

A Microfluidic Approach to Chemically Driven Assembly of Colloidal Particles at Gas–Liquid Interfaces

Jai Il Park¹, Zhihong Nie¹, Alexander Kumachev¹, Ahmed I. Abdelrahman¹, Bernard P. Binks², Howard A. Stone³, Eugenia Kumacheva¹

¹Department of Chemistry, University of Toronto, 80 Saint George Street, Toronto, ON M5S 3H6, Canada

²Surfactant & Colloid Group, Department of Chemistry, University of Hull, Hull, HU6 7RX, United Kingdom

³School of Engineering and Applied Sciences, Harvard University, 308 Pierce Hall, Cambridge, MA 02138, USA

ABSTRACT

Dissolution of CO₂ bubbles in a suspension of colloidal particles chemically leads to the assembly of particles on the surface of shrunken bubbles, and thus yields rapid continuous formation of a colloidal armour.

KEYWORDS: colloids, interfaces, microfluidics, surface chemistry

INTRODUCTION

Bubbles encapsulated with a close-packed monolayer of solid particles have extremely high stability to coalescence, the ability to acquire anisotropic shapes, and the capability to arrest the dissolution of the entrapped gas [1-4]. These properties make particle-coated bubbles applicable to the fabrication of new materials with high structural stability.

THEORY

Bubbles are intrinsically unstable due to their dissolution and coalescence. The former is caused by the Laplace pressure difference while the latter is by the rupture of the thin liquid film between bubbles. Recently, it has become possible to prevent both of them by applying the concept of “Pickering emulsions” (liquid/liquid interfaces) to bubbles (gas/liquid interfaces) [1-4]. Colloidal particles with appropriate wettability strongly adsorb to the gas-liquid interfaces. They are irreversibly adsorbed since the size of the particles makes the desorption energies orders of magnitude greater than thermal energy [5].

EXPERIMENTAL

Photolithographic masters were prepared using SU-8 50 photoresist (MicroChem) in bas relief on silicon wafers. The microfluidic devices were fabricated in PDMS by using a standard soft lithography procedure [6].

RESULTS AND DISCUSSION

We used a microfluidic T-junction device to produce CO₂ bubbles in an aqueous dispersion of anionic polymer particles, poly (styrene-co-acrylic acid), PS-co-PAA. The CO₂ thread periodically broke up to release monodisperse CO₂ plugs, which un-

derwent a dramatic decrease in volume and acquired a spherical shape (Figure 1A). A uniform dissolution in the microchannels yielded armored bubbles with a narrow size distribution (Figure 1B). The particles formed a close-packed two-dimensional crystalline shell on the bubble surface (Figure 1C). The cross-section image of the bubble confirmed that the particles formed a monolayer-thick shell (Figure 1D). We explain the formation of armored bubbles as follows. The dissolution of CO_2 was combined with the reaction $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$ at $\text{pH} \geq 10$ [7]. Consequently, this reaction led to a local decrease in the pH of the liquid adjacent to the bubble surface, which reduced the wettability of water on the polymer surface. The generality of the strategy was demonstrated by controlling the size of the encapsulated bubbles (Figure 2) and by coating the bubbles with a variety of colloidal particles (Figure 3).

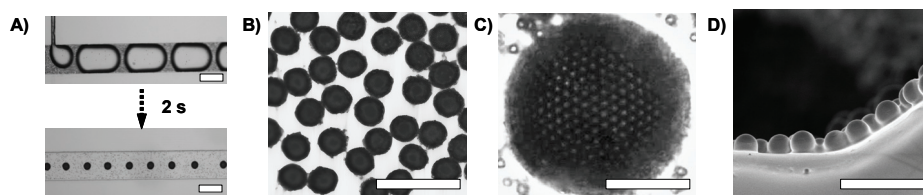


Figure 1. Microfluidic generation of armored bubble by dissolving CO_2 . A) Optical microscopy images of the CO_2 plugs generated at $\text{pH}=14$, $\text{PCO}_2=5$ psi, $Q_L=10.5$ mL hr^{-1} , $C_p=1.5$ wt%. (top); progression of the plugs to spherical armored bubbles (bottom). B, C) Optical microscopy images of armored bubbles generated as in (A) and collected at the outlet of the microfluidic device. Scale bars: 200 μm (A, B) and 25 μm (C). D) SEM image (side view) of the shell of the armored bubble infiltrated with poly(ethylene glycol) diacrylate. Scale bar: 10 μm .

