

Preparations of the Artificial Plastron Device by Self-Organized Honeycomb-Patterned Films*

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Oxygen is an indispensable resource for action of humans or autonomous underwater vehicles in water. However, it is limited in the present situation because of a capacity of O₂ cylinders. In nature, there are some insects, which utilize superhydrophobic hair structures as physical gills, semipermanently living in water. We focused on this physical gill of the plastron and prepared artificial plastrons by using self-organized honeycomb-patterned films. As result, durable honeycomb-patterned films resisting water pressure were obtained, and O₂ transferred from air to water through the films. This phenomenon suggests the honeycomb-patterned films showed possibility of use as artificial plastrons.

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I. INTRODUCTION

Recent years, biomimetics, which is a material and device fabrication research field by mimicking or inspiring from nature functional surfaces, attract much attention due to their possibilities for sustainable society [1–3]. Especially, we focused on a superhydrophobic plastron [4]. Though pulmonary respiration, some insects live in water. They use air bubbles trapped at the plastron, which is superhydrophobic hair structures, for breath in water. In this case, when insect uses O₂ in trapped air bubbles for breath, a concentration of O₂ is decreased and that of CO₂ is increased. Carbon dioxide is easily dissolved in water. Therefore, air bubbles would be shrinking. However, air bubbles are supported by superhydrophobic hairs, so air bubbles can not become small and O₂ is supplied from water by a partial pressure. As result, insects can continuously stay in water by using plastrons as physical gills [5]. By mimicking the plastron, we can obtain new oxygen supply device instead of limited air cylinder for use in water [6].

For fabrications of artificial plastron devices, there are three key factors; superhydrophobic surfaces, porous materials, and durable materials. Superhydrophobicity is required for trapping air bubbles in water, and porous materials are needed for gas exchange between inside and outside of an O₂ consumption place. Durability is also important for resisting water pressure because inside area is filled by air in many applications. We have reported honeycomb-patterned porous polymer films are easily obtained by self-organization process [7–9]. The honeycomb-patterned films are not superhydrophobic surfaces, but it is hard to get water into the micropores because hydrophobic spherical micropores trap air bubbles in water. Furthermore, the honeycomb-patterned films can be prepared from wide variety of hydrophobic polymers, which

can be dissolved in a hydrophobic solvent. So, we can obtain durable honeycomb-patterned films made from engineering plastics, such as Poly(Bisphenol A carbonate) (PC, Fig. 1(a)), Polysulfone, and so on. In this report, we attempted the honeycomb-patterned films to an artificial plastron device. Herein, a construction of O₂ transmittance measuring setup and O₂ exchange properties through the honeycomb-patterned films are shown.

II. EXPERIMENTAL

The honeycomb-patterned films were prepared by casting 4.4 g/L chloroform solutions of PC ($M_w = 22,000\text{--}40,000$ g/mol, purchased from Sigma-Aldrich, USA) and an amphiphilic polyacrylamide derivative (Cap, Figure 1(b), $m : n = 4 : 1$, synthesized by free-radical polymerization as described elsewhere [10]) (PC : Cap = 10 : 1) on 20×10 cm glass substrates. The casting volume of the polymer mixture solution was 19 mL. Moist air (temperature 38°C, relative humidity c.a. 90%) was applied to the solution surface at a flow rate of c.a. 51 L/min.

Experimental setup for measuring O₂ exchange properties through the films was shown in Fig. 2. To investigate a function of honeycomb-patterned films as plastron, O₂ transmittances from inside the bottle filled by air to water were measured. The honeycomb-patterned films were removed from the glass substrate, and fixed on polystyrene (PSt) bottles (Inside volume is 20 mL) with mm-scale pores (Pore diameters were 1.5 mm, total pore surface area was 353 mm² and 3.3 mm, total pore surface area was 513 mm², respectively. See Appendix.) by a

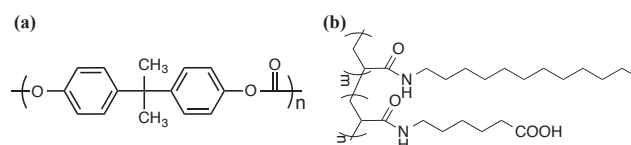


FIG. 1. Structural formulas of (a) PC and (b) Cap ($m : n = 4 : 1$).

