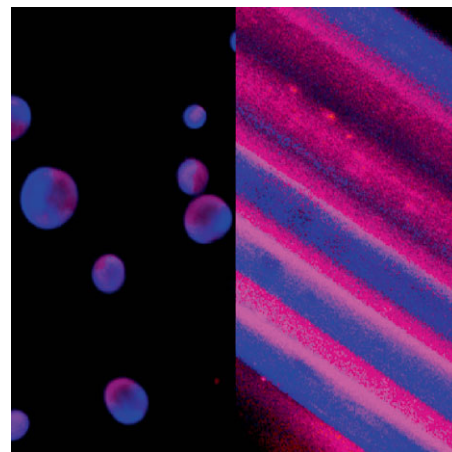


Compartmentalized Photoreactions within Compositionally Anisotropic Janus Microstructures^a

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We demonstrate spatially controlled photoreactions within bicompartamental microparticles and microfibers. Selective photoreactions are achieved by anisotropic incorporation of photocrosslinkable poly(vinyl cinnamate) in one compartment of either colloids or microfibers. Prior to photoreaction, bicompartamental particles, and fibers were prepared by EHD co-jetting of two compositionally distinct polymer solutions. Physical and chemical anisotropy was confirmed by confocal laser scanning microscopy, Fourier-transformed infrared spectroscopy, and scanning electron microscopy. The data indicate adjustment of polymer concentrations of the jetting solutions to be the determining factors for particle and fiber structures. Subsequent exposure of poly(vinyl cinnamate)-based particles and fibers to UV light at 254 nm resulted in spatially controlled crosslinking. Treatment of the crosslinked bicompartamental colloids with chloroform produced half-moon shaped objects. These hemishells exhibited a distinct porous morphology with pore sizes in the range of 70 nm. Based on this novel synthetic approach, Janus-type particles and fibers can be prepared by EHD co-jetting and can be selectively photocrosslinked without the need for masks or selective laser writing.



Introduction

Fabrication of anisotropic colloidal polymer particles with complex shapes, surface patterns, and bulk compartment-

alization has been an emerging area of material science,^[1] because of a range of potential applications of these particles in diagnostics, drug delivery,^[2] micromotors or actuators,^[3] and scaffolds.^[4] Contemporary particle fabrication methods include stretching,^[5] particle replication in non-wetting templates (PRINT),^[6] seeded polymerization,^[7] and microfluidic processing.^[8] Anisotropic surface properties can also be prepared by selective decoration of particle surface leading to “patchy particles.”^[9]

Especially, particles and microfibers, which are comprised of different compartments, provide a unique opportunity to combine orthogonal physical properties on the same micro-object.^[10–15] For instance, if such “bipolar” particles contain drugs loaded in polymer

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matrices that have different crosslinking densities of each compartment, sequential drug release may be achieved. In addition, multicompartmental fibers are currently investigated for their potential biomedical applications.^[15] One can easily contemplate scaffold structures, where one compartment is loaded with drugs or nutrients that are released in a controlled fashion, while the other compartment supports mechanical integrity of the fiber mesh. Such multicompartmental fibers may address an important challenge in tissue engineering, as drug release from the fibers can be decoupled from maintaining mechanical support properties.^[16]

In principle, spatially controlled photoreactions are well suited for selective modification of particles and a range of photolithographic methods have been used for fabrication of particles with novel shapes and anisotropy.^[10] Our group has recently used maskless photolithography for creation of surface patterns on colloidal particles.^[17] While these processes are in principle applicable to smaller scales, the actual particles are often relatively large, and methods, such as maskless photopatterning of coated microbeads, are strictly limited to the modification of surfaces. In order to prepare Janus particles with anisotropic bulk compositions, various technical approaches have been developed so far including microfluidics,^[10] solvent evaporation methods,^[11] and self-assemble methods.^[12] Among them, electrohydrodynamic (EHD) co-jetting in a side-by-side geometry may provide a number of advantages, if compositional diversity, broad control of shapes and architectures, and experimental simplicity are required.^[13–15] Recent work underpins the potential of the EHD co-jetting technology to control the internal and external structure of Janus particles and fibers.^[14] Beyond polymers, we have reported that inorganic nanomaterials can be selectively incorporated into one side of bicompart-mental particles.^[18]

We now report on spatially controlled photoreactions within anisotropically structured colloids and microfibers. This approach allows for fabrication of biphasic particles and fibers with different mechanical properties in each compartment, as well as selective removal of sacrificial compartments.

