

Fabrication of Free-floating Nanohybrid Microparticles with ZnO Nanowire Surfaces

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A photopolymerization technique with UV-photocurable materials using optofluidic maskless lithography (OFML) provides great flexibility in generating microstructure in microfluidic channels, such as continuous flow lithography¹ and optofluidic lithography.² These techniques enable the production of various microstructures with freeform shapes and high throughput because of its continuous synthetic process. Photocurable materials can generate polymeric microstructures with tunable internal structures, shapes, and surface properties. They have potential applications in particle-based technologies such as encoded chemical-laden microparticles, QR-encoded polymeric microparticles, and functional microparticles with complex nanostructured compartments.³ Recently, polymeric microstructures have been widely used in cell biology, including in scaffolding materials, tissue regeneration, and cellular studies,⁴ they can be used as three-dimensional (3D) tissue-like structures assembled by biological structures. Most researches on nanowire technology for cellular physiology have been based on nanowires on a two-dimensional planar substrate. For more flexible and scalable expansion of biomimetic surface for cellular study, we have focused on three-dimensional tissue-like structures assembled with microscale building blocks. In bottom-up approach for forming biomimetic extracellular matrix including nanowires, the unit of the structure is required to have nanowires on its surface.

We present a novel nanohybrid microparticle inspired by a natural extracellular matrix composed of an interlocking mesh of fibrous proteins and carbohydrate polymers that can be used as a biomimetic material. The novel polymeric microparticle is a 3D shape with spiked ZnO nanowires on its surface. ZnO nanowires have been used for biochemical sensing devices that detect proteins, viruses and pH levels. Moreover, ZnO nanowire structures are an effective extracellular matrix to guide cell migration or control cell differentiation.^{5,6}

Herein, we introduce fabrication of free-floating nanohybrid microparticles with a ZnO nanowire surface. The fabrication process of nanohybrid microparticles is composed of two main steps. First, freeform shapes of microparticles are generated by photopolymerization using an OFML system. After preparation of the microparticles, silica layers are deposited to provide texture seeds for the ZnO nanowires. Then, the ZnO nanowires are grown on the surface

of microparticles via a hydrothermal reaction process. We can control the density of the ZnO nanowires on the microparticle during seeding processes.

In order to produce nanohybrid microparticles, we prepare an UV-photocurable resin, ethoxylated trimethylolpropane triacrylate (ETPTA, Sigma-Aldrich, St. Louis, MO) and UV photoinitiator (2,2-dimethoxy-2-phenylacetophenone, Sigma-Aldrich, St. Louis, MO) for synthesis of polymeric microparticles. For silica layer deposition, we also prepare 98% tetraethyl orthosilicate (TEOS, Sigma-Aldrich, St. Louis, MO) and a mixed solution that consists of deionized water, 99% ethanol (Daejung, Korea), and 25-28% ammonium hydroxide (Daejung, Korea). After synthesizing polymeric microparticles by photopolymerization of the mixture consisting of ETPTA and 10 wt % photoinitiator using maskless lithography, polymeric particles are incubated in solution for the silica-coating reaction by periodically injecting TEOS into the mixed solution using the Stöber method.⁷ The surface of elastic polymeric microparticles is coated with an inelastic silica film forming a core-shell structure.

Texture seeds are used for ZnO nanowire synthesis on the surface of the microparticles. A solution that contains 0.005

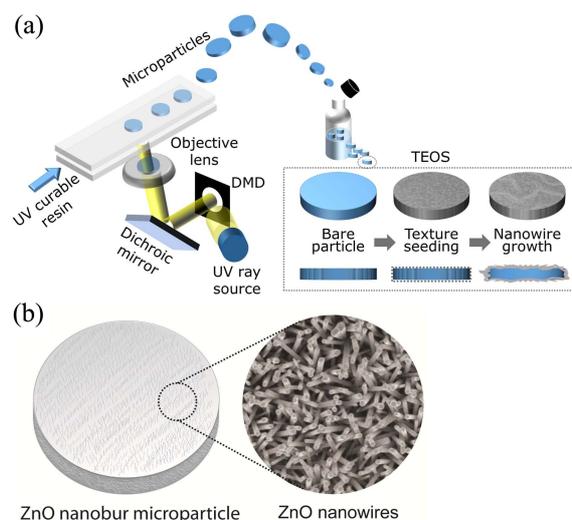


Figure 1. A schematic illustration of the free-floating nanohybrid microparticle fabrication and ZnO nanowires surface. (a) Fabrication and synthetic process of the nanohybrid microparticle. (b) Image of the synthesized ZnO nanowires on the polymeric microparticle surface.