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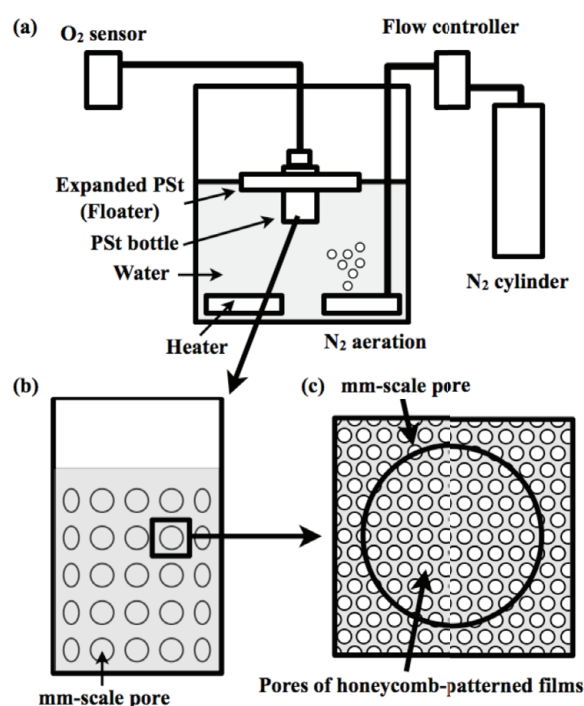


FIG. 2. (a) A schematic illustration of experimental setup. Magnified schematic illustrations of (b) a PSt bottle and (c) a mm-scale pore.

common glue. The oxygen sensor (JKO-O2LJD3, JIKCO Ltd., Japan) was fixed to the PSt bottle top, and PSt bottles with or without honeycomb-patterned films were soaked in deionized water (Water temperature was kept at 26°C by a heater). An oxygen concentration of water was decreased by N₂ aeration at flow rate of 3 L/min to keep almost 0 mg/mL. Surface structures of honeycomb-patterned films were observed by using optical microscope (LEXT OLS4000, OLYMPUS COOPERATION, Japan), and water contact angles (WCAs) of the films were measured by using WCA analyzer (DM500, Kyowa Interface Science Co. LTD., Japan) with 3 μ L ultra pure water.

III. RESULTS AND DISCUSSION

Figure 3(a,b) displays optical microscope images of honeycomb-patterned films. Hexagonally arranged 5.8 μ m pores were formed at the topside. At the backside of the films, there were thin polymer layer located at micropores. Strictly, honeycomb-patterned films with penetrated pores were more prefer for O₂ transmittance, however, that types of the films were mechanically weak. Therefore, the honeycomb-patterned films with non-penetrated pores were used in this experiment. Figure 3(c,d) shows WCAs on a PC flat surface and the honeycomb-patterned films. WCAs were enhanced by surface structures of honeycomb-patterned films. Although honeycomb-patterned films were not superhydrophobic surface, it is hard to put water into micropores of the films because of trapped air of inside pores. After fixing the honeycomb-patterned films on PSt bottles with mm-scale pores, PSt bottles were soaked in wa-

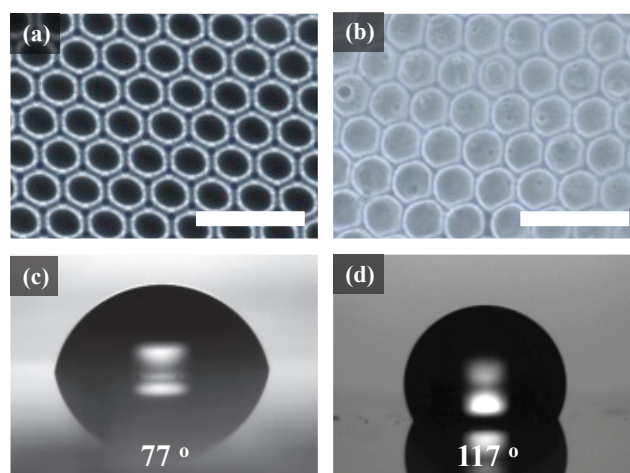


FIG. 3. Optical microscope images of honeycomb-patterned films (a) topside and (b) backside (Bars; 20 μ m). WCAs of (c) PC flat surface and (d) honeycomb-patterned films.

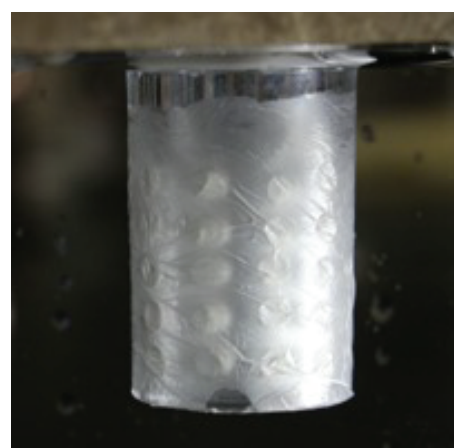


FIG. 4. A photograph of the PSt bottle with honeycomb-patterned films in water.

ter. Silvery appearance caused by total reflection between trapped air and water interface were observed (Fig. 4). And water did not go into the PSt bottle inside with breaking the honeycomb-patterned films. This result indicates the honeycomb-patterned films prepared from PC have enough durability for measuring a gas exchange experiment.

