

Electronic Supporting Information

One-pot microfluidic fabrication of graphene oxide-patched hollow hydrogel microcapsules with remarkable shell impermeability

Aram Byun,^a Jongwon Shim,^b Sang Woo Han,^a Bohyun Kim,^c Pil Seok Chae,^a

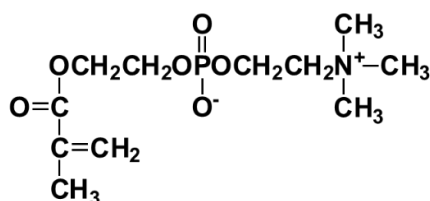
Hyeong Seok Shin,^d and Jin Woong Kim^{a,c}

^aDepartment of Bionano Technology, Hanyang University, Ansan 426-791, Republic of Korea;

^bAmore-Pacific Co. R&D Center, Yongin, 446-729, Republic of Korea; ^cDepartment of Applied Chemistry, Hanyang University, Ansan, 426-791, Republic of Korea; ^dHansol Bio Inc., Seongnam, 463-824, Republic of Korea.

Experimental section

Materials: 2-methacryloyloxyethyl phosphorylcholine (MPC, Scheme S1) was kindly supplied from KCI Co. (Korea). Cetyl PEG/PPG-10/1 dimethicone (Abil EM 90, Evonik, Germany), and hexyltrimethoxysilane (TCL, Japan) were used as received. Isopropanol was purchased from Samcheon (Korea). Paraffin oil, N, N'-methylenebisacrylamide (BIS), 2-hydroxy-2-methylpropiophenone (Darocure 1173, 97%), fluorescein sodium salt (FSS), kerosene oil, glycerol ($\geq 99.5\%$ purity), and polyvinyl alcohol (PVA, Mw 13,000-23,000, 87-89 % hydrolyzed) were all purchased from Sigma-Aldrich (USA). All other chemicals were reagent grades and used without further purification.



Scheme S1. Molecular structure of 2-methacryloyloxyethyl phosphorylcholine (MPC).

Synthesis of graphene oxide: Aqueous graphene oxide (GO) dispersion was prepared from graphite powders by a modified Hummer's method.¹⁻⁴ 20 g of graphite and 460 mL of sulfuric acid (H₂SO₄) were mixed in a flask. Then, 60 g of potassium permanganate (KMnO₄) were slowly added over 1 h and, stirring was continued for 2 h in an ice bath. Then, the mixture was stirred vigorously for 18 h at room temperature. After the completion of oxidization, 920 mL of deionized water was added and, the

solution was stirred for 10 min in an ice bath. 50 mL of H₂O₂ (30 wt% aqueous solution) was then added and, the mixture was stirred for 2 h at room temperature to cease the oxidization reaction. The resulting mixture was precipitated and filtered to separate graphite oxide powder, which was washed with 10-fold-diluted hydrogen chloride (HCl, 37%) several times to remove impurities. After vacuum filtering, graphene oxide was vacuum-dried at room temperature. The dried solid powder was re-dispersed in deionized water to remove residual ionic or acidic impurities by dialysis (Spectrum Laboratory, Inc., MWCO of membrane = 8000). The dialysis was performed for two weeks, highly pure graphene oxide solution was finally obtained.

Fabrication of glass capillary-based microfluidic devices: To generate o/w/o double emulsions in a single step, we used a glass capillary-based microfluidic device that consisted of two cylindrical glass capillaries (outer diameter = 1.0 mm, World Precision Instruments, USA) within a square glass capillary (inner diameter = 1.0 mm, Atlantic International Technology, Spain). The two cylindrical capillaries were tapered with a pipette puller (Model P-97, Sutter Instruments, USA), their tips were adjusted by using a microforge station (Micro Forge MF 830, Narishige, Japan). Typically, the diameter of injection capillary and collection capillary were 20 μm and 200 μm, respectively. The two capillaries were treated with 1 wt% of hexyltrimethoxysilane in toluene to make their surfaces hydrophobic, thereby preventing any wetting of the middle aqueous phase. For this, the capillaries were dipped in the hexyltrimethoxysilane/toluene solution for 30 sec and then dried at 50 °C for 6 h. Lastly, the cut-down needles (Korea Vaccine Co., Ltd., Korea) were glued at the junction between capillaries or their ends on a glass microscope slide.

Generation of uniform O/W/O double emulsions: Monodisperse O/W/O double emulsion drops were produced with the microfluidic device. Each fluid was loaded into a glass syringe (Hamilton Gastight, USA) that was fitted with a 20G luer-stub. The luer-stub was connected with a polyethylene (PE) tube having an outer diameter of 1.32 mm (PE-5, Scientific Commodity, USA). The outer and middle fluids were injected through the interstices between the round injection capillaries and the square collection capillary, respectively. The inner fluid was injected through the injection capillary. The flow rates were precisely adjusted using the syringe pumps (Pump 11 Elite, Harvard Apparatus, USA).

