JANUS HYDROGEL BEADS FOR ELECTRONIC PAPER USING SHRINKAGE-GELATION TECHNIQUE

Kyouhei Aketagawa[1]**, Hirotada Hirama**[1]**, Hiroyuki Moriguchi**[2]**, Toru Torii**[1]
[1]*Graduate School of Frontier Sciences, The University of Tokyo, Japan,* [2]*RIKEN, Japan*

ABSTRACT

A novel fabrication technique of Janus hydrogel beads whose morphology was controlled using shrinkage-gelation technique was developed. Aggregation of inoganic nanoparticles in an incompartible solvent was also applied to the fabrication. Small-size Janus particles for electronic paper were formed from bigger size sodium alginate droplets composed of inorganic nanoparticles by applying this technique which can avoid clogging problem of microchannels.

KEYWORDS

microfluidics, calcium alginate gel, magnetic beads, osmotic pressure, monodisperse.

INTRODUCTION

Janus particles for electronic paper had been developed using monodisperse droplet formation technique using microchannels [1]. However, the resolution of electronic paper using the particles is still low compared to other electronic paper devices because of the particle size, although that with 50µm was used and analysed showing that small-size Janus particles were useful to improve its resolution [2].

Fabrication of small-size Janus particles with inorganic nanoparticles is difficult because microchannel size is dominant for the control of droplet size and the Janus particle contains many nanoparticles which lead to clogging problem of microchannels [3,4].

A new shrinkage-gelation technique has been developed in which small-size hydrogel beads were formed from bigger sodium alginate droplets (Fig. 1) [5]. Shrinkage and gelation is generated at the interface between oil and Ca^{2+}-loaded hydrogel which can avoid clogging problem.

In this paper, we describe a fabrication method of small-size Janus hydrogel beads using its technique and aggregation of inorganic nanoparticles in an incompartible solvent.

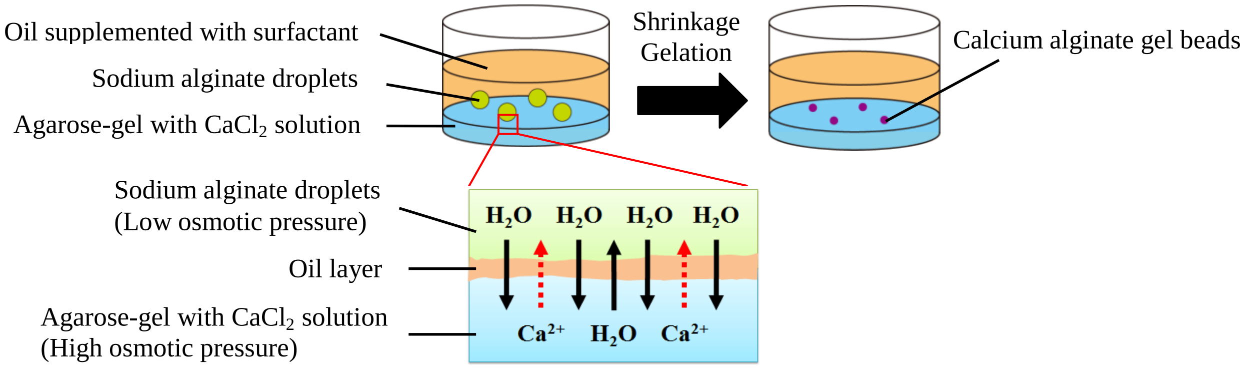
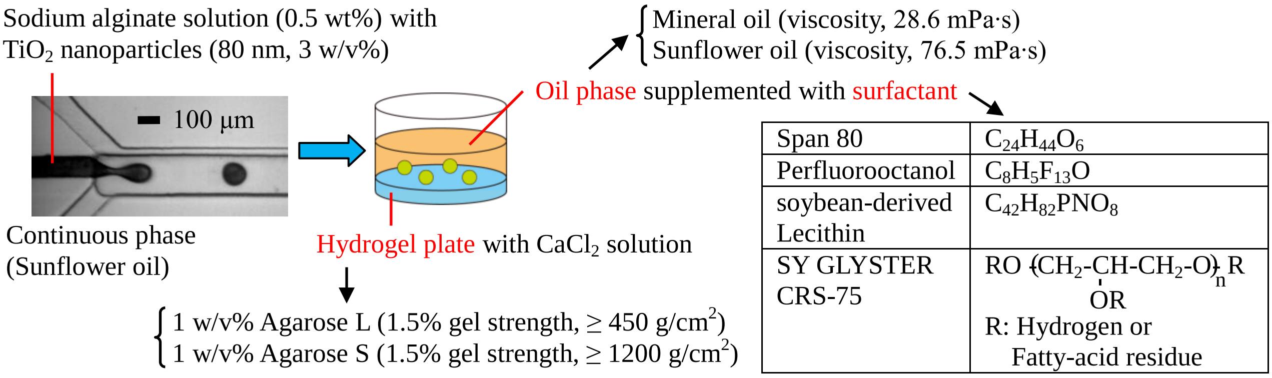


