Current Topics in Electrochemistry
Vol. 15, 2010

Original Communication

Droplet-assisted synthesis of polypyrrole capsules

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ABSTRACT

Two types of polymeric microcapsules were fabricated through the deposition of polymer onto liquid droplets. The microstructures were synthesized either by chemical or photochemical polymerization of pyrrole. In the first step an oil-in-water or water-in-oil emulsion was prepared and the liquid droplets were subsequently adsorbed onto glass or quartz slides. Then the polymer was deposited onto the surface of the droplets which resulted in the formation of polymeric capsules.

KEYWORDS: microcapsules, polypyrrole, emulsion, scanning electron microscopy, photo-polymerization

INTRODUCTION

Conducting polymers are very important material in science and industry due to their remarkable optical, electrical and catalytic properties. In recent years preparation of various nano- and microstructures was reported. Martin was one of the first who developed hard template synthesis of conducting polymers through chemical or electrochemical polymerization of monomers within the pores of filtration membranes [1]. Another kind of templates that can be applied to the synthesis of polymeric nano- and micro-structures, are soft templates. These include micelles, droplets, gaseous bubbles, etc. [2]. For instance, three-dimensional spherical structures of poly-(2-methoxaniline) fabricated with gas bubbles have been reported recently [3]. Nano- and microstructures have many potential applications in medicine as drug delivery systems or in gene therapy [4]. They are also used in electronics as displays [5] and in catalysis [6].

EXPERIMENTAL

Materials and methods

All chemicals were of the highest quality commercially available. In the photopolymerization experiments a UV-Vis mercury lamp Polamp-5 (Poland), 80 W was used. The images of the samples were recorded using LEO 1530 or LEO 435 VP Scanning Electron Microscopes.

Procedures and materials

To support polymeric capsules, glass or fused silica slides were used. The substrates were placed in contact with the respective oil-in-water (O/W) or water-in-oil (W/O) emulsion and then the pyrrole was polymerized either in chemical or photochemical reaction.

O/W emulsion

P-xylene/water emulsion was prepared by addition of p-xylene (100 µl) to water (3 ml), shaking and then sonicating for 30 s at 400 W. The glass slides were immersed for 5 minutes. Then the emulsion was exchanged for the polymerization bath. The polymerization solution was prepared by mixing 2 ml of aqueous 0.1 M pyrrole with 2 ml of aqueous 0.05 M $FeCl_3$ solution.

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W/O emulsion

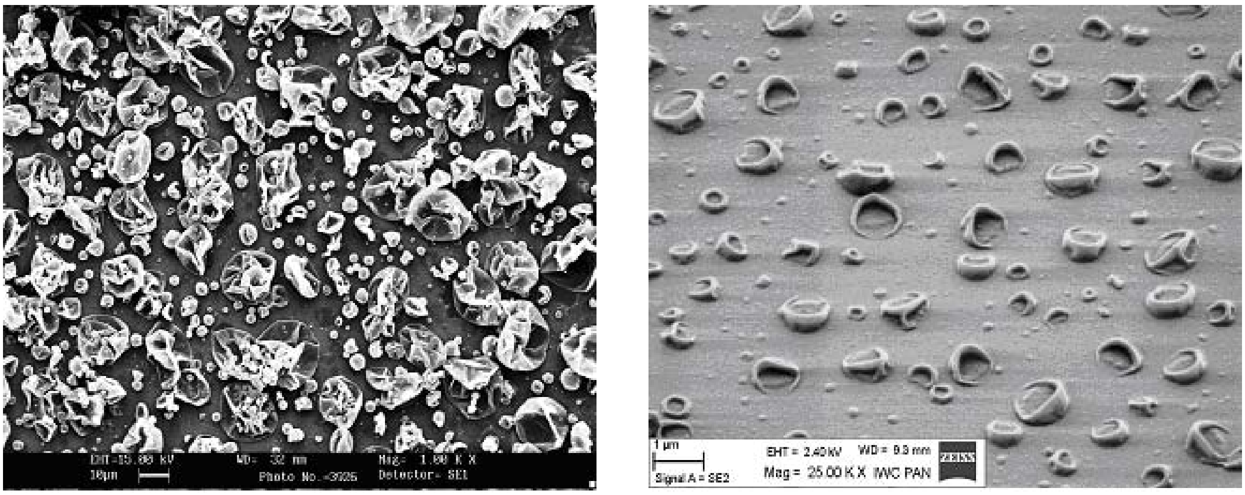
Water/dichloromethane emulsion was prepared by addition of 25 µl water to 5 ml dichloromethane containing 200 µl pyrrole and then sonication for 30 s at 400 W. One side of the quartz slide was placed in contact with the emulsion and then the sample was irradiated with UV light for 5 minutes at the distance of 23 cm from the quartz window side to photopolymerize the monomer.