Characterizations: The generation of double emulsion drops was monitored using an inverted microscope equipped with a high-speed camera (Phantom Miro eX2, Vision Research Inc., USA). The morphology of the collected double emulsion drops and hydrogel shell microcapsules was imaged using a bright-field microscope (NSI-100, Samwon, Korea). The surface topology of GO-patched PMPC microcapsules were observed with a scanning electron microscope (SEM, MIRA3, TESCAN,

Czech Republic). We also observed the fluorescence intensity of probe molecules by using a fluorescence microscope (Axio Vert.A1, ZEISS, Germany). The presence of GO in the microcapsules was confirmed by using a Raman spectroscopy (RM 1000, Renishaw, UK). The interfacial tension was determined with a force tensiometer (Attension Sigma 700, Biolin Scientific, Sweden).

Experimental data

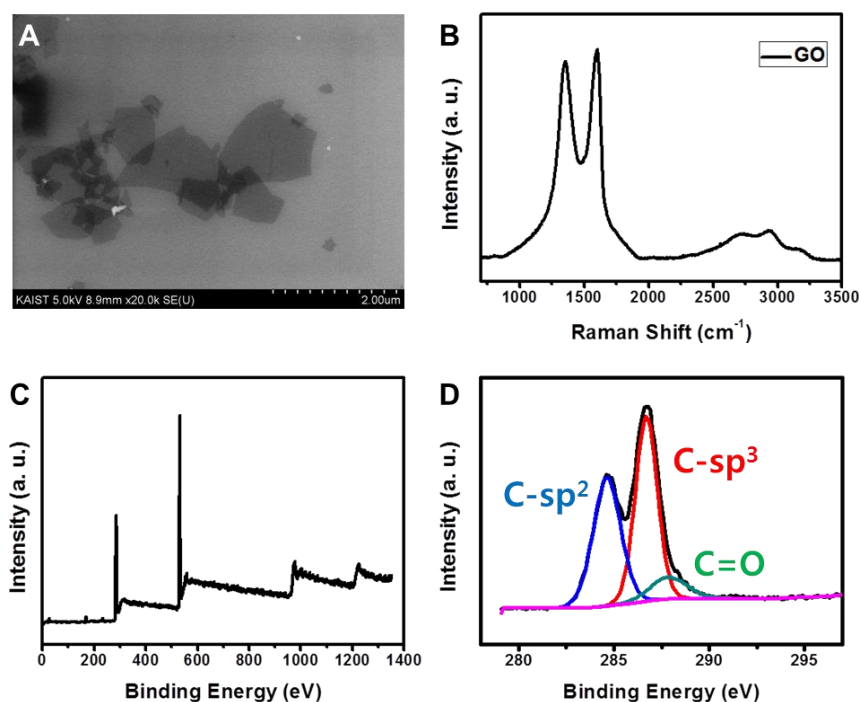


Figure S1. (A) SEM image showing GO platelet sheets. (B) Raman spectrum of GO platelet. (C, D) XPS spectra (C1s) for GO platelets.

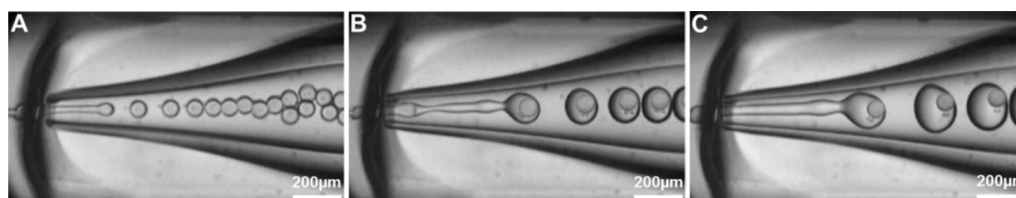


Figure S2. Control over the shell thickness of double emulsion drops by changing flow rates. (A) $Q_{IF}=1500 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{MF}=1000 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{OF}=4500 \mu\text{L}\cdot\text{h}^{-1}$, (B) $Q_{IF}=500 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{MF}=2600 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{OF}=4500 \mu\text{L}\cdot\text{h}^{-1}$, (C) $Q_{IF}=500 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{MF}=4500 \mu\text{L}\cdot\text{h}^{-1}$, $Q_{OF}=4500 \mu\text{L}\cdot\text{h}^{-1}$.

