GENERATIOIN AND SELF-REPLICATION OF MONOLITHIC, DUAL-SCALE POLYMER STRUCTURES BY TWO-STEP CAPILLARY FORCE LITHOGRAPHY

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ABSTRACT

Inhibition effects in UV radiation curing by oxygen were utilized for fabricating monolithic, micro/nanoscale hierarchical polymer structures via two-step UV-assisted capillary force lithography (CFL). It was found that the UV exposure time for the partial curing of microstructure was a crucial parameter; a shorter exposure time induced collapse of the underlying microstructure while a longer time gave rise to non-fluidity of the microstructure. The partial curing is attributed to inhibition of UV crosslinking by trapped or permeated oxygen within mold cavities. Using this method, various dual-scale hierarchical structures were fabricated with minimum resolution to 50 nm over a large area (5×5 cm^2) in a fast and reproducible manner.

KEYWORDS: Micro/nano, Dual-scale structure, Oxygen inhibition, UV radiation curing

INTRODUCTION

The effects of oxygen on UV radiation curing have been studied extensively in thin film coatings because the oxygen inhibits free radical polymerization by scavenging initiator radicals, resulting in several negative influences including undercured, tacky surface, loss of optical and surface properties and reduction in the rate of polymerization [1-2]. For these reasons, the oxygen in radiation curing has been considered as a negative factor and several methods have been developed to overcome O_2 inhibition in photopolymerization [1-2].

In the current approach, this oxygen-induced partial curing was exploited for fabricating various micro/nanoscale hierarchical structures by a two-step molding process. Micro/nanoscale combined hierarchical structures are potentially useful for the development of diverse biomimetic, photonic, electronic and micro/nanofluidic devices because multiscale structures enhance structural functionalities and often lead to totally different properties compared to those of single length scale.

THEORY

We hypothesize that the partial curing has to do with trapped or permeated oxygen in a molding process. Although the flexibility of the polyurethane acrylate (PUA) mold (~50μm thickness) can minimize the trapped air inside the mold cavity, there remains trapped air as the PUA mold is impermeable to air. In the case of polydimethyl siloxane (PDMS) mold, the surface of the molded polymer film is exposed to air that is permeated through a porous PDMS mold. The trapped or perme-

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ated oxygen inhibits UV curing by scavenging radicals generated from the photoinitiator by UV [1-2]. Thus, the surface of the PUA resin in contact with the air remains tacky whereas the resin beneath the surface cures completely. There is some predissolved oxygen in the liquid resin, which is rapidly consumed under UV exposure due to high mobility and reactivity of oxygen with a large amount of initial radicals. Therefore, the formation of a tacky surface is attributed to the diffusion of oxygen that is trapped in the mold cavity or permeated out of the mold.

EXPERIMENTAL

Figure 1 shows a schematic diagram of the two-step UV-assisted capillary force lithography. For fabricating a microstructure (1st step), a micropatterned PDMS or PUA mold was placed onto a spin-coated, UV-curable PUA resin on a solid substrate followed by partial curing by exposure to UV light for 5-21 s (λ =250-400 nm, dose=100 mJ/cm^2). Nanofabrication on the preformed microstructure (2nd step) was subsequently carried out by using a high-resolution nanopatterned PUA mold, which was recently introduced for sub-100-nm patterning [3]. While PDMS is difficult to be used for sub-100 nm patterning due to low elastic modulus (~1.8 MPa), the PUA mold is not only sufficiently rigid (Young's modulus of hundreds of MPa) but also flexible (~50μm thickness), allowing for nanopatterning over a large area. The PUA mold replicated from the complementary nanopatterned Si master was placed on top of the as-prepared microstructure with a low pressure (10^3 Pa) followed by an additional UV exposure for 10 s.

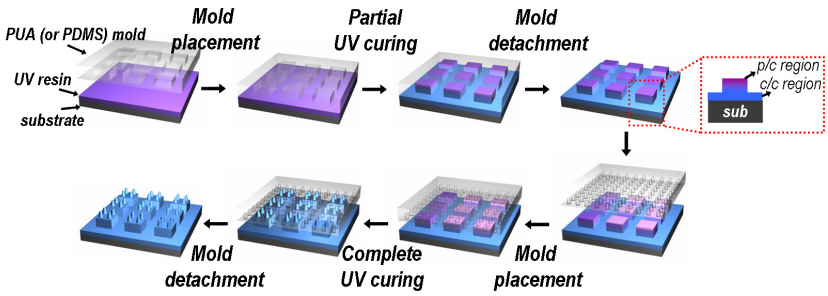

Figure 1. A schematic illustration for the fabrication of dual-scale hierarchical structures by two-step UV-assisted capillary force lithography

RESULTS AND DISCUSSION

Figure 2a demonstrates the capability of large area fabrication (~5 × 5 cm^2) of the two-step CFL procedure. Figure 2b-f shows SEM images of various hierarchical structures on PET (~50μm thickness) film substrate. Nanopillars of 100nm diameter (a-c) and 400nm diameter (d-f) were uniformly formed on top of (a-b) 280×75μm^2 lattices (spacing of 25 μm, height of 4.5 μm), (c) 30μm posts (spacing of 40 μm, height of 50 μm), or 40μm boxes (80μm spacing and 40μm height). Although not shown, 50nm lines, whether positive (features sticking out) or negative (features sticking in), were faithfully integrated with the underlying microstructure. In this method, UV irradiation

time for the partial curing of microstructure was a crucial parameter. If the curing time was too short, the microstructures were easily collapsed in the presence of a small mechanical loading. If the time was too long, on the other hand, the nanostructures could not be formed on the completely cured microstructure due to non-fluidity of the PUA. With a suitable curing time, the upper part of the microstructure is still fluidic (tacky), allowing for subsequent formation of nanostructure over the preformed microstructure.

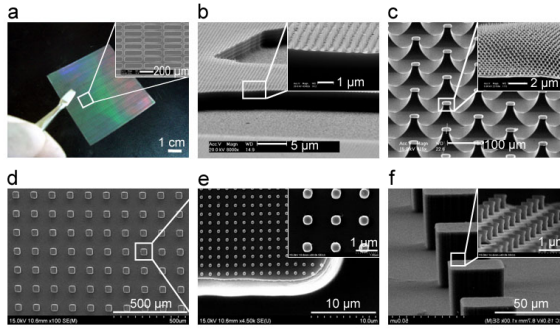

Figure 2. Various dual-scale hierarchical structures fabricated by two-step UV-assisted capillary force lithography

CONCLUSIONS

In conclusion, we have presented a highly efficient method for fabricating well-defined micro/nanoscale hierarchical structures over a large area by using two-step UV-assisted capillary molding technique. Using this approach, various dual scale polymer structures have been created within a few minutes with precise control over geometrical parameters. It was found that the trapped or permeated air plays an important role. By controlling UV exposure time or trapped/permeated oxygen, various strategies could be pursued from simple micro/nanostructures to hierarchically organized structures.

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