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Polypyrrole Microcontainers: Electrochemical Synthesis and Characterization

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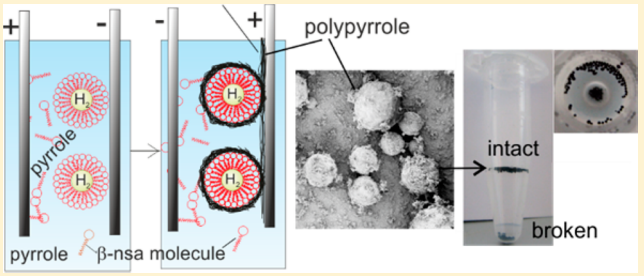
Supporting Information

ABSTRACT: We present electrochemically controlled synthesis of polypyrrole microcontainers on electrogenerated hydrogen gas bubbles acting as a template. We performed structural characterization of the obtained microcontainers to gain insight into the growth kinetics of the polypyrrole shell. Experimental results showed that surfactant-mediated polymerization of pyrrole at the hydrogen microbubble surface under controlled electrochemical biasing led to the synthesis of various micro/nanostructures. Dependent upon the electrochemical conditions, such as the number of redox cycles and scan rate, the containers with spherical globules and bowl-like structures, which become lantern-like with increasing the number of cycles, are formed, as revealed by scanning electron microscopy. Their diameter can range between 40 and 200 μm, and wall thickness can be varied from 2 to 70 μm, depending upon the electropolymerization conditions.



INTRODUCTION

Design of new types of sorbents is one of the developing areas in modern industry and technology. This is especially important for the removal of organic contaminants from water, like cleaning of oil and chemical spill accidents,[1] which are caused by human mistakes and carelessness, deliberate acts, such as vandalism, war, and illegal dumping, or natural disasters, such as hurricanes or earthquakes. Offshore and shoreline waters can be polluted by accidents involving oil tankers or container ships, runoffs from offshore oil explorations and productions, and spills from ship loading and unloading operations.[2]

There are three major classes of chemical sorbents, namely, inorganic mineral products, organic synthetic products, and organic natural products.[3,4] At present, most of the commercially available sorbents for removal of the liquid chemical hazards are organic synthetic products, such as polypropylene and polyurethane.[4] However, they are non-biodegradable and cannot be easily recycled after use as a result of their xenobiotic nature.

Various natural absorbers[5] and synthetic mineral products, such as expanded perlite[6] and zeolites,[7] exfoliated graphite,[8] vermiculites,[9] organoclay,[4] silica aerogel,[4] spongy graphene[10] and diatomite organic material wool fiber,[11] activated carbon, and sawdust,[12] were tested as pollution sorbents because of their microporosity. However, these materials have low sorption capacity. Microporous polymers were studied because of their large specific surface area and hydrophobicity.[13,14] Polymer sorbents already demonstrated high absorption ability and applications in different areas; however, the cost of these sorbents is quite high, and the environmental and ecological risks of these polymers in application are still present and not studied well. Such limitations of the existing sorbents led to the recent interest in developing new alternative products.

Hollow polymer containers can be one of the promising types for a new generation of sorbents. They possess high loading capacity as a result of low density and high inner lumen and can be of both hydrophobic and hydrophilic nature of the shell components as a result of the versatility of the container assembly techniques: layer-by-layer assembly,[15] interfacial polymerization,[16] co-precipitation during synthesis,[17] chemical cross-linking,[18] adsorption,[19,20] etc. Despite such a high level of the potential perspectives, there are no published works on the application of the polymer containers for collection of the liquid chemical hazards.