Figure 1. A schematic drawing of the shrinkage-gelation process of sodium alginate droplets on an interface between oil and Ca^{2+}-loaded hydrogel. (Due to surfactant molecules which serve as carriers, water molecules and calcium ions transfer through oil layer, resulting in shrinkage and gelation of sodium alginate droplets.)

EXPERIMENT

First, we examined the effect of surfactant, oil phase and hydrogel plate on shrinkage of sodium alginate droplets composed of inorganic nanoparticles. The experimental system is shown in Figure 2.



Span 80	$C_{24}H_{44}O_6$
Perfluorooctanol	$C_8H_5F_{13}O$
soybean-derived Lecithin	$C_{42}H_{82}PNO_8$
SY GLYSTER CRS-75	RO $\left(CH_2\text{-}\underset{OR}{CH}\text{-}CH_2\text{-}O\right)_n$ R R: Hydrogen or Fatty-acid residue

Figure 2. Examination of optimal conditions for shrinkage of sodium alginate droplets composed of nanoparticles.

Figure 3A shows a fabrication method of small-size Janus hydrogel beads using the shrinkage-gelation technique and aggregation of TiO_2 nanoparticles (80 nm) in hydroxyethyl methacrylate. 1:10 mixture of hydroxyethyl methacrylate and sodium alginate solution (1.0 wt%) and pure water in which TiO_2 nanoparticles were dispersed were injected separately through two inlets causing two-phase parallel stream in microchannel. This stream then enters continuous flow of oil phase which contains surfactant, resulting in the formation of droplets. Once the droplets are formed, mixing due to the diffusion occurs across the interface inside the droplet. Because TiO_2 nanoparticles aggregate in the droplet (Fig. 3B), small-size Janus calcium alginate gel beads were fabricated by the shrinkage-gelation process.

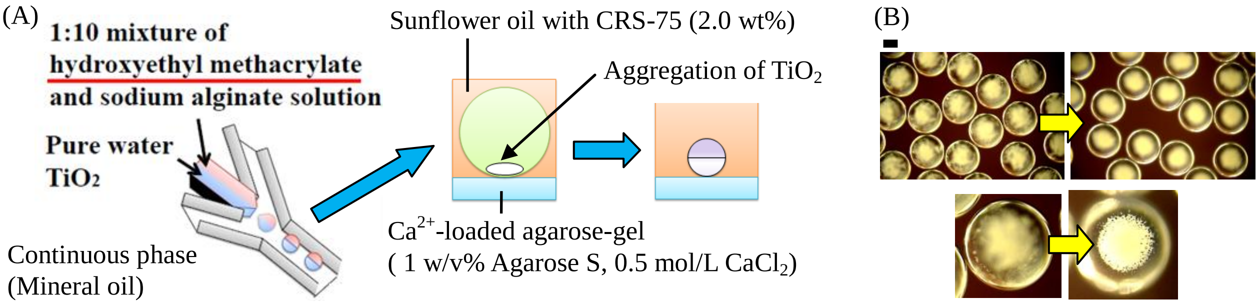


Figure 3. (A) Fabrication procedure of small-size Janus hydrogel beads by the shrinkage-gelation technique. (B) Aggregation of TiO_2 nanoparticles in droplets. Scale bar is 100 μm.

RESULTS AND DISCUSSION

Table 1 shows the effect of surfactant, oil phase and hydrogel plate on shrinkage of sodium alginate droplets composed of TiO_2 nanoparticles. If we used monomeric surfactant, the droplet ruptured during shrinkage process. By contrast, in case that polymeric surfactant was used, the droplet shrank without rupture. This result indicates that shrinkage of droplets composed of nanoparticles requires strong stabilization capabilities of thick and flexible films formed by polymeric surfactant. However, if we used low-viscosity oil as the oil phase and low-strength agarose-gel as the hydrogel plate, the droplet ruptured during shrinkage process in spite of using polymeric surfactant. This suggests that using high-viscosity oil as the oil phase and high-strength agarose-gel as the hydrogel plate is also important for achievement of the shrinkage. Therefore, optimal conditions were using SY GLYSTER CRS-75 (Sakamoto Yakuhin Kogyo Co.Ltd) as the surfactant, sunflower oil as the oil phase and agarose S as the hydrogel plate.

