FABRICATION OF TUNABLE WRINKLE PATTERNED MICROPARTICLE VIA SILICA-COATING

Hyung Jong Bae[1,2], Arang Lee[2], Sangkwon Han[1,2], Lily Nari Kim[3], Sunghoon Kwon[1,2], Wook Park[4]

[1]Seoul National University, Korea, [2]Inter-university Semiconductor Research Center, Korea, [3]Konkuk University, Korea, [4]Kyung Hee University, Korea

ABSTRACT

Patterning of microstructure and nanostructure on a planar substrate has been widely studied in diverse fields such as cell analysis and biomimetic applications. In this paper tunable wrinkle patterned microparticles are fabricated by coating the surface of the polymeric particle with silica. Microparticles with various shapes are produced using optofluidic maskless lithography (OFML) and wrinkling is induced by a silica-coating process. We control the wrinkle pattern in two aspects; direction and characteristic wavelength of the wrinkle. The wrinkle direction is guided by changing the internal structure of the particle and the wavelength is regulated by varying the amount of ultraviolet (UV) light during photopolymerization. This wrinkle structure based on the particle substrate will be useful as a new platform for cell analysis or other related research areas.

KEYWORDS

Wrinkle, microparticle, silica-coating, wrinkle directionality, wrinkle characteristic wavelength

INTRODUCTION

Patterned substrates including microstructures and nanostructures consist of line, pillar, or fiber, have received a lot of attention because they are valuable to mimic an extracellular environment to observe cell morphology or differentiation of stem cell.[1] Recently, the importance of these structures fabricated by the bottom-up process has become significant because of its high scalability and inexpensive fabrication cost compared to the top-down process. However, few studies patterned microstructure on the particle substrate compared to the planar substrate.

Here, we demonstrate a fabrication of tunable wrinkled microparticles by controlling the particle shape and UV light dose. First, a large number of polymeric microparticles with various shapes were generated using an OFML system.[2] Then the wrinkles were fabricated via a silica-coating process based on the modified version of Stöber method.[3, 4] We did not use conventional methods widely utilized in the two-layer system for wrinkling such as thin metal film deposition with thermal expansion or drying during the sol-gel process.[5, 6] This wrinkle pattern is tunable in that the directionality of the wrinkle can be controlled by punching holes inside of the particle and the wavelength of the wrinkle can be modulated by changing the dose of UV light during the photopolymerization process.

EXPERIMENT

A schematic view of the fabrication process of the wrinkled particle is shown in Figure 1. Polymeric microparticles were polymerized from prepolymer resin consisting of ethoxylated trimethylopropane triacrylate (ETPTA), 3-(trimethoxysilyl) propyl acrylate (TMSPA), and photoinitiator, DAROCUR. Particles with various shapes were easily synthesized using the OFML system. Then a silica layer was coated on the surface of these particles by the condensation of tetraethoxysilane (TEOS) in a mixture of deionized water, ethanol, and ammonium hydroxide aqueous solution with vortexing. Then wrinkling occurs during this silica-coating process.

