

Supplementary Material (ESI) for Chemical Communications

## Supporting Information

### **Golf ball-shaped PLGA microparticles with internal pores fabricated by simple O/W emulsion**

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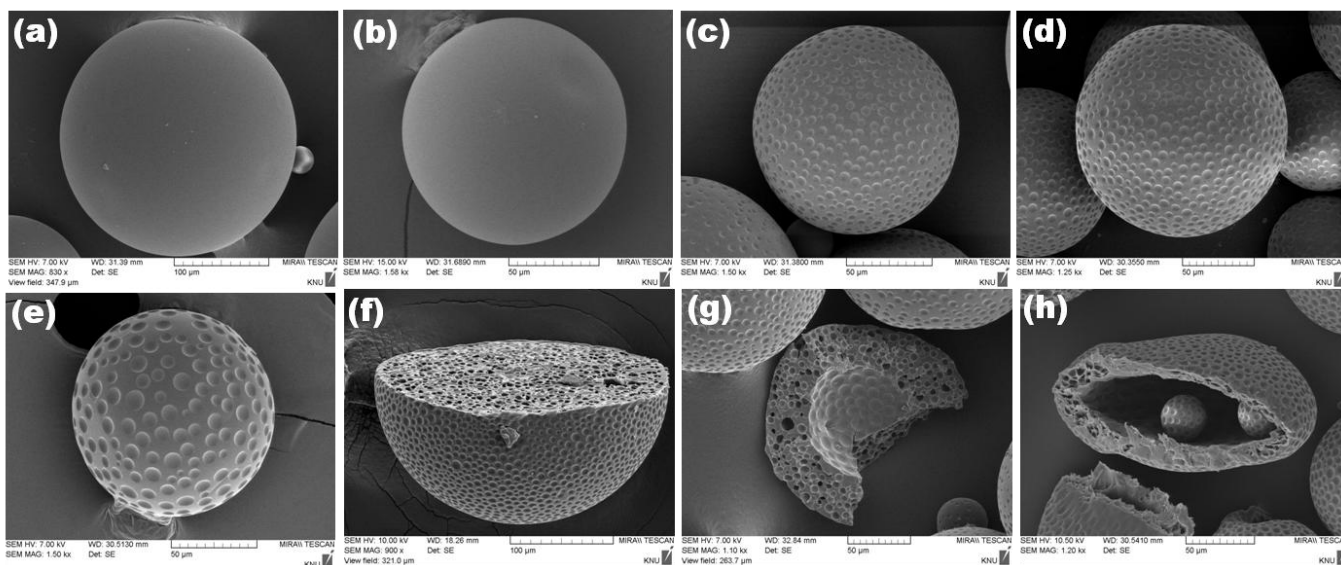
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#### **Fabrication of microsphere**

Polymer and phase change material (PCM) were dissolved in dichloromethane (DCM) which served as an organic phase. The ratio of DCM to the mixture of polymer and PCM was fixed to 9:1 by weight. The amount of polymer and phase change material was varied. The ratios of polymer to PCM were 10:0, 9:1, 8:2, 7:3, and 6:4. After complete dissolution of polymer and PCM in DMC, the organic phase was placed in a syringe, which was equipped with a 21G needle. The organic phase was introduced drop by drop into a 300 ml aqueous solution containing 1 wt% of PVA, 0.02 wt% of Tween 20, 0.01 wt% of sodium azide while the magnetic bar was stirred at the speed of 300 rpm. DCM in the oil phase was evaporated at ambient temperature for 3 h. After the fabrication of microparticles, microparticles were washed with distilled water three times and collected by centrifugation at 3,500 rpm for 4 min. Final product was first air dried in a hood for 24 h and samples are separated into two groups (1) vacuum drying and (2) air drying in a hood. Vacuum drying was conducted for 1 day, while air drying took more than three days for complete removal of water. From the comparison of air dried samples with vacuum dried samples, there was no detectable difference in SEM images.