Polypyrrole (PPy) containers have very good potential for successful application as a chemical sorbent. The selection of PPy as container shell material has the following advantages. First, PPy is not toxic. PPy extraction solution showed no evidence of acute and sub-acute toxicity, pyretogen, hemolysis, allergen, and mutagenesis.[21] Second, perfect adsorption of the low-molecular-weight substances made PPy an interesting and perspective material for the sorption of chemical spills. Third, hydrophobic/hydrophilic properties of the PPy film can be easily varied, changing the chemical nature of the counterion in the oxidized state of PPy.[22,23] The preparation of the PPy

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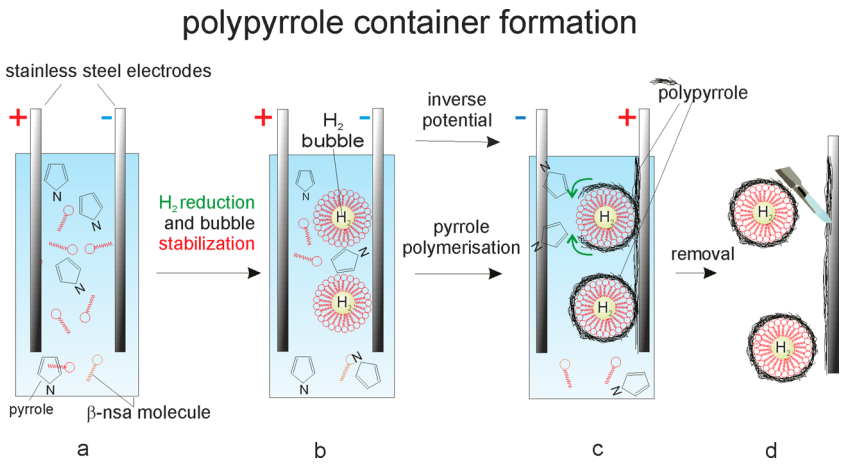

Figure 1. Schematic presentation of electrochemical fabrication of PPy containers: (a) electrochemical cell containing solution of surfactant (β-nsa) and pyrrole, (b) formation of the hydrogen microbubbles on the working electrode stabilized by the surfactant, (c) application of reverse potential on the working electrode, with the pyrrole being polymerized around pre-made, stabilized hydrogen microbubbles, and (d) detachment of prepared containers from the electrode.

microcontainers was shown using hard template microparticles (polystyrene), followed by further modification of the resulting PPy shell with Fe_3O_4 and Pd nanoparticles for reduction of 4-nitrophenol.[24,25] An emulsion-based template method was used for encapsulation of water-insoluble active materials, like Nile Red for biomedical applications[26] or polydimethylsiloxanes for redox-responsive self-healing coatings.[27] One of the recent interesting methods for the formation of the solvent-filled PPy microcontainers is photopolymerization of the pyrrole monomer at the water/solvent interface of the emulsion droplet.[28]

We previously demonstrated the formation of the 5−20 μm PPy containers on the oxygen microbubble on an anode electrode.[29] However, they were not able to store oxygen for a long time and float on the water surface as a result of their thin and porous shell. Here, we show for the first time the possibility of using an electrochemical method for making large (100−500 μm or even larger depending upon the electropolymerization conditions), hydrogen-filled PPy microcontainers, which store hydrogen and are able to float on the water surface collecting liquid chemicals. Such electrochemical fabrication of hollow containers based on the electropolymerization of pyrrole on the hydrogen bubbles stabilized by a surfactant was demonstrated before. PPy microcontainers can be easily prepared by electrochemical polymerization of pyrrole in substantial quantities without any additional need of the expensive reagents or template particles. Various parameters, like scanning speed (volts per second), number of cycles, and voltage range, have a strong influence on the amount and structure of the PPy shell deposited on the bubble template. Modification of cyclovoltammetric parameters allows one to keep a balance between shell thickness, size, and stability of PPy microcontainers.

EXPERIMENTAL SECTION

Materials. Pyrrole and β-naphthalene sulfonic acid (β-nsa) were purchased from Aldrich and used without further purification.

Fabrication of PPy Containers. The growth of the PPy microcontainers was carried out at 20 °C in a 50 mL electrochemical cell (Radiometer Analytical, France) with a CompactStat potentiostat/galvanostat (Ivinum, Netherlands) under personal computer (PC) control. Working and counter electrodes were two stainless-steel foils, of 1 cm^2 surface area each, placed 0.5 cm apart. All potentials were referred to the saturated Ag/AgCl electrode (Radiometer Analytical, France).

