Microfluidic Fabrication of Microcapsules Encapsulating Mineral Oil and Evaluation of Self-Healing of Self-Cleaning Performance

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Keywords: microfluidics, oil-encapsulated microcapsules, self-healing, self-cleaning

Abstract ID No : 51

ABSTRACT

This research presents self-cleaning surface formed with hydrophobic microcapsules including mineral oil to address self-healing. The self-cleaning surface is consisted of hydrophobic microcapsules with nano structures on the outer surface of the capsule. In specific, the nano structures on the outer surface of the microcapsules were formed by PANI(polyaniline) treatment. The self-healing can be examined by releasing oil when the capsule is broken by external forces such as impact of rain or mechanical scratch. The self-cleaning and self-cleaning microcapsules were fabricated successfully in a microfluidic channel with multi-step inlets and the self-healing of self-cleaning performance was evaluated. The contact angle was measured and compared before and after the relaease of oil.

INTRODUCTION

Self-healing technology is self-restoration without any external intervention such as cellular tissue restoration or natural purification. The scanning electron microscope (SEM) reveals the surface topology of a lotus leaf (Figure 1). It is structured with micropappilaes and nanocilia covered with wax and exhibits superhydrophobic water repellency, resulted in self-cleaning[1-3].

There are various methods to fabricate self-cleaning surface such as silicon etching, polymer molding and surface deposition. But these methods have disadvantage that cannot restore after it destroyed. Thus, in this study a novel method to fabricate self-cleaning surface with long term reliability is suggested. For the technical analogue of lotus leaf, we present a mimicking surface sprayed with the nanostructured microcapsules encapsulating mineral oil. Also, self-healing has been examined by measuring contact angle after releasing oil out when the surface is ruptured.

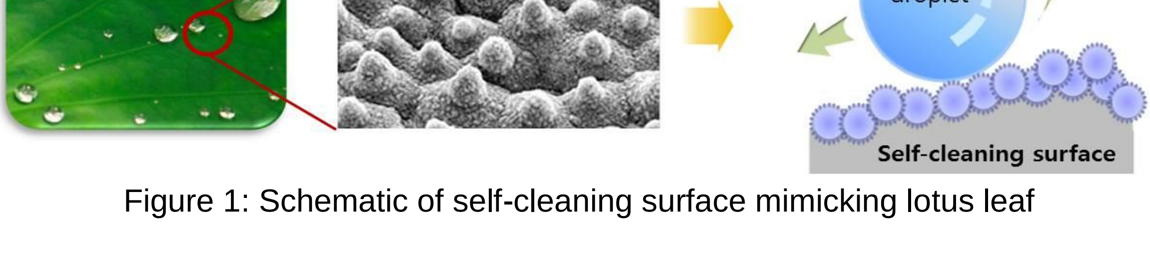


Figure 1: Schematic of self-cleaning surface mimicking lotus leaf

1. MATERIALS AND METHODS

To produce the microcapsules encapsulating mineral oil, the microfluidic device fabricated by bonding with PDMS(polydimethylsiloxace) polymer and a transparent slide glass. A 100 ㎛-thick layer of the SU-8 photoresist(SU-8 2050, MicroChem) was spin-coated onto a polished silicon wafer with the spread cycle ramping to 500 rpm for five seconds and sequentially to 2000 rpm and was maintained for 30 seconds. Two stage soft baking to evaporate solvent and to increase density of film was conducted at a condition of three minutes, 65 ℃ and nine minutes, 95 ℃ in a baking oven. The SU-8 photoresist was then patterned by UV exposure under I-line of 365 nm for 30 seconds and was cross-linked. Finally, the SU-8 patterned mold was prepared by developing in the SU-8 developer for three minutes, followed by rinsing with isopropyl alcohol.

The PDMS pre-polymer was mixed with the curing agent at a volumetric ratio of 10 :1. The mixture was then degassed in a vacuum until air bubbles were removed completely. The PDMS was then poured onto the prepared SU-8 mold and cured at 65 ℃ for 30 min. The patterned PDMS was detached from the SU-8 mold. The PDMS layer was treated by oxygen plasma(Plasma cleaner PDC-32G, Harrick Plasma) and immediately brought in contact with the slide glass for bonding. The plasma power used was 10.5 W and the chamber pressure was set to 200 mTorr. The plasma exposure was maintained for two minutes. Finally, the PDMS layer was bonded with slide glass to form the microfluidic chip. The width and depth of the microchannel are 100 ㎛ each.