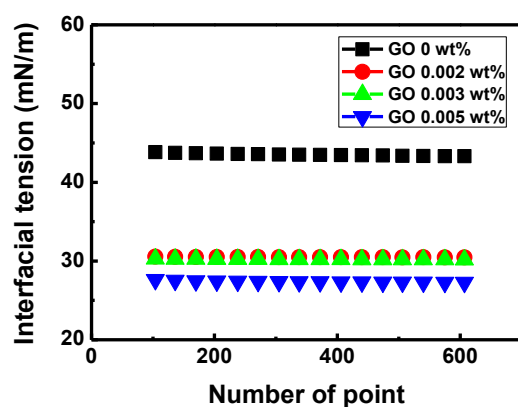


Figure S3. Variation of interfacial tensions with increase in the concentration of GO in water. The interface consisted of paraffin oil and water.

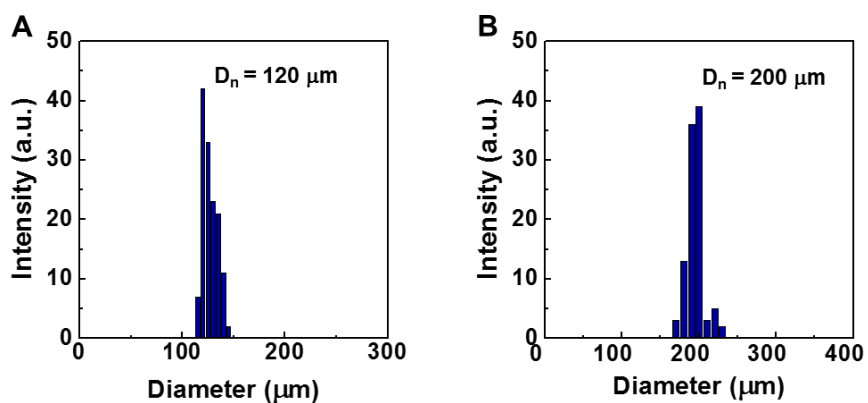


Figure S4. Drop size and size distributions of (A) double emulsion drops and (B) GO-patched PMPC hydrogel microcapsules.

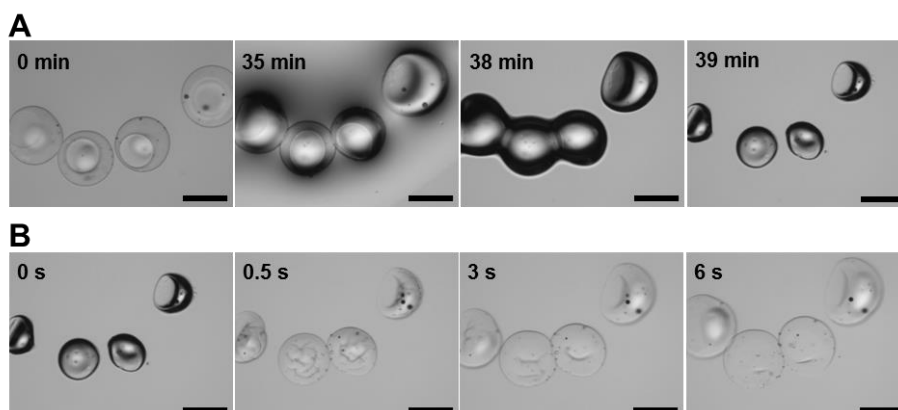


Figure S5. Maintenance of hollow structure of GO-patched PMPC hydrogel microcapsules after drying at ambient temperature (A) and consecutive swelling with water (B). The scale bars are 200 μ m.

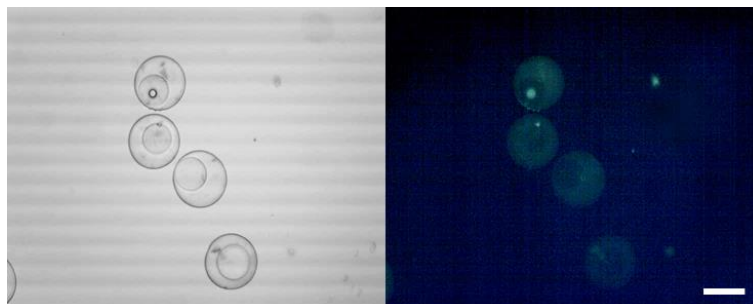


Figure S6. Optical and fluorescence microscope images of FSS-loaded GO-patched PMPC hydrogel microcapsules after storage for 100 day at room temperature. The scale bar is 200 μm .

References

- 1 J. E. Kim, T. H. Han, S. H. Lee, J. Y. Kim, C. W. Ahn, J. M. Yun, and S. O. Kim, *Angew. chem. Int. Ed.* 2011, 50, 3043-3047.
- 2 K. E. Lee, J. E. Kim, U. N. Maiti, J. Lim, J. O. Hwang, J. Shim, J. J. Oh, T. Yun, and S. O. Kim, *ACS Nano* 2014, 8, 9073-9080.
- 3 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* 1958, 80, 1339.
- 4 H. Bai, C. Li, X. Wang, and G. Shi, *Chem. Commun.* 2010, 46, 2376-2378.