Cyclovoltammetry scanning was performed in a 0.5 M pyrrole aqueous solution with the addition of 0.5 M β-naphthalene sulfonic acid (pH 3). The solution was deaerated with the pure nitrogen gas flow for 15 min before container formation. The first scanning cycle was performed from 0 to −1.6 V versus Ag/AgCl electrode to generate hydrogen bubbles on the working electrode (Figure 1a). After the first cycle, the scanning potential range was changed from 0 to +1.6 V for pyrrole electropolymerization on stabilized hydrogen bubbles (panels b−d of Figure 1). Scan rates were varied for each sample (the same scan rate for first and other cycles): 0.02, 0.1, 0.2, and 0.5 V/s. The presence of β-naphthalene sulfonic acid in solution not only stabilizes hydrogen bubbles and provides time enough to form the PPy shell but also, as a large organic counterion, makes the PPy wall more hydrophobic. Pyrrole electropolymerization was performed with a variable number of oxidation cycles, from 1 up to 14 cycles, depending upon the sample. After electropolymerization, hollow PPy microcontainers were mechanically removed from the electrode and separated from the rest of PPy by washing in water.

Characterization. The morphology of PPy containers was investigated by scanning electron microscopy (SEM, LEO-1550, Carl Zeiss, Germany). Size distribution and wall thickness were derived from SEM images. Statistical image analysis was performed using ImageJ (NIH, http://rsb.info.nih.gov/ij/) software based on the calculation of 30 microcontainers per sample.

RESULTS AND DISCUSSION

The PPy containers templated on the stabilized hydrogen microbubbles were synthesized on the stainless-steel working electrode. The time of PPy deposition, which is related to the number of cycles and speed, has a strong influence on the pyrrole polymerization and, consequently, amount of polymerized pyrrole in the container shell (Figure 1).

Scan potential window was set in the negative range (from 0 to −1.6 V) during the first cycle, and the hydrogen microbubbles were produced on the working electrode and stabilized by the surfactant (Figure 1a). Afterward, the scan potential window was changed to the positive values (from 0 to +1.6 V). Hydrogen stopped being generated, and pyrrole polymerization started covering β-nsa-stabilized hydrogen microbubbles with the PPy shell (panels b−d of Figure 1). The amount of pyrrole deposition is dependent upon the time of polymerization. We can control this parameter in two

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different ways: changing the number of cycles or scanning speed.

The influence of the number of cycles was investigated at two different scanning speeds: 0.02 and 0.2 V/s. The SEM images of the obtained PPy structures are presented in Figures 2 and 3.

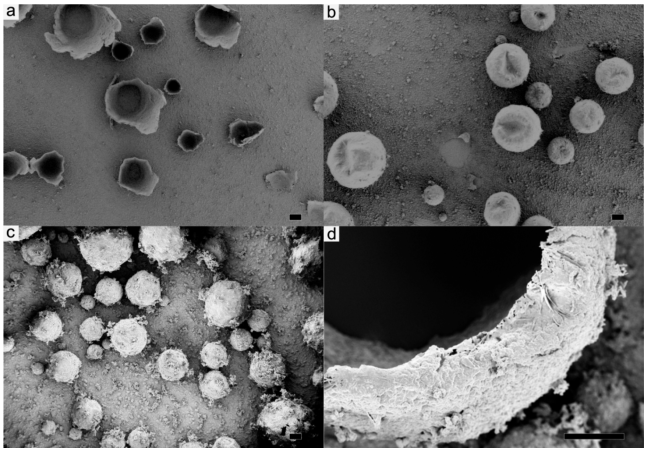

Figure 2. SEM images of the PPy containers obtained at a constant speed of 0.02 V/s and different numbers of cycles: (a) 1 cycle, (b) 2 cycles, and (c and d) 3 cycles. Wall thickness is 1.5, 7, and 70 μm, respectively. Scale bar = 100 μm.