A microfluidic device with two successive inlet cross-channels prepared to obtain the double-layered droplets. The mineral oil mixed with Rhodamine-B was introduced into the center inlet of the first inlet cross-channel with a flow rate of 5 ㎕/min and 1wt% PVA solution into two side inlets with a flow rate of 10 ㎕/min. The CH_2Cl_2 containing PS-b-PMMA injected into two side inlets of the second inlet cross-channel with a flow rate fo 30 ㎕/min. The double-layered droplets of O/W/O were generated (Figure 2(a)). They were collected and dried. Figure 2(b) shows the SEM(scanning electron microscope) of the oil-encapsulating microcapsules in the range of 20-40 ㎛ sizes.

Also, to form nanocilia on the microcapsule surface, polyaniline was coated on the surface[4]. The microcapsules were immersed in an aqueous solution containing 1 M $HClO_4$, 6.7 mM ammonium persulfate and 10 mM aniline monomer at 0-4 ℃ for 12 hours. Then, they were washed to remove the residual of polymers. Figure 3 shows the SEM image of the nanostructures on the microcapsule and the chemical compounds by measuring EDAX.

2. RESULTS AND DISCUSSION

In order to evaluate the recovery of self-cleaning function, we measured the contact angle on the glass substrate. The self-healing of the self-cleaning surface was demonstrated by measuring the incresed contact angle on a glass surface withe the released hydrophobic oil and the fractured microcapsules fragments.

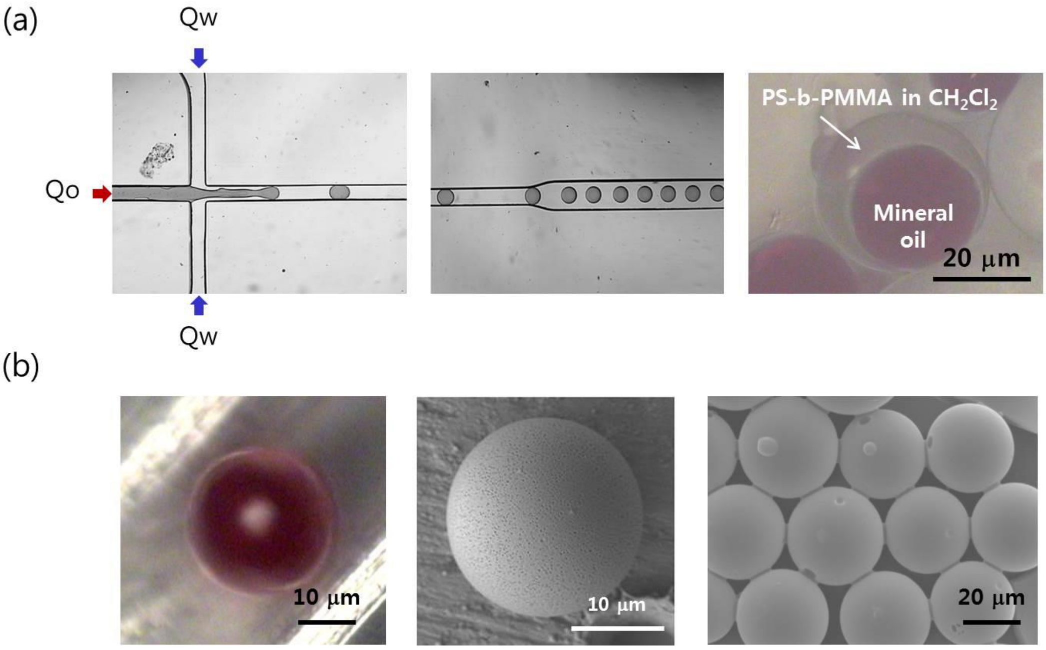
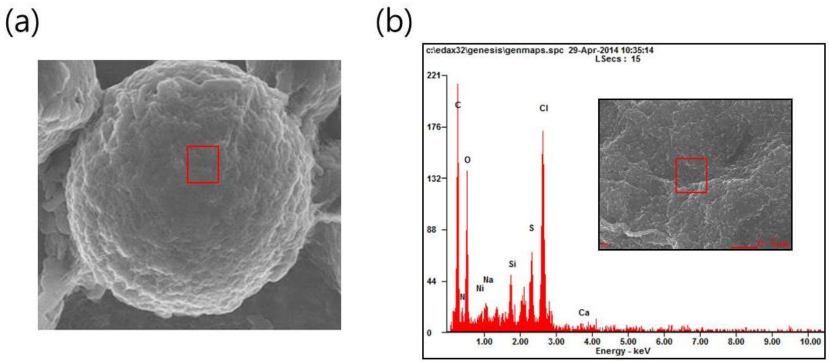