Figure 5 shows graphs of O₂ concentrations of inside the PSt bottles. In the case of the blank system (PSt bottles without mm-scale pores and honeycomb-patterned films), O₂ concentration was gradually decreased to c.a. 17% after 10 h. Cause of this O₂ concentration decline was supposed to the O₂ transmittance of bottle materials or O₂ consumptions by the O₂ sensor, which is consisted of a galvanic cell. In the case of PSt bottles with honeycomb-patterned films, decreasing rates of O₂ concentration were larger than the blank system, and differences between two types of PSt bottles with honeycomb-patterned films were related to mm-scale pore surface area. These results suggested that honeycomb-patterned films acted as an artificial plastron even though O₂ exchange rates were still

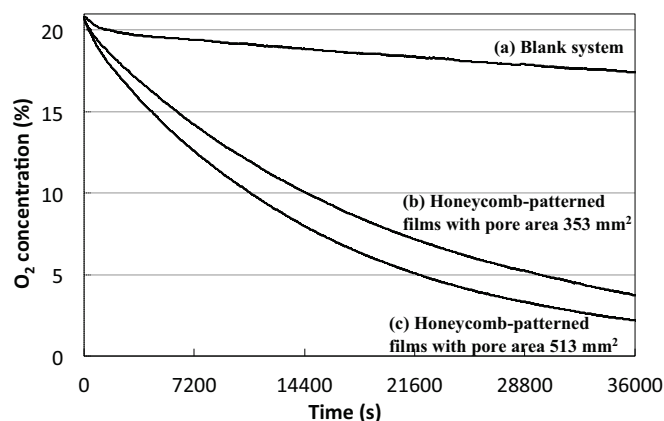


FIG. 5. A graph of O_2 transmittance. (a) Blank system (Non mm-scale pores on a PSt bottle), PSt bottles with (b) 1.5 mm diameter pores and (c) 3.3 mm diameter pores surrounded by honeycomb-patterned films, respectively.

not enough for practical use of applications, such as an O_2 supply source of autonomous underwater vehicles.

IV. CONCLUSIONS

In conclusions, we demonstrated an application of honeycomb-patterned films as an artificial plastron. The

honeycomb-patterned films with 5.8 μm pores were successfully obtained. Prepared films from PC have enough durability for water pressure during O_2 transmittance measurements. However, O_2 transmittance ability of honeycomb-patterned films was insufficient to use for autonomous underwater vehicle or other application. We should prepare honeycomb-patterned films with more durable hydrophobic polymers for the fabrication of the films with penetrated type micropores, because O_2 transmittance rate of it might be higher than that of non-penetrated type films.

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APPENDIX

Photographs of the PSt bottles are available in Supplementary materials (https://www.jstage.jst.go.jp/article/ejsnt/13/0/13.90/_article/supplement).

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- [1] P. Ball, *Nature* **400**, 507 (1999).
 - [2] D. W. Bechert, M. Bruse, W. Hage, and R. Meyer, *Naturwissenschaften* **87**, 157 (2000).
 - [3] T. L. Sun, L. Feng, X. F. Gao, and L. Jiang, *Accounts of Chemical Research* **38**, 644 (2005).
 - [4] M. R. Flynn and J. W. M. Bush, *J. Fluid Mech.* **608**, 275 (2008).
 - [5] R. S. Seymour and P. G. D. Matthews, *J. Exp. Biol.* **216**, 164 (2013).
 - [6] N. J. Shirtcliffe, G. McHale, M. I. Newton, C. C. Perry, and F. B. Pyatt, *Appl. Phys. Lett.* **89**, 104106 (2006).
 - [7] G. Widawski, M. Rawiso, and B. Francois, *Nature* **369**, 387 (1994).
 - [8] N. Maruyama, T. Koito, J. Nishida, T. Sawadaishi, X. Cieren, K. Ijiro, O. Karthaus, and M. Shimomura, *Thin Solid Films* **329**, 854 (1998).
 - [9] Y. Hirai, H. Yabu, Y. Matsuo, K. Ijiro, M. Shimomura, *J. Mater. Chem.* **20**, 10804 (2010).
 - [10] H. Yabu, Y. Hirai, and M. Shimomura, *Langmuir* **22**, 9760 (2006).