RESULTS AND DISCUSSION

We demonstrate a facile preparation of three-dimensional nano- and microcapsules through deposition of polypyrrole onto the surface of liquid droplets. The droplets act as soft templates that direct polymer growth in form of liquid-filled micro- or nanocontainers. Two experimental approaches are reported - the deposition of polymer onto oil and aqueous droplets.

In the first case, an oil-in-water emulsion was prepared and the oil droplets (p-xylene) were adsorbed onto the glass substrate. Then the polymerization solution (monomer and oxidant) was added which resulted in the deposition of polypyrrole onto both the substrate and the droplets' surface [7]. This procedure yields the polymeric capsules filled with organic solvent, supported on the surface of glass. Shown in Fig. 1a is the scanning electron microscopy (SEM) image of the polymeric microcapsules. Their average diameter is ca. 9 µm. When imaged with SEM, the structures resemble collapsed doughnuts rather than the expected hemispheres. This is due to the evaporation of p-xylene from the capsules during the sample drying which results in the collapse of the containers.

In the second approach, a water-in-oil emulsion was used to fabricate the polymeric containers with an aqueous filling. We prepared the water-in-dichloromethane emulsion and the polymer was grown onto the droplets' surface. The main problem encountered during the synthesis is the polymerization of pyrrole in the organic medium (dichloromethane). The standard polymerization reaction cannot be used here (as it was applied in the case of p-xylene filled capsules) since the oxidant ($FeCl_3$) is not soluble in the dichloromethane phase. To overcome this problem a new polymerization approach based on the photochemical polymerization was proposed. We observed that the UV-irradiation of pyrrole in dichloromethane solution through a quartz window yields the polypyrrole adlayer on its surface. A detailed characterization of the photopolymerized pyrrole is to be published elsewhere [8], thus we only demonstrate here that this new polymerization protocol can be applied to grow



a) b)

Fig. 1. a) Scanning electron microscopy images of solid-supported polypyrrole capsules: a) grown on dichloromethane droplets; b) grown on aqueous droplets.

the three-dimensional containers (capsules) on silica slides. To synthesize the polypyrrole capsules the water-in-dichloromethane emulsion was used, and the monomer was dissolved in the organic phase. Then, the emulsion was irradiated with UV light through a quartz window. This procedure yielded micrometer-sized capsules (ca. 600 nm in diameter) on the quartz surface as shown in Fig. 1b (similarly as for the dichloro-methane-filled capsules, the structures are collapsed due to the evaporation of the solvent). The explanation of the formation of these capsules is as follows. First, the aqueous droplets are adsorbed on the substrate. Then, the UV light is switched on and the polymerization reaction is initiated both at the quartz/dichloromethane and droplet/dichloromethane interfaces. The growing polymer covers the substrate with a thin poly-pyrrole adlayer that encapsulates the droplets forming the three-dimensional microcontainers.

CONCLUSIONS

The solid-supported polypyrrole capsules filled with p-xylene or water were prepared through chemical or photochemical polymerization. The size of the obtained structures depends on the type of emulsion used in the experiment and varies from several hundreds of nanometers (water filled capsules) to several micrometers (p-xylene filled capsules).

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science and Higher Education through the National Centre for Research and Development, Project No. PBR 0923/R/T02/2010/10.

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