Table 1. Effect of surfactant, oil phase and hydrogel plate on shrinkage of sodium alginate droplets composed of inorganic nanoparticles.

Surfactant (molecular weight)	Oil phase (viscosity, 25.5℃)	Hydrogel plate (1.5% gel strength)	Concentration of $CaCl_2$ solution	Shrinkage
Span 80 (428)	Sunflower oil (76.5 mPa·s)	agarose-gel 1 w/v% Agarose L ($\geq$ 450 g/cm^2)	$\leq$ 0.5 mol/L	× (rupture)
Perfluorooctanol (364)				× (rupture)
Lecithin (759)				× (rupture)
SY GLYSTER CRS-75 Polyglycerol esters of fatty acids (number avg. 2089)	Mineral oil (28.6 mPa·s)			× (rupture)
	Sunflower oil (76.5 mPa·s)			○
			$\geq$ 1 mol/L	× (rupture)
		agarose-gel 1 w/v% Agarose S ($\geq$ 1200 g/cm^2)	$\leq$ 0.5 mol/L	○
			$\geq$ 1 mol/L	○

Figure 4A shows time course of the shrinkage of sodium alginate droplets composed of TiO_2 nanoparticles at a variety of the concentration of calcium chloride contained in agarose-gel plate under optimal conditions (SY GLYSTER CRS-75, sunflower oil, agarose S). Figure 4B shows relation between shrinkage rate and difference between osmotic pressure of calcium chloride solution and sodium alginate solution at a variety of original droplet size. Shrinkage rate is defined as the slope of the linear approximate curve in Figure 4A. Shrinkage rate was positively correlated with osmotic pressure. Figure 4C shows relation between shrinkage factor and osmotic pressure. Shrinkage factor became saturated at high osmotic pressure. Saturated shrinkage factor was about 80 percent. The difference of osmotic pressure between calcium chloride and sodium alginate was dominant in the shrinkage rate of alginate droplets and the size of resulting hydrogel beads.

Figure 5 shows small-size Janus calcium alginate gel beads fabricated by shrinkage-gelation technique made from the 1:10 mixture of hydroxyethyl methacrylate and Sodium alginate solution. Morphology of resulting Janus hydrogel beads was controlled by adjusting the concentration of TiO_2 nanoparticles dispersed in pure water.

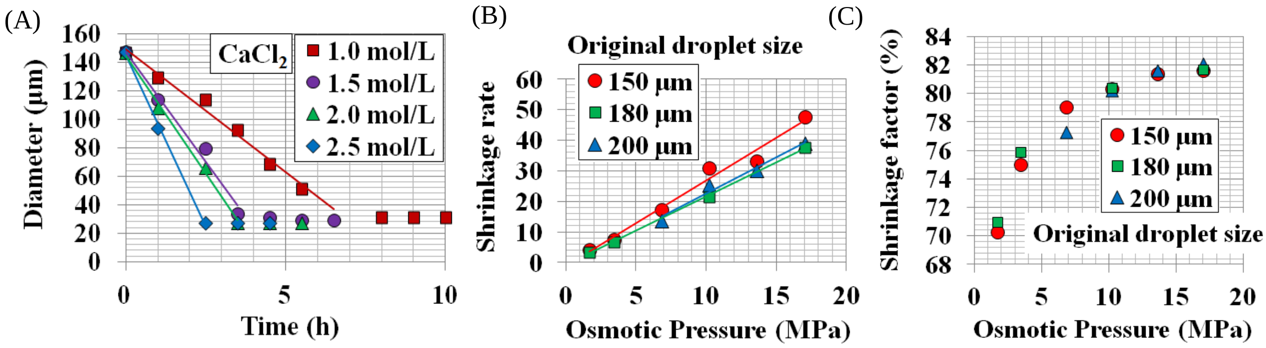


Figure 4. (A) Time course of the shrinkage of sodium alginate droplets composed of TiO_2 nanoparticles at a variety of the concentration of calcium chloride contained in agarose-gel plate.(B) Relation between shrinkage rate and difference between osmotic pressure of calcium chloride solution and sodium alginate solution. (C) Relation between shrinkage factor and difference between osmotic pressure of calcium chloride solution and sodium alginate solution.