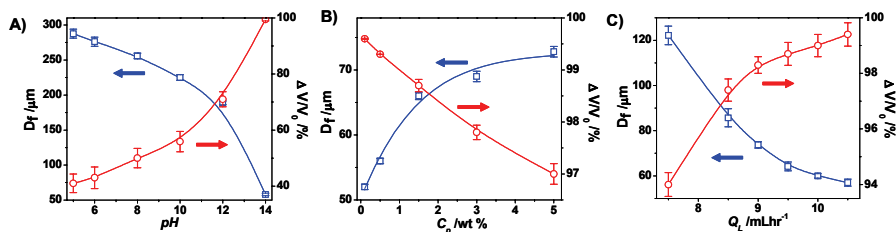


Figure 2. Effect of experimental variables on the final diameter D_f of armored bubbles (\square) and on the fractional change in volume of the CO_2 plugs (\circ). A) Effect of initial pH value, B) Effect of the particle concentration, C_p . C) Effect of the flow rate Q_L of the continuous phase.

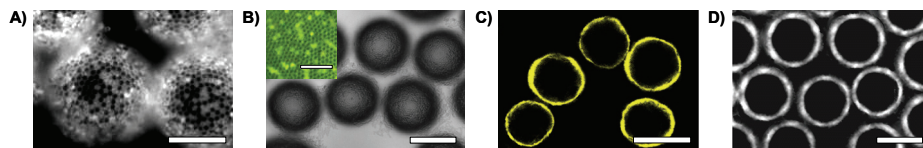


Figure 3. Generation of bubbles with various types of colloidal armour. A) Fluorescence microscopy image of bubbles coated with HY-labelled PS-co-PAA particles and 3.5 μm diameter PS-co-PAA particles. Scale bar: 50 μm . B) Optical microscopy image of bubbles coated with carboxylated silica particles. Scale bar: 100 μm . The inset shows a fluorescence microscopy image of the surface of an armored bubble coated with carboxylated silica particles and HY-labelled PS-co-PAA polymer particles. Scale bar: 25 μm . C) Confocal microscopy image of bubbles encapsulated with carboxylated silica nanoparticles loaded with CdSe/ZnS. Scale bar: 100 μm . d) Fluorescence microscopy image of armoured bubbles engulfed with the FITC-BSA shell. Scale bar: 100 μm .

CONCLUSIONS

The described approach can provide a new route to the fabrication of materials with advanced properties such as optical resonators and 3D foams with ordered structures. Further, the deposition of cationic particles can be achieved by dissolving, for example, NH_3 and increasing the pH in the region adjacent to the surface of the bubbles. Controllable transfer of one of the components of the gaseous mixture to the continuous phase would provide the ability to control the composition of the bubbles and the surrounding medium, and activate a particular reaction on demand.

ACKNOWLEDGEMENTS

E.K. thanks the Canada Research Chair (NSERC Canada) for the financial support of this work. J.I.P. thanks the Graduate Student Conference Travel Grant for the financial support for attending MicroTas 2009.

REFERENCES

- [1] J. I. Park, Z. H. Nie, A. Kumachev, A. I. Abdelrahman, B. P. Binks, H. A. Stone, and E. Kumacheva, *Angew. Chem. Int. Ed.* **2009**, DOI: 10.1002/anie.200805204.
- [2] A. B. Subramaniam, M. Abkarian, L. Mahadevan, H. A. Stone, *Nature* **2005**, 438, 930.
- [3] M. Abkarian, A. B. Subramaniam, S. H. Kim, R. J. Larsen, S. M. Yang, H. A. Stone, *Phys. Rev. Lett.* **2007**, 99, 188301.
- [4] B. P. Binks, R. Murakami, *Nat. Mater.* **2006**, 5, 865.
- [5] B. P. Binks, *Curr. Opin. Colloid Interface Sci.* **2002**, 7, 21.
- [6] Y. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, 37, 550.
- [7] P. V. Danckwerts, *Gas-Liquid Reactions*, McGraw-Hill, New York, **1970**.