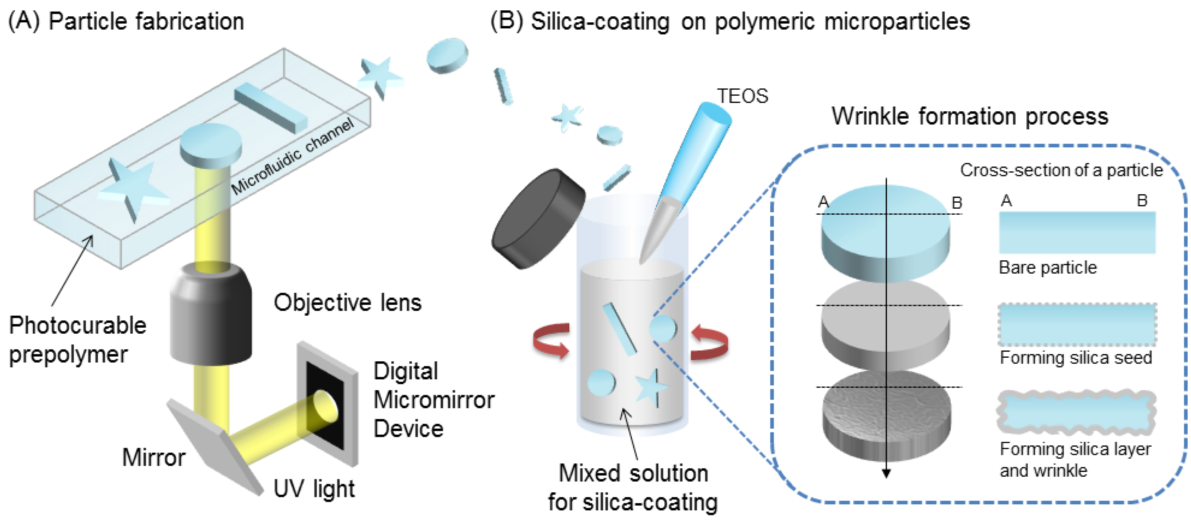

Figure 1. *A schematic view of the fabrication process of wrinkled particles. (A) Fabrication of microparticles using OFML system. Various shapes of particles are fabricated by changing the digital micromirror device (DMD) pattern. (B) Wrinkle generation via the silica-coating process. Silica seeds are formed then the silica layer covers the surface of the particle and wrinkles start to occur.*

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) images of fabricated wrinkled microparticle are shown in Figure 2(A). The silica layer has been fully grown on the surface of the particle as shown in the magnified images. The wrinkles were generated during the silica-coating process. When the reaction in mixed solution for silica-coating was performed for 200 minutes, wrinkles were generated (Figure 2(C)). However, when we reduced the coating time to half, wrinkling did not occur and the surface of the particle was smooth (Figure 2(B)). In the silica-coating process, silica seeds are formed first. Then a silica layer is developed by condensation of TEOS, which is done in a relatively short period compared to forming seeds (Figure 1(B)). Buckling does not occur until the silica layer covers the surface of the polymer particle. Therefore, enough coating time is essential for generating wrinkles.

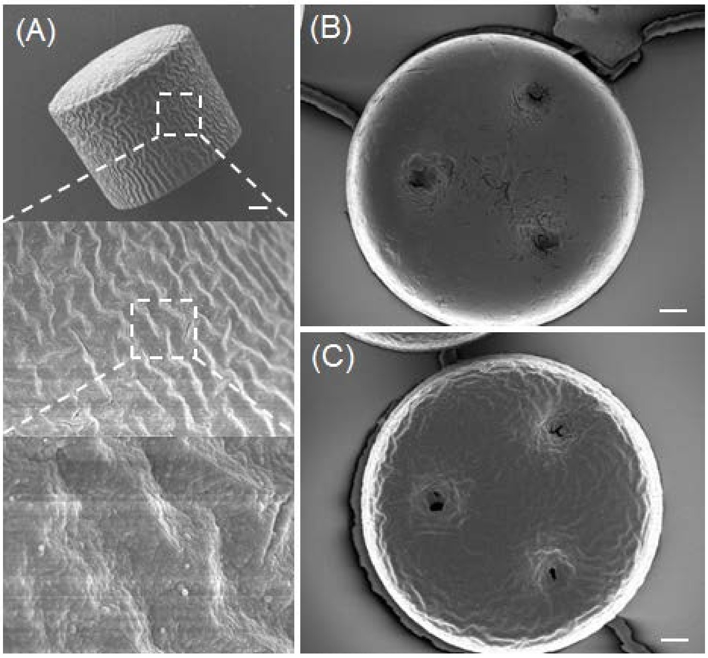

Figure 2. *SEM images of wrinkled microparticles. (A) Silica-coated surface of wrinkled particle. (B) No wrinkle on the particle coated for 100 minutes. (C) Wrinkles on the particle coated for 200 minutes (Scale bar 10μm).*

Wrinkle patterned microparticles with different shapes were fabricated as shown in Figure 3. It is simple to generate wrinkles on the surface of the particle regardless of the shape of it by using the OFML system and the silica-coating process. Also, wrinkle patterns were different depending on the shape of the substrate. Therefore, we can generate diverse wrinkle patterns by changing the shape of the particle.