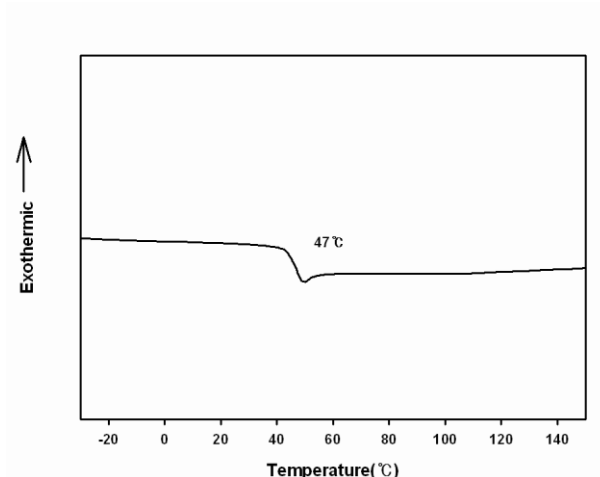
**Figure S1.** Photo image of fabrication of single O/W emulsion.



**Figure S2.** SEM images of PLGA(LA:GA=65:35) microspheres prepared by single O/W emulsification/solvent evaporation method varying the weight ratio of PLGA to PCM in the DCM. (a) 10:0, (b) 9:1, (c) 8:2, (d) 7:3, (e) 6:4, (f) 7:3, a cross-sectional image illustrating polydisperse porous structures, (g) 7:3, a cross-sectional image illustrating a hollow core and porous shell structure, and (h) 6:4, a cross sectional image illustrating a hollow core and porous shell structure. The weight ratio of DCM to the mixture of polymer and PCM was fixed at 9:1 for all of the samples. The aqueous phase is 1 wt% PVA in distilled water.

## Glass transition temperature ( $T_g$ ) of PLGA

Glass transition temperature was measured using Differential Scanning Calorimeter (DSC) at the heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  in the range of  $-50\text{ }^\circ\text{C} \sim 190\text{ }^\circ\text{C}$ .



**Figure S3.** DSC thermogram of PLGA used in this work.

## Surface tension, interfacial tension, and spreading coefficient calculated for PLGA

**Table S1.** Surface tension of the materials used.

Surface tension	PLGA(65/35) <sup>[a]</sup>	Water <sup>[a]</sup>	2-methylpentane <sup>[b]</sup>
$\gamma_i$ (mN/m)	35.6	72.7	17.1

[a] Ref. [S1] [b] calculated by group contribution using Ref. [S2].

**Table S2.** Interfacial tension between A and B

Serial	A	B	$\gamma_{AB}$ (mN/m)
1 <sup>[a]</sup>	PLGA in DCM (5% Conc.)	Water	22.6
2 <sup>[b]</sup>	Water	2-methylpentane	50.3
3 <sup>[c]</sup>	PLGA	2-methylpentane	18.6
4	PLGA	water	23.4 <sup>[d]</sup> or 10.4 <sup>[e]</sup>

[a] Ref.[S3] [b] Ref.[S4] [c] calculated from eqn 1 using surface tension from Table S1 and measured contact angle . [d] Advancing contact angle from Ref.[S1]) is used for calculation. [e] contact angle of PLGA ( $69.7^\circ$ ) from goniometric method is used for calculation.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \quad (\text{eqn. 1})$$

As a PLGA (LA:GA = 65:35) film for “s”, “l” for liquid drop, and “v” as air, “sv” is surface tension of PLGA and “lv” is surface tension of liquid, and “sl” is interfacial tension between polymer and liquid. When we used 2-methylpentane, contact angle was lower than 5°. Thus we inserted for  $\theta=5^\circ$  for calculation.

