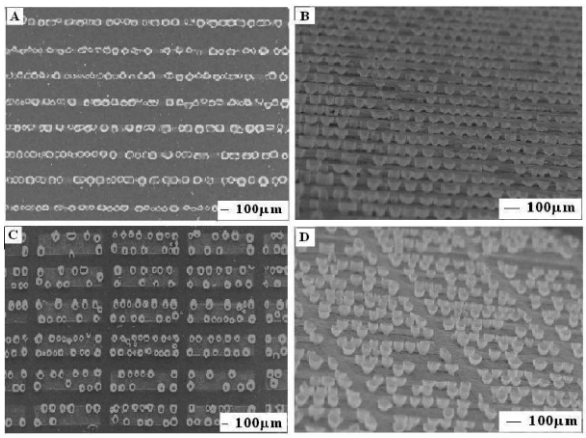


Fig. 2 SEM images of PPy micro-containers generated by electrolysis of 0.5 M Py in the aqueous solution of 0.7 M (+)-CSA at a constant applied potential of 1.0 V for 100 s. The margin between the two neighboring silicon micro-electrodes was 200 μm, and the widths of clean silicon electrode lines were 50 μm (A, B) and 200 μm (C, D), respectively.

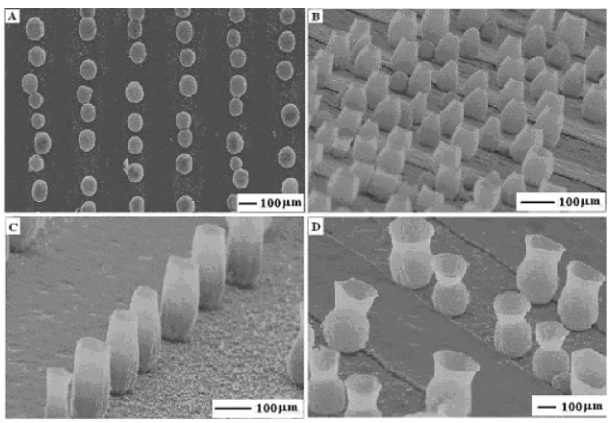
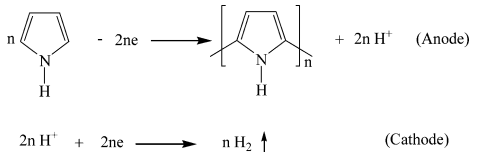


Fig. 3 SEM images of PPy micro-containers prepared by electrolysis of 0.5 M Py in 0.7 M aqueous solution of (+)-CSA under different experimental conditions. (A) was obtained by electrolysis at 0.8 V for 60 s and successively at 1.2 V for 90 s; (B) was prepared by CV scanning in the potential scale of 0–1.1 V for 2 cycles; (C) was formed by electrolysis at 1.1 V for 150 s and (D) was generated by electrolysis at 1.2 V for 60 s and successively at 1.0 V for 60 s.

DOI: 10.1039/b400614c

However, on the electrode surface with width of 200 μm, most of the micro-containers (> 90%) arranged into two lines (Fig. 2C, D). Our previous studies demonstrated that the micro-containers were generated because of the assembled hydrogen gas bubbles on the working electrode acted as soft templates. The hydrogen gas bubbles were released from the counter electrode during the electrolysis process, mainly due to the following reactions:[5c]



In the aqueous solution of (+)-CSA (a typical surfactant), small gas bubbles were enwrapped by the surfactants with negative charges and dispersed in the aqueous solution. As a positive potential was applied, the gas bubbles close to the anode zone were assembled on the surface of the working electrode under the function of an electric field (Fig. 1). The assembled gas bubbles can be observed by naked eye or with an optical microscopy. Their sizes were measured to be around 50 μm.[5c] This is why only one line of micro-containers were grown on the 50 μm wide electrode. However, on the 200 μm silicon micro-electrode surface, the micro-containers grew along the two edges of the micro-electrode. This is mainly due to the surface tensions of the gas bubbles being decreased by the interactions between the walls of the polymeric photoresist and the gas bubbles (capillary interaction),[8] which led the gas bubbles to self-assemble linearly along the two edges of the silicon electrode. On the surfaces of the electrodes with widths of 100 and 150 μm, the micro-containers also tended to grow along the two edges of the electrode, however, the densities of micro-containers were relatively low because of both space limitation and fewer gas bubbles per unit length of the electrode (Fig. 4A, B). On the other hand, if the width of the electrode pattern was much higher than 200 μm (*e.g.* 500 μm), the micro-containers also could be arranged in two lines (Fig. 4C). Also, as the silicon line width was much narrower than that of the gas bubbles (*e.g.* 25 μm), the micro-containers seldom can be generated in good quality (Fig. 4D). These results also confirmed the gas bubble template model of micro-container growth. The height of the polymer photoresist also can influence the quality of the linear self-assembled PPy micro-containers. As the polymer film was thinner than 2 μm, the capillary effect was too weak to lead the gas bubbles to be arranged linearly. A thick polymer film (> 5 μm) is unnecessary and may result in the formation of micro-containers with irregular shapes. 3–5 μm thick films were found to be most suitable for generation of high quality linearly arranged micro-containers.

In conclusion, polypyrrole micro-containers formed by electrolysis of pyrrole in an aqueous solution of (+)-CSA can be arranged in one or two lines on patterned silicon micro-electrode surfaces with line widths of 50 or 200 μm, respectively. The hydrogen gas bubbles generated during electrolysis acted as the templates for micro-container growth. The positive electronic field and capillary interaction led the gas bubbles self-assembling to the edges of the linear silicon micro-electrode, which made the arrangement of polypyrrole containers. The self-assembly arrangement technique developed here can be extended to synthesize other materials with similar microstructures by changing monomers and surfactants.

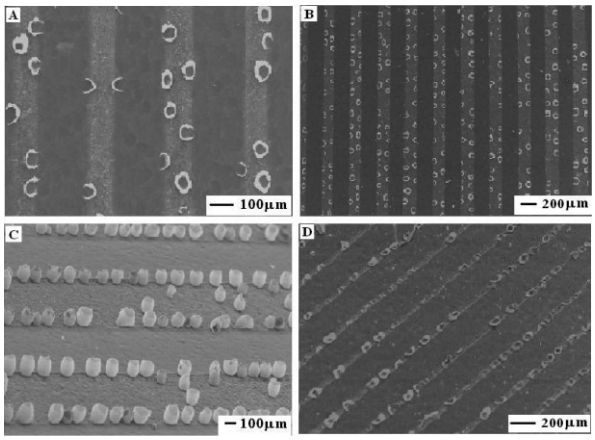


Fig. 4 SEM images of PPy micro-containers obtained by electrolysis of 0.5 M Py in an aqueous solution of 0.7 M (+)-CSA at a constant applied potential of 1.0 V. The margin between the two neighboring silicon micro electrodes was 200 μm (A, B, C) or 500 μm (D), and the widths of clean silicon electrode lines were 100 μm (A), 150 μm (B), 500 μm (C) and 25 μm (D) respectively.

This work was supported by the National Natural Science Foundation of China with Grant Nos. 50225311,50373023, 20374034 and 973 Project with Grant No. 2003CB615700.

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