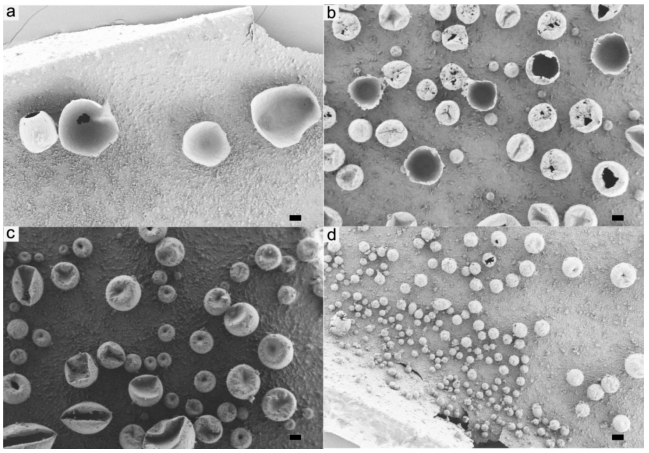

Figure 3. SEM images of the PPy containers obtained with speed of 0.2 V/s at different numbers of cycles: (a) 6 cycles, (b) 10 cycles, (c) 12 cycles, and (d) 14 cycles. Scale bar = 100 μm.

The amount of PPy deposited on the stabilized hydrogen bubbles can be defined at the low speed. After 1 cycle, the PPy deposition does not fabricate a stable spherical structure (Figure 2a). Gas microbubbles are not completely covered with PPy. After 2 cycles, gas microbubbles are completely covered with the PPy shell and the wall thickness is increased from 1.5 to 7 μm (Figure 2b; see also the Supporting Information for other SEM images demonstrating the wall thickness). Increasing the number of cycles to 3 created very dense containers (Figure 2c), with wall thickness around 70 μm (Figure 2d). The better control over the wall thickness and final mass of containers can be performed by the increasing of the deposition speed to 0.2 V/s (Figure 3). Increasing the number of cycles to more than 10 gives us stable containers with hydrogen inside (Figure 3c). Thus, the facile mechanism of mass and wall thickness control for PPy containers was achieved by simple changing of the electropolymerization conditions.

Separation of the microcontainers from the steel template was performed by scratching, and microcontainers were washed with water from PPy pieces. Dense PPy pieces and cracked containers are sediment, while intact H_2-containing containers can be collected from the water surface (Figure 4).

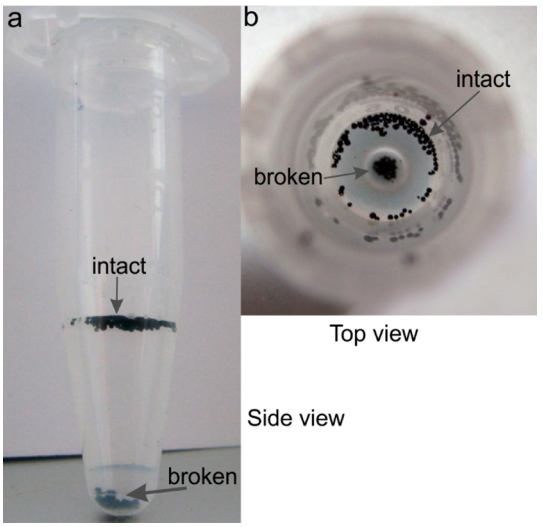

Figure 4. (a) Side view and (b) top view of hydrogen-filled containers, cracked containers, and PPy pieces in water. Containers were prepared at 0.2 V/s, with 14 cycles of pyrrole polymerization, and detached.

The floating ability of containers is very important for their use as a sorbent on the water surface. The light density of PPy prefilled with hydrogen gives a good opportunity to use it in perspective as a liquid sorbent from the water surface. The net forces acting on the either filled or empty containers can be expressed by the following equation:

$$F_{net} = mg - \rho_w V_p g$$

where ρ_w is the density of water, V_p is the volume of PPy particles, and

$$m = \rho_{pp} 1/6\pi(d^3 - (d - l)^3) + \rho_{oil} 1/6\pi(d - l)^3$$

where ρ_{pp} is the PPy density, l is the wall thickness, d is theparticle diameter, ρ_{oil} = 820 kg m^{-3}, ρ_{pp} = 1500 kg m^{-3}, and ρ_w = 1000 kg m^{-3}.