Hence, we provide an experimental approach toward confinement of photoreactions to specific compartments and use this approach to create controlled particle and fiber shapes.

Experimental Part

Materials

Chemical reagents including poly(lactide-co-glycolide) (PLGA, ratio of lactide and glycolide: 85:15, 40 000–75 000 g·mol⁻¹ of \bar{M}_w), poly(vinyl cinnamate) (PVCi, \bar{M}_w : 200 000 g·mol⁻¹), chloroform,

and dimethylformamide (DMF) were purchased from Sigma–Aldrich Co. (USA) and used without further purification. Polythiophene polymers (PDS306PT and ADS406PT), which were used as photoluminescent red and blue dyes, respectively, were purchased from American Dye Source Co. (USA).

Electrohydrodynamic (EHD) Co-jetting from Dual Needles with Side-by-side Geometry

For EHD co-jetting, two jetting solutions were prepared, which contained either PLGA in CHCl₃/DMF (95:5 v/v) or a 1:1 w/w mixture of PLGA and PVCi in CHCl₃/DMF (95:5 v/v). The total polymer concentration for electrohydrodynamic co-jetting experiments was 7.5% w/v in case of particles and 30% w/v for fibers. In addition, photoluminescent dyes were added to the polymer solutions at a concentration of 0.5 wt.-%.

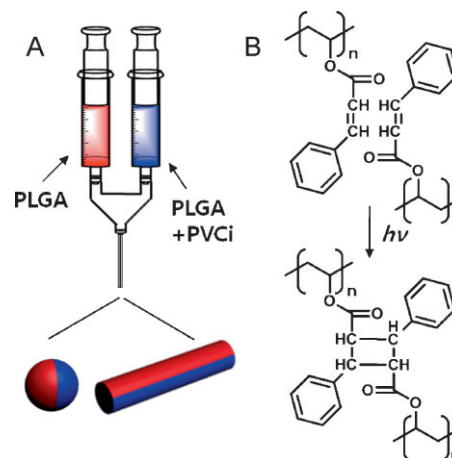
Using a standard syringe pump (Kd Scientific, USA), each polymer solution was pumped through a dual-needle set-up with a side-by-side geometry (Scheme 1A). Needles were connected to the cathode of a DC voltage source, and a positive electrical potential of 7 kV (for particle) and 15.5 kV (for fiber) was applied. The flow rates of each polymer solution were adjusted to 0.2 ml·h⁻¹ for particles and 0.1 ml·h⁻¹ for fibers using a syringe pump. The counter electrode was linked to aluminum foil, which was used as the collector.^[13–15]

Photocrosslinking of Poly(vinyl cinnamate) (PVCi)

Microstructures prepared by EHD co-jetting were stored in a desiccator under a reduced pressure for 12 h to remove any residual solvent. Next, the solid products were irradiated for 10 min at 254 nm with a UV light source (ABM Inc. controlled by Illumination Controller of Radiation Power Systems Inc., USA).