Controlling the wrinkle pattern was demonstrated in both direction and characteristic wavelength of the wrinkle. First, we guided the direction of waves by punching holes at a particular location in the particle. The wrinkle showed random directionality when the particle had no holes (Figure 4(A)). However, wrinkles tended to converge toward the hole when holes existed because the waves align perpendicular to the direction of maximum compressive stress (Figure 4(B) ~ (F)). We controlled the stress field by constructing structures like a hole, which confine the internal structure of the particle. Therefore the wrinkle pattern can be controlled by several parameters which confine the inside region of the particle such as the number, location, or shape of holes.

In addition, UV light exposure time regulated the characteristic wavelength of wrinkle patterns during photopolymerization (Figure 5). Fast Fourier transform (FFT) analysis revealed that the characteristic wavelength was 5.52μm when we illuminated UV light for 0.15 second during lithography while the wavelength was 4.14μm for 0.25 second. The shorter illumination time resulted in the longer characteristic wavelength. It seems because shorter illumination resulted in a softer polymer particle substrate, which means the substrate has a smaller elastic modulus. This smaller elastic modulus of the substrate induced longer wavelength because wavelength is inversely proportional to it.[5]

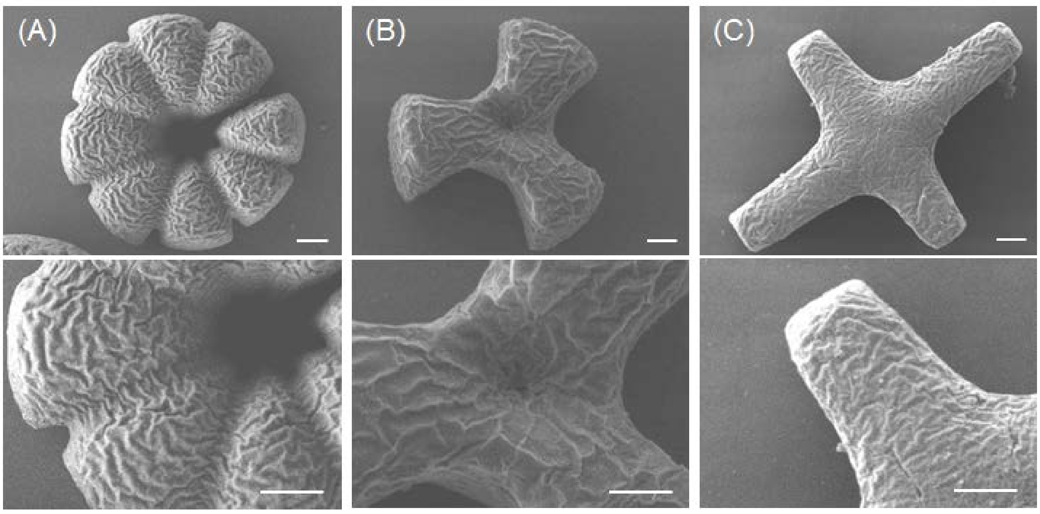

Figure 3. *SEM images of wrinkle-patterned microparticles with different shapes. (A) Petal-like shape. (B) Boomerang shape. (C) Cross shape (Scale bar 10μm).*

