Fluorinated Colloidal Emulsion of Photochangeable Rheological Behavior as a Sacrificial Agent to Fabricate Organic, Three-Dimensional Microstructures

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Three-dimensional organic microfabrication, an emerging technology, faces the challenge of lacking a sacrificial agent (SA) to temporarily support the formation of microscale geometries, which can be removed after a microstructure is constructed. In this study, an ultradense oil-in-organofluorine colloidal emulsion with photopolymerizable submicrometer droplets (diameter ~500 nm) was prepared and used as the required SA. Upon exposure to light, the colloidal emulsion undergoes a significant rheological change, which hardens the emulsion and presents the molding/protecting function that an SA must have. Importantly, the emulsion includes a synthesized fluorophilic/fluorophobic block copolymer surfactant to stabilize the droplet compartments, facilitating the dissolution of the postexposure SA. Two successfully built, complex, organic 3D microstructures show the effectiveness of using this novel SA material.

Introduction

In recent years, 3D organic-based microfabrication has gained significant attention in several emerging areas including tissue engineering, organic electronics, micro/nano-optics, and biochemical sensors.[1−6] Compared to the inorganic materials for semiconductor-based microfabrication, organic materials provide an abundance of chemical properties, material multifunctionality, and flexibility that metals and metal oxides cannot.[4] However, the development of this technology is challenged by the lack of an effective sacrificial agent (SA).[7] A SA is a temporary supporting material that can be transformed from a fluid (gas or liquid) to a solid phase when manufacturing microstructures. Solidified SA forms a template for developing microgeometries; it is also applied to cover a microstructure and separate it physically and chemically from other microstructures being formed. Most importantly, a solidified SA can be removed efficiently without affecting the microstructures underneath. The SA materials developed for semiconductor-based technology, such as silicon dioxide and photoresists, are designed for harsh environments; they are applied or removed under extreme temperatures or pH values and are unsuitable for organic-based microfabrication.[7]

One candidate material for synthesizing SAs for organic-based microfabrication is organofluorine compounds. Some chemically inert organofluorine fluids, such as perfluorotripentylamine and perfluorinated poly(propylene glycol), are effective water/oil repelling agents, and they provide the molding/protecting
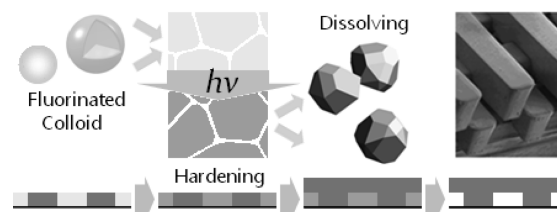

Figure 1. Colloidal emulsion for organic microfabrication.

function that SA materials must have. The challenge of synthesizing an SA from these organofluorines is to achieve the aforementioned phase transformation and material removability. This problem can be solved by developing a close-packed, compartmentally polymerizable oil-in-organofluorine colloidal emulsion (as illustrated in Figure 1). This kind of emulsion contains submicrometer droplets of cross-linkable monomers. Upon polymerization, the cross-linked droplets significantly change the rheological behavior of the emulsion and harden the emulsion. As shown in Figure 1, a microstructure can be fabricated using this solid support. The solidified emulsion can be dissolved afterwards by dispersing the postpolymerized droplet compartments.

Having an effective fluorophilic/fluorophobic surfactant is the key to stabilizing a dense organofluorine emulsion and guaranteeing the removability of SA. Surfactant syntheses for water-in-organofluorine and oil-in-organofluorine systems are reported elsewhere;[8,9] however, these procedures were for different purposes, and our experiments showed that these surfactants fail to keep the close-packed droplets separated upon polymerization. For example, upon photopolymerization, dense polymerizable droplets with the surfactant in ref 9 were found to cross link each other and form clusters that were millimeters in size. Through a

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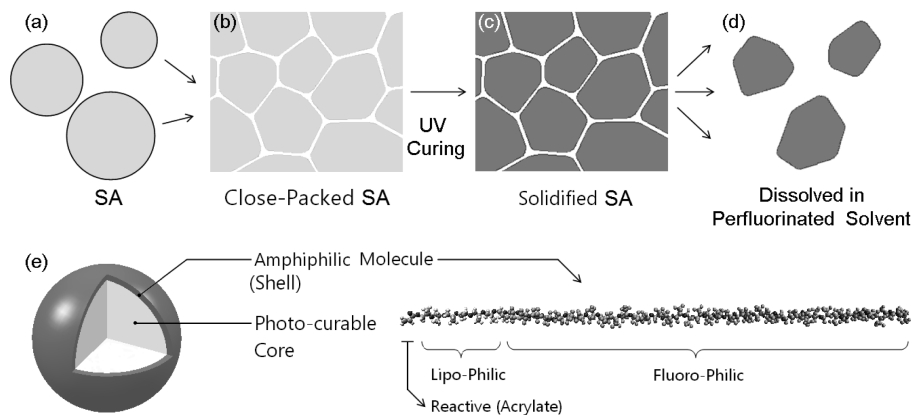
Figure 2. Fluorinated colloidal emulsion of photochangeable rheological behavior.