Results and Discussion

Electrospinning or electrospaying are efficient techniques to obtain micron- to nanometer-scale fibers and particles by



Scheme 1. (A) Schematic diagram of EHD co-jetting in a side-by-side configuration; one side contains PLGA only and the other side is composed of a mixture of PVCi and PLGA. (B) The chemical structures of PVCi before and after photocrosslinking.

applying a high DC voltage to a jetting solution exiting a macroscopic outlet.^[19] Under the influence of the electrical field, the fluid droplet becomes truncated and forms a narrow cone, the so-called Taylor cone, which acts as a barrier-free, ultra-thin nozzle.^[20] In this work, we use a modification of this process, EHD co-jetting, to produce biphasic microparticles and fibers containing the photo-reactive polymer PVCi, which is selectively localized in one compartment only. The chemical structure of PVCi is illustrated in Scheme 1B. After UV irradiation (254 nm), the double-bonds in neighboring cinnamate groups form cyclobutane rings resulting in intra- or inter-chain cross-linking.^[21]

The EHD process allows for co-localization of different polymers within defined compartments of the same particle or fiber.^[13–15] Whereas one jetting solution can contain PLGA only, a mixture of PVCi and PLGA can be introduced into a second jetting solution, which forms an additional compartment (Scheme 1A). Because PVCi and PLGA are immiscible at higher concentrations, phase separation may occur in the PVCi/PLGA compartment. A variety of experimental conditions have to be considered during the EHD co-jetting process, such as choice of polymer, polymer concentration, solvent, flow rate of jetting solutions as well as applied electrical voltage. Recently, we have reported the systematic investigation on EHD jetting of the bicompartamental particles that were

made of PLGA in both compartments and studied the variation of shape in terms of polymer concentrations and flow rates.^[14a] In general, formation of particles is favored, when lower polymer concentrations are used. As the concentration of polymer is increasing, beads-on-a-string fibers and fully cylindrical fibers can be produced.

Initial studies confirmed that addition of PVCi to one of the jetting solutions did not alter the overall jetting conditions dramatically. This is somewhat surprising because the addition of PVCi can create large difference in physical properties between two jetting solutions, which may interfere with the formation of a stable jet. Similar to the case, when PLGA is used in both compartments, EHD co-jetting of PVCi/PLGA solutions with relative low polymer concentrations in the range of 7.5% w/v resulted in microparticles having two well-defined and distinct compartments, as confirmed by confocal laser scanning microscopy (CLSM). Figure 1A, B, and C, show CLSM images of bicompartamental microparticles, with PVCi localized in one compartment. In these images, blue fluorescence can be attributed to the fluorescence dye ADS406PT, which was added to a PVCi/PLGA mixture (Figure 1A), and the red fluorescence came from ADS306PT, which was used to visualize the PLGA compartment (Figure 1B). It is important to note, that the CLSM images shown in Figure 1A, B, and C were obtained prior to photocrosslinking. Under these conditions, the PVCi does not show appreciable autofluor-