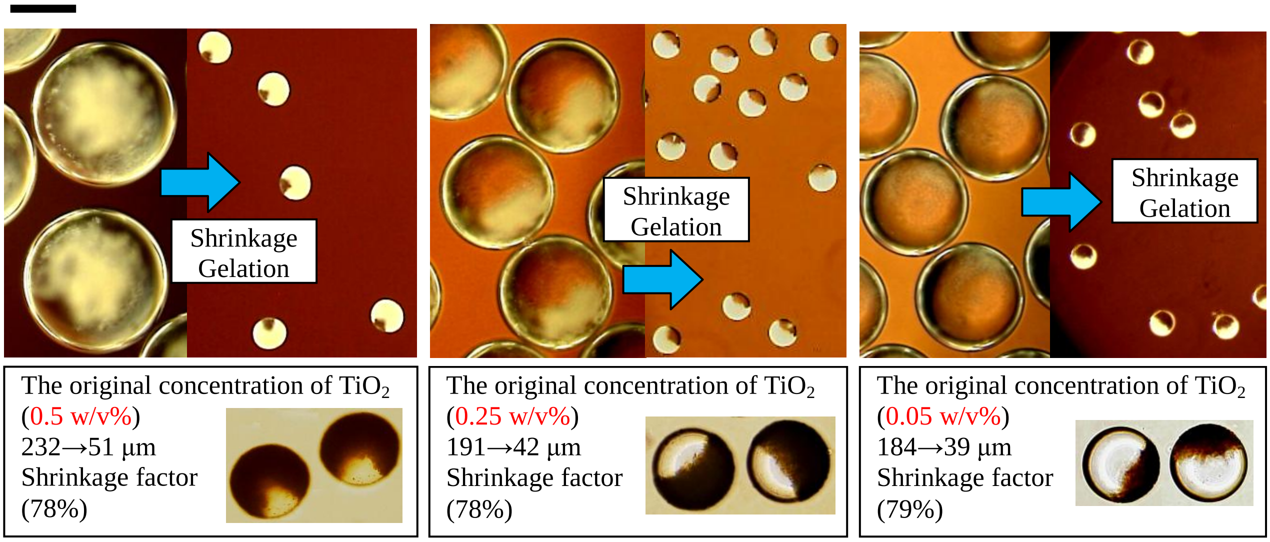


Figure 5. Janus calcium alginate gel beads were fabricated by shrinkage-gelation technique made from the 1:10 mixture of hydroxyethyl methacrylate and Sodium alginate solution. A ratio of gel with TiO_2 to that without TiO_2 in resulting Janus hydrogel beads decreases with decrease in the concentration of TiO_2 nanoparticles in original sodium alginate droplets. Scale bar is 100 µm.

CONCLUSION

A novel fabrication technique of small-size Janus hydrogel beads whose morphology was controlled using shrinkage-gelation technique was developed. Aggregation of inoganic nanoparticles in hydroxyethyl methacrylate was also applied to the fabrication. This technique can avoid clogging problem of microchannels and be applied to fabrication of Janus hydrogel beads with not only electric characteristics but also magnetic characteristics. Therefore, it has potential for fabrication of small-size Janus particles for electronic paper.

REFERENCES

[1] T. Nisisako, T. Torii, *et al.*, "Novel microreactors for functional polymer beads", Chemical Engineering Journal, **101**, pp. 23-29, (2004).

[2] J. M. Kim, Trends and Future of e-Paper Technologies, 16th IDW, (2009).

[3] D.R. Link, D. A. Weitz, *et al.*, "Electric Control of Droplets in Microfluidic Devices", Angewandte Chemie International Edition, **45**, pp. 2556-2560, (2006)

[4] Su-Na Yin, Su Chen, *et al.*, "Versatile Bifunctional Magnetic-Fluorescent Responsive Janus Supraballs Towards the Flexible Bead Display", Advanced Materials, **23**, pp. 2915-2919, (2011)

[5] K. Aketagawa, H. Hirama, T. Torii, *et al.*, FABRICATION OF TITANIA MICROSPHERES USING ALGINATE MICRODROPLETS ON AN OIL/HYDROGEL INTERFACE, Proc. Micro TAS 2011, pp. 1615-1617, (2011).

CONTACT

K. AKETAGAWA, tel: +81-4-7136-5654; aketagawakyouhei@dt.k.u-tokyo.ac.jp, http://www.dt.k.u-tokyo.ac.jp/