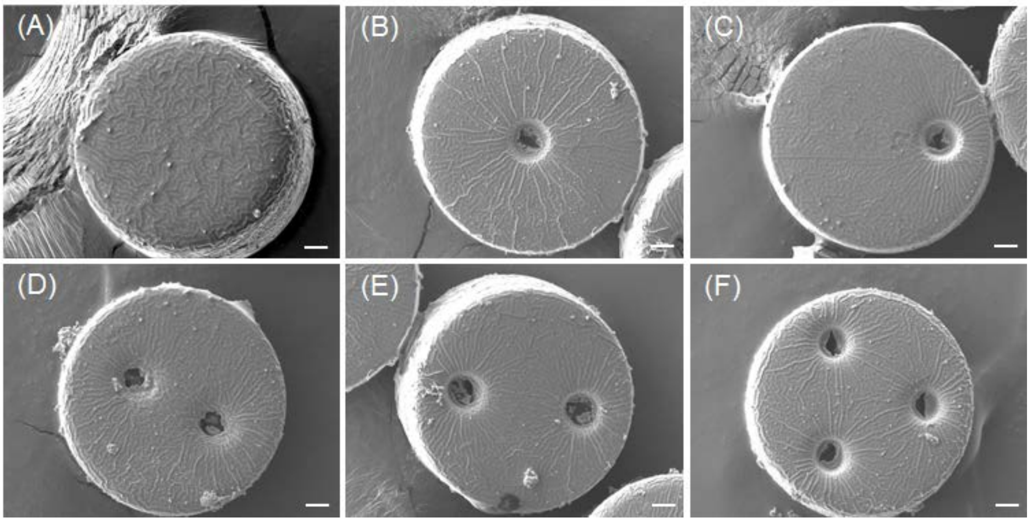

Figure 4. *Guiding of the wrinkle direction by punching holes inside the particle. (A) Random directionality with no hole. (B)-(F) Converging directionality near the hole. Also linear directionality between the adjacent holes (Scale bar 10μm).*

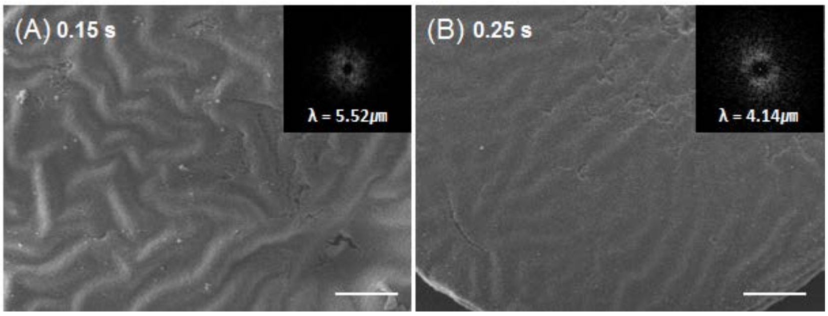

Figure 5. *Controlling of the characteristic wavelength of wrinkles by changing the dose of UV light illumination during the process of photopolymerization. (A) 0.15 second exposure time. The inset (FFT analysis) reveals that the wavelength is 5.52μm. (B) 0.25 second exposure time. The wavelength is 4.14μm. The shorter illumination time induces the longer wavelength (Scale bar 10μm).*

CONCLUSION

Wrinkle patterned miccroparticles were fabricated by the OFML system and the silica-coating process. Wave patterns were controlled in the directionality and the wavelength by the internal structure and the amount of UV light illumination. This wrinkle structure could provide the new three-dimensional extracellular topology for cellular bioassays based on microparticle technology.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2011-0030269 and NRF-2011-35B-D00015).

REFERENCES

[1] D-H. Kim, H. Lee, Y. K. Lee, J-M. Nam, and A. Levchenko, *Biomimetic Nanopatterns as Enabling Tools for Analysis and Control of Live cells*, Advanced Materials, vol. 22, pp. 4551–4566, (2010).
[2] S. E. Chung, W. Park, H. Park, K. Yu, N. Park, and S. Kwon, *Optofluidic maskless lithography system for real-time synthesis of photopolymerized microstructures in microfluidic channels*, Applied Physics Letters, vol. 91, pp. 041106, (2007).
[3] W. Stöber, A. Fink, and E. Bohn, *Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range*, Journal of Colloid and Interface Science, vol. 26, pp. 612-69, (1968).
[4] J. Ge and Y. Yin, *Magnetically Tunable Colloidal Photonics Structures in Alkanol Solutions*, Advanced Materials, vol. 20, pp. 3485–3491, (2008).
[5] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, and G. M. Whitesides, *Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer,* Nature, vol. 393, pp. 146–149, (1998).
[6] S. J. Kwon, J-H. Park and J-G. Park, *Wrinkling of a sol-gel-derived thin film*, Physical Review E, vol. 71, 011604, (2005).

CONTACT

Prof. Sunghoon Kwon +82-2-880-1736 or skwon@snu.ac.kr
Prof. Wook Park +82-31-201-3465 or parkwook@khu.ac.kr