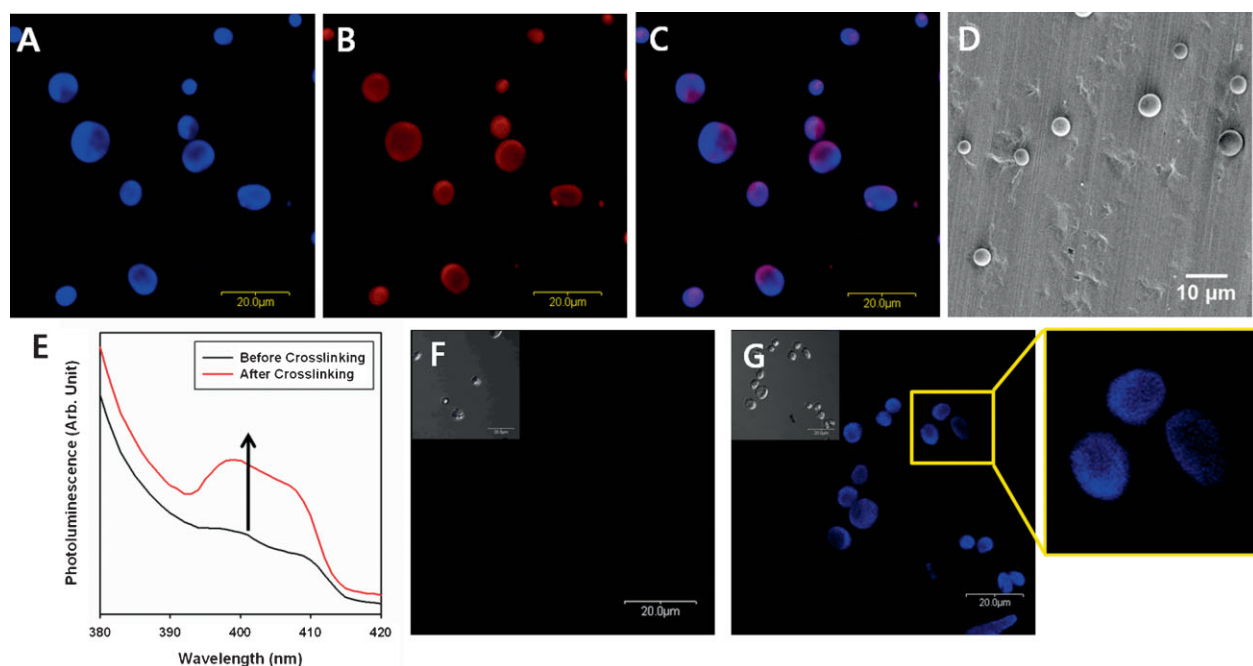


Figure 1. Confocal laser scanning microscopy (CLSM) images of biphasic microparticles; (A) blue emission, (B) red emission, and (C) corresponding overlay image. (D) SEM image of biphasic microparticles. (E) Photoluminescence spectra of a PVCi film before and after photocrosslinking. (F) and (G) CLSM image (blue emission) of biphasic microparticles without incorporation of organic dyes before (F) and after (G) photocrosslinking (insets are corresponding DIC images).

escence and the blue color can be attributed to the ADS406PT dye. Figure 1C represents an overlay of the corresponding images. A clear separation of dyes can be observed in the image overlays, confirming that bicompartamental particles with PVCi localized in one compartment are successfully prepared via EHD co-jetting. Analysis of the scanning electron microscope (SEM) image (Figure 1D) revealed a particle diameter distribution of $8 \pm 2 \mu\text{m}$.

Once the ability to selectively compartmentalize PVCi in colloids and microfibers was established, we sought to confirm that selective photoreactions were possible within colloids and microfibers. The polymer PVCi is the well-known photocrosslinkable polymer, even in the solid state.^[21] To confirm occurrence of photoreactions, particles or fibers were collected onto the counterelectrode and were directly irradiated at 254 nm with a UV source. After photocrosslinking, PVCi emits sufficiently high levels of fluorescence to be detectable by CLSM (Figure 1E). Figure 1F and G present the CLSM images before and after photocrosslinking of biphasic microparticles, which were prepared without organic dyes. As shown in Figure 1G, hemisphere-like blue emission can be observed after photocrosslinking, whereas no emission was observed before crosslinking (Figure 1F) under an identical experimental conditions; i.e., the same laser intensity, gain width, and offset for pseudo-color. This result establishes strong evidence for the occurrence of spatially controlled photoreaction in microparticles. Not only was the bicompartamental character of the colloids retained during EHD co-jetting and particle solidification, but compartmentalization was maintained after photocrosslinking as well.

UV-Vis spectra of biphasic particles containing PVCi before and after photocrosslinking are illustrated in Supporting Information Figure S1 along with a detailed description of the experimental method. Before crosslinking, PVCi showed strong UV absorption in the range of 250–300 nm in wavelength, which was mainly attributed to conjugation between double bonds and benzene rings of cinnamate pendent groups. After photocrosslinking, the double bonds were converted to cyclobutane groups and the UV absorption diminished. In addition to the UV-Vis study, the photoreactions were further verified by infrared spectroscopy. During the photocrosslinking reaction, double bonds of the cinnamate groups are converted into cyclobutane and unsaturated ester bonds will disappear. Figure 2 shows the Fourier transform infrared (FTIR) spectra of biphasic particles before and after photocrosslinking, which are obtained by potassium bromide pellets. Before photocrosslinking, characteristic IR stretches of PLGA and PVCi are clearly displayed: C–H bands of polymer backbone at $2800\text{--}3000 \text{ cm}^{-1}$; C=O bands of PLGA at 1754 cm^{-1} ; C=O stretches of unsaturated ester groups in PVCi at 1716 cm^{-1} , C=C bands of the cinnamate groups at 1631 cm^{-1} , as well as several vibrational modes related