The positive and negative values of the equation demonstrate the possibility of microcontainer floating (negative) or sedimentation (positive). In Figure 5, we showed how to manage this properly by modulation of the wall thickness for 200 μm containers presented in Figure 3d. This theoretical model demonstrates the control over the container position on either the surface of water or the bottom. After diffusion of hydrogen through the container walls, the container interior is filled with air or solvent (oil). The positive value of net force means that the containers sink. The containers with wall thickness less than 6 μm do not sink either with or without oil inside. Starting from 7 μm, the containers filled with oil continuously sink in water compared to the containers filled with air. This difference remains until 30 μm wall thickness. Above 30 μm, the quantity of PPy is 0.3 of the whole container volume and the microcontainers become heavy enough to sink by their own weight without additional filling.

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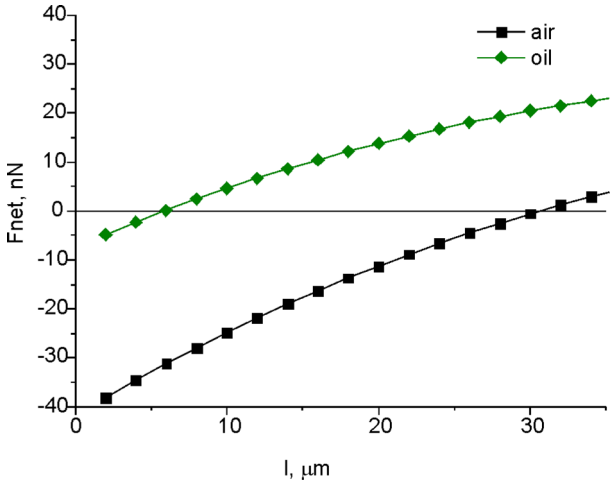

Figure 5. Simulation of the net force (F_{net}) for PPy containers filled with air (square) and oil (diamond) with a fixed diameter (d = 200 μm) depending upon container wall thickness (l). A positive net force indicates that containers sink.

Both size and wall thickness have a strong influence on container floating. Figure 6 presents a simulation of the net

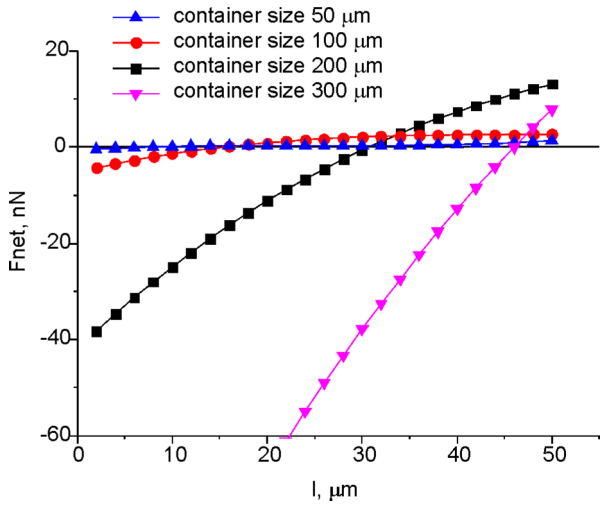

Figure 6. Simulation of the net force (F_{net}) depending upon container wall thickness (l). Simulation was performed for air-filled containers with different diameters (d): d = 50 μm (triangle), d = 100 μm (circle), d = 200 μm (square), and d = 300 μm (reverse triangle). A positive force indicates that containers sink.

force for air-filled containers with different sizes and wall thicknesses. If the net force has a 0 value, the wall thickness increase leads to the container immersion into the water. Larger containers need thicker walls to become immersed into water. For example, for 50 μm containers, the wall thickness of 8 μm is enough to be sunk, while a 300 μm container needs 42 μm walls.

CONCLUSION

In summary, we demonstrated facile and rapid electrochemical synthesis of hollow PPy containers with a micrometer size range, which has an easy upscaling ability for industrial application by increasing the surface area of the electrodes. The size and wall thickness of microcontainers can be easily controlled by changing parameters of the electrochemical oxidation of pyrrole: scanning speed and number of polarization cycles. We observed that hydrogen was successfully encapsulated and intact containers are floating on the water/air interface. The potential application of the resulting nontoxic PPy microcontainers as a sorbent for collection of the liquid chemical hazards from a water surface was theoretically analyzed depending upon the container size and wall thickness.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b01931.

SEM images of the PPy containers with a cut section for thickness determination (PDF)

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Notes

The authors declare no competing financial interest.

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