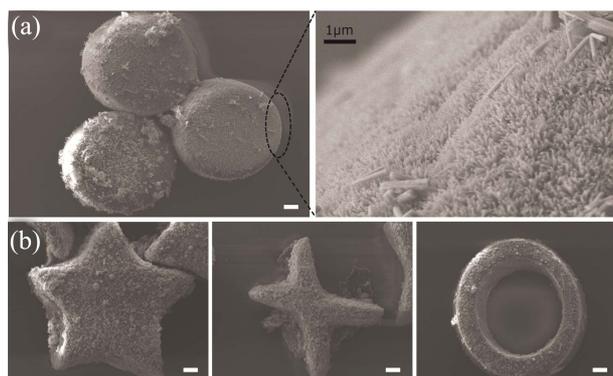


Figure 2. SEM images of freeform-shaped nanohybrid microparticles: (a) Circular-shaped microparticle and magnified ZnO nanowires grown on microparticle surface, (b) Nanohybrid microparticles with freeform shapes (ring, cross, and star shapes), scale bar: 10 μm .

M zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in ethanol is added to a vial containing the microparticles. Then, the microparticles are rinsed with ethanol and annealed in the vial at 350 $^\circ\text{C}$ for 20 min. We fill the vial containing the seeded microparticles with aqueous solutions of 25 mM zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 25 mM hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$). The microparticles are heated at 95 $^\circ\text{C}$ for 3 h by a heating plate and are rinsed with DI water.

Figure 1 shows a schematic illustration of ZnO nanobur microparticles and their fabrication process. Figure 1(a) shows the freeform shapes of microparticles generated by photopolymerization using an optofluidic maskless lithography system. After preparation of the microparticles, silica layers are deposited for texture seeding of ZnO nanowires. Then, the ZnO nanowires are grown on the silica layer of the microparticle by a hydrothermal reaction process. The diameter of the ZnO nanowires is approximately 100 nm, and their length is around 1 μm . Various shapes of microparticles are generated by the photopolymerization process using the OFML system followed by synthesis of ZnO nanowires on their surface (Figure 1(b)).

Figure 2 shows SEM images of nanohybrid microparticles. Figure 2(a) shows the ZnO nanowires grown on circular microparticles. The nanowires extend from the polymeric microparticle surface. Also, Figure 2(b) shows the production of the freeform nanohybrid microparticles (ring, cross, and star shapes). We regulated the density of the ZnO nanowires by controlling the number of seeds.

Figure 3 shows SEM images of nanohybrid microparticles with a ZnO nanowire surface under different ZnO texture seeding conditions. The images of (a), (b), and (c) underwent 2, 5, and 10 ZnO texture seeding processes, respectively. SEM images indicate that the density of the ZnO nanowire increases with the number of texture seeding

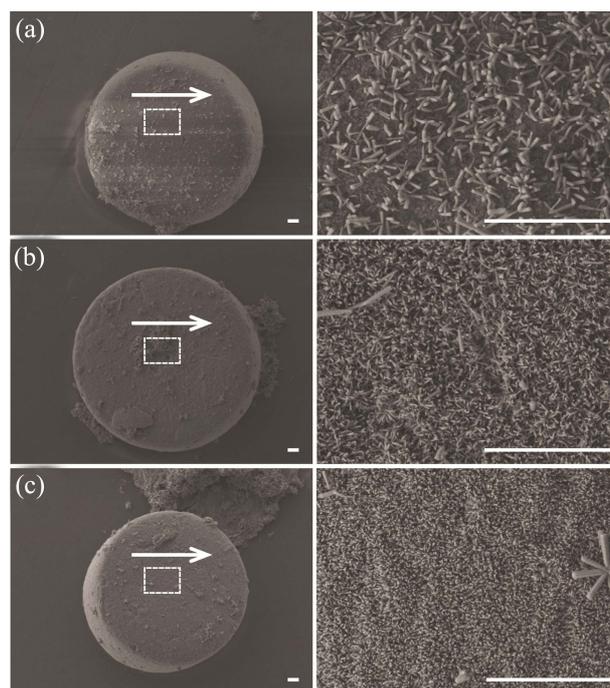


Figure 3. SEM images of ZnO nanowire density control during the texture-seeding process. ZnO nanowire surface of a microparticle that underwent (a) 2, (b) 5, and (c) 10 seeding processes. Scale bar: 5 μm .

processes. The measured surface densities of ZnO nanowires are approximately 5, 30, and 83 wires/ μm^2 at 2, 5, and 10 ZnO texture seeding processes, respectively.

In this paper, we introduce the fabrication process for freeform-shaped 3D polymeric microparticles with a ZnO nanowire surface. Furthermore, we expect that the nanohybrid microparticles may be utilized in drug screening assays and local gene delivery tools.

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