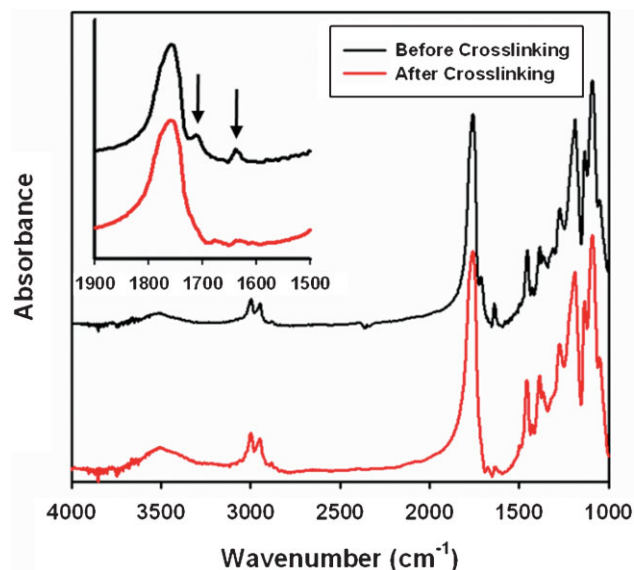


Figure 2. Fourier transform infrared (FTIR) spectra of biphasic microparticles before and after photocrosslinking at 254 nm.

to the benzene rings of the cinnamate groups.^[21b,c] After UV irradiation, the signals for double bonds at 1631 cm^{-1} (right arrow in inset of Figure 2) were significantly reduced, indicating successful conversion of the cinnamate groups. In addition, the signal at 1716 cm^{-1} (left arrow in inset of Figure 2) was shifted to higher wavenumbers, where it overlapped with C=O stretches of PLGA.^[21b]

Based on CLSM, IR, and UV-vis analysis of bicompartamental particles, we concluded that EHD co-jetting in conjunction with spatially controlled photocrosslinking reactions can yield novel types of particles and fibers, where each compartment has highly distinct physical and chemical physical properties including degradation rates, solvent resistance, and mechanical properties.

When polymer solutions with higher concentrations were used, microfibers with a uniform diameter of ca. $20 \mu\text{m}$ were obtained, as shown in Figure 3A. The EHD co-jetting makes it possible to assemble fibers into aligned scaffolds, while maintaining their unique bicompartamentalized architecture. Accordingly, a distinct boundary is revealed at the interface of the blue and red compartments of the fibers shown in Figure 3B. In this case, the fibers were prepared without the addition of blue dyes in the jetting solutions of PLGA/PVCi. The blue fluorescence is originated from crosslinked PVCi,^[21d] confirming that PVCi is incorporated into just one compartment of the fibers. The SEM image in Figure 3C provides a cross-sectional view on an aligned fiber scaffold. Clear differences in the surface morphology can be observed between the two hemispheres of the microcylinders. Several PVCi microfibers with smaller diameter are embedded into one compartment of a large PLGA fiber. The characteristic morphology in the PVCi