Interfacial tensions of PLGA/water are calculated on the basis of either advanced contact angle of 80.3° or contact angle from goniometric method.

$$\gamma_{sl} = 35.6 - 72.7 \times \cos(80.3^\circ) = 23.4 \quad \gamma_{sl} = 35.6 - 72.7 \times \cos(69.7^\circ) = 10.4$$

Spreading coefficient is defined by following eqn.

$$\lambda_j (\lambda_j = \gamma_{jk} - \gamma_{ij} - \gamma_{ik}) \quad (\text{eqn. 2})$$

Droplets of immiscible liquids [PCM (phase1) and PLGA in DCM (phase 3)] is brought into immiscible liquid [Water (phase 2)] which satisfy the condition of is  $\gamma_{12} > \gamma_{23}$ .

Then three possible combinations of  $\lambda_j$  were obtained.

$\lambda_1 < 0; \lambda_2 < 0; \lambda_3 > 0,$	Core-shell structure
$\lambda_1 < 0; \lambda_2 < 0; \lambda_3 < 0,$	Acorn structure
$\lambda_1 < 0; \lambda_2 > 0; \lambda_3 < 0,$	Two separate droplets

Since the interfacial tension can be obtained between two immiscible components, it has limitation on the measurement of interfacial throughout the whole evaporation process, generally initial interfacial tensions are used for interpretation. However, we also considered not only PLGA in DCM/water but PLGA/water.

By the calculation using eqn 5 spreading coefficient is obtained.

$$\lambda_1 = 22.6 - (18.6 + 50.3) < 0$$

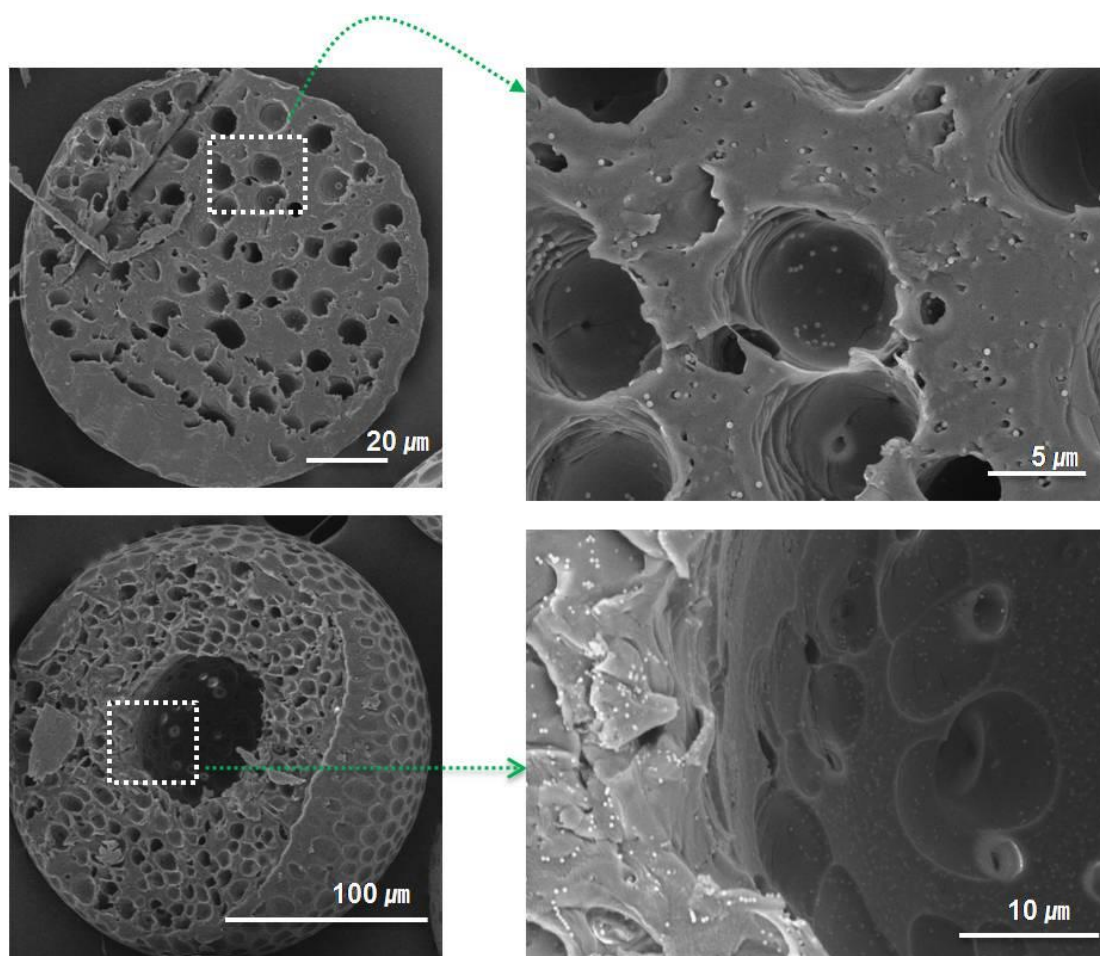
$$\lambda_2 = 18.6 - (22.6 + 50.3) < 0$$