Figure 2 : Visualization of encapsulating mineral oil in the microchannel
(a) Droplet generation and encapsulated result, (b) Evaluation of mineral oil encapsulated in the microcapsules



Element	Wt%	At%
C	52.97	65.43
N	07.57	08.02
O	19.05	17.66
Ni	01.13	00.29
Na	00.89	00.57
Si	01.82	00.96
S	03.52	01.63
Cl	12.62	05.28
Ca	00.43	00.16
Matrix	Correction	ZAF

Figure 3 : Evaluation of surface nano structure by PANI(polyaniline) polymerization by FE-SEM and EDAX
(a) Morphology of nano structure, (b) Analysis results of chemical compounds after synthesis

The nanostructured microcapsules were sprayed on a glass surface and the contact angle was measured to examine self-cleaning performance. As shown in Figure 4(a) and 4(b), the contact angle on bare glass was 14.6 °, while that coated with oil only was 90.1 °, respectively. The glass coated with microcapsules were broken mechanically and the oil release was observed. It is shown that the contact angle was increased to 120.1°. This indicates that the self-cleaning performance can be recovered successfully by the breakage of the microcapsules, leads to the self-healing of the surface.

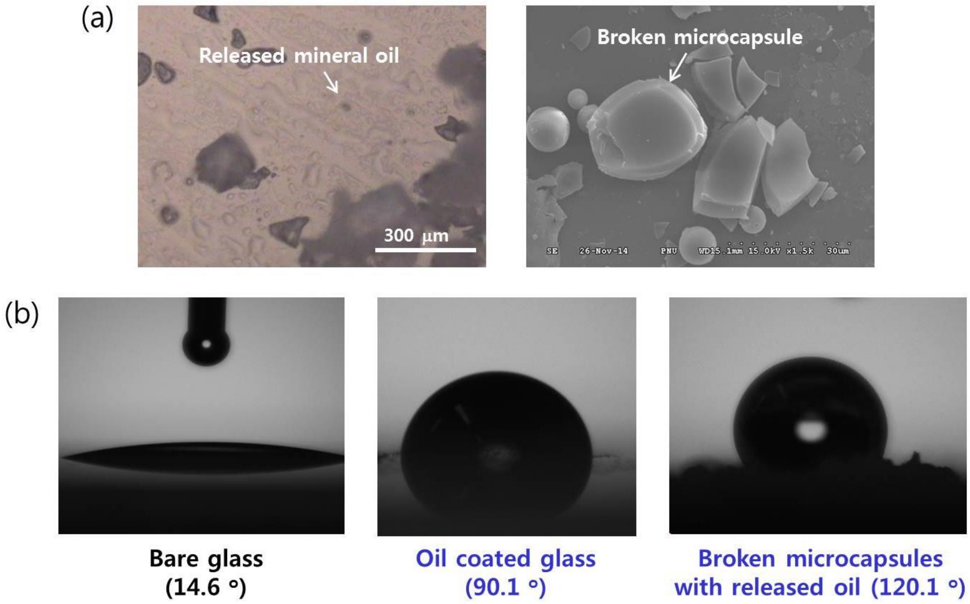


Figure 4. Performance evaluation of self-cleaning function
(a) Broken microcapsules with released mineral oil of self-cleaning surface,
(b) Contact angle comparison with bare glass and after capsule broken

3. CONCLUSION

Double-layered microdroplets were produced in two step inlet cross microchannel. The mineral oil-encapsulated hydrophobic microcapsules of 20-40 ㎛ with nanostuructures of about 200 nm were successfully fabricated by using the self-assembly of block copolymers. The micro-nano hybrid structures formed by the microcapsules and nanostructures obtained by PANI treatment demonstrated the self-cleaning surface with a large contact angle. Also, their self-healing performance is shown by releasing the oil with the breakage of the capsules.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MOE) (No. NRF-2014R1A1A2057489).

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