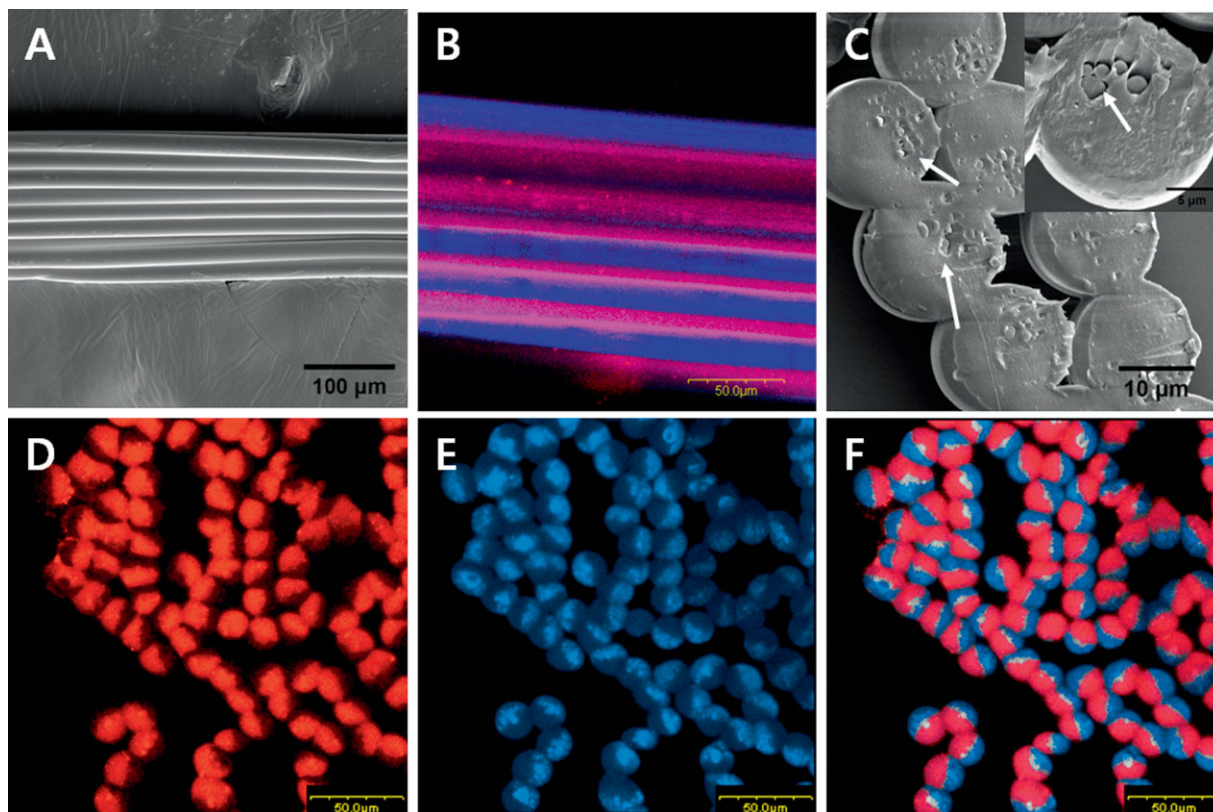


Figure 3. Aligned bicompartmental microfibers. (A) SEM image, (B) CLSM image of top view of microfibers, (C) cross-sectional SEM image, (D, E, and F) cross-sectional CLSM images of red, blue, and overlay images, respectively.

compartment is caused by the phase separation between PVCi and PLGA during the fiber spinning process. Figure 3D, E, and F show cross-sectional CLSM images of biphasic microfibers (red, blue, and their overlay, respectively). While red color is uniformly emitted over the entire compartment, several bright spots from blue compartments can be depicted, which are caused by crosslinked PVCi. Microfibers that contain crosslinked polymers in one compartment can offer several advantages for developing functional scaffold materials. If scaffolds for tissue engineering are intended, release of drugs from the polymer fibers is based on polymer degradation and thus associated with loss of mechanical properties. However, if release and mechanical stability are provided by two different compartments, a physically and chemically durable backbone can be maintained, while simultaneously allowing for polymer degradation and drug delivery. Ultimately, it is expected that unique drug release profiles can be generated by compositionally anisotropic fibers.