$$\lambda_3 = 50.3 - (22.6 + 18.6) > 0$$

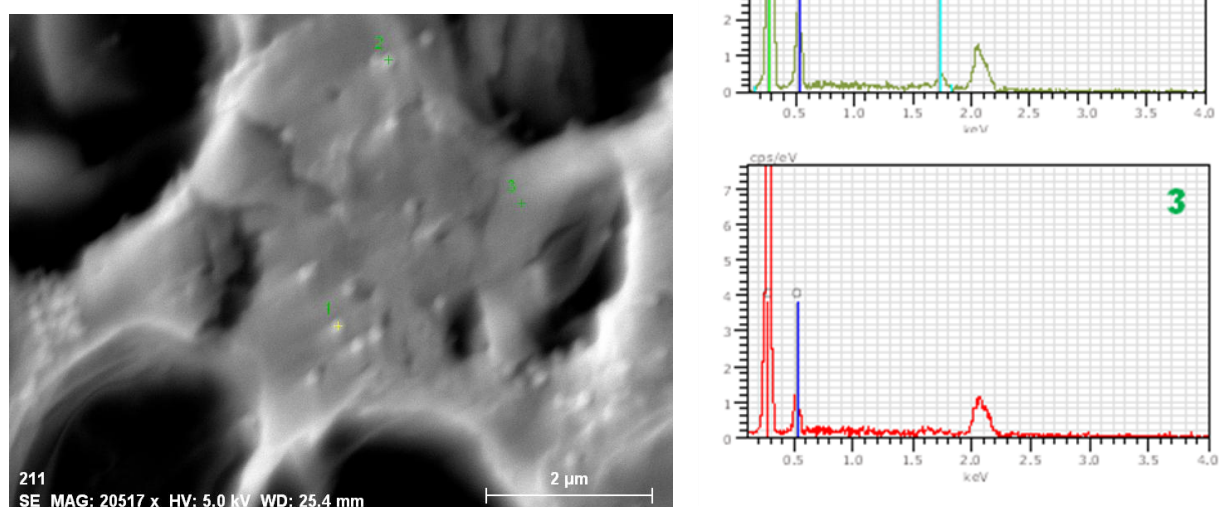
In  $\lambda_3$ , replacement of value 22.6 to 23.4 does not change the result.

By the calculation, we could predict core-shell morphology based on spreading coefficient.

### Cross-sectional SEM images of the silica particle encapsulated microspheres



**Figure S4.** Cross-sectional SEM images of PLGA golf ball-like microspheres encapsulating monodisperse hydrophilic silica colloids.



**Figure S5.** Atomic compositions measured by EDX coupled with SEM. Encapsulated silica particle (1 and 2). PLGA matrix (3).

## References

- [S1] E. I. Vargha-Butler et al., *Colloid Polym. Sci.* **2001**, 279, 1160-1168
- [S2] D. W. Van Krevelen, *Properties of Polymers: Their Correlation with Chemical Structures*, Elsevier Science, New York, 1990.
- [S3] E. Pisani et al., *J. Colloid Interface Sci.* **2008**, 326, 66-71.
- [S4] C. G. Aranda-Bravo et al., *Ind. Eng. Chem. Res.* **2009**, 48, 1476-1483.