Spatially controlled photoreaction in biphasic particles and fibers was further confirmed by selective dissolution of the compartment, which was comprised of PLGA. Figure 4 shows SEM images of biphasic microparticles and fibers after solvent exposure. When the biphasic particles are

treated with chloroform, semicapsules containing small pores on their surface can be obtained (Figure 4A). The average pore sizes of the semicapsules shown in Figure 4A are ≈ 70 nm. When bicompartmental fibers were exposed to chloroform to dissolve the PLGA, PVCi fibers with average diameters of ≈ 300 nm were isolated (Figure 4B). During jetting, the concentration of polymers continuously increases until phase separation of the two polymers occurs. A direct consequence is the formation of PVCi fibers in the compartment containing both PLGA and PVCi, which are revealed after removal of PLGA with chloroform.

Conclusion

In summary, biphasic microparticles and fibers containing photocrosslinkable polymer in one side were successfully prepared by EHD co-jetting. Careful CLSM analysis revealed distinct boundaries between two compartments in bicompartmental colloids and microfibers. SEM analysis further indicates well-established surface morphologies. FTIR analysis and solvent treatment of products confirms spatially controlled photoreactions. Because of rapid solvent evaporation during jetting, hemicapsules with

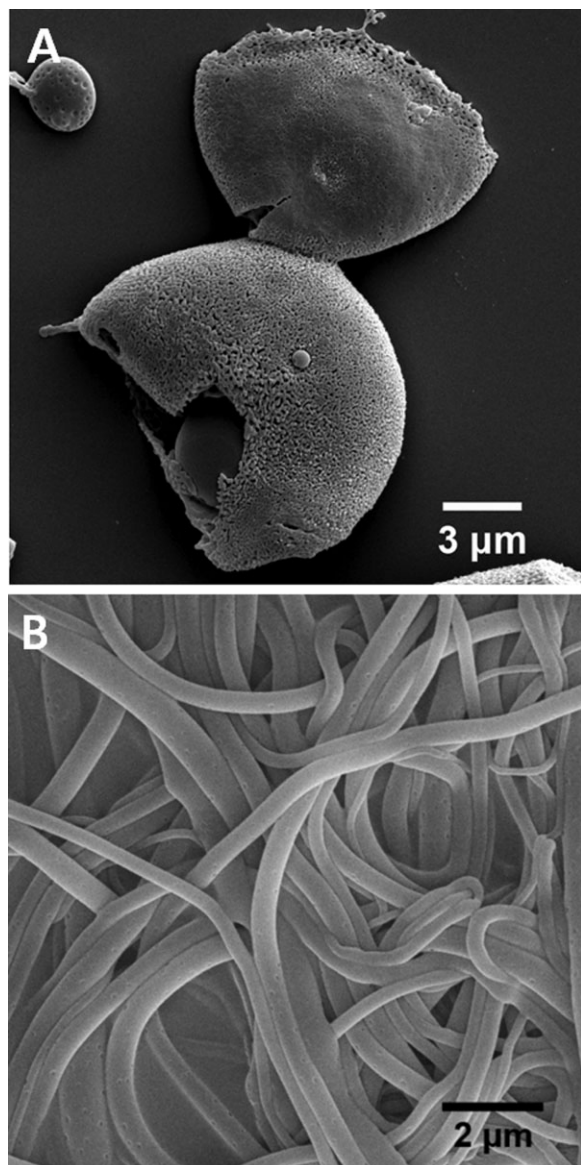


Figure 4. Scanning electron microscope (SEM) images of biphasic microstructures after solvent treatment. (A) Hemicapsules containing lots of small pores on the surface obtained from biphasic particles and (B) PVCi microfibrils with smaller diameters after exposure of the biphasic fibers to chloroform.

porous morphologies were obtained after selective removal of PLGA with chloroform. The bicompartamental particles and fibers prepared in this study may potentially find uses as drug delivery carriers or scaffolds for regenerative medicine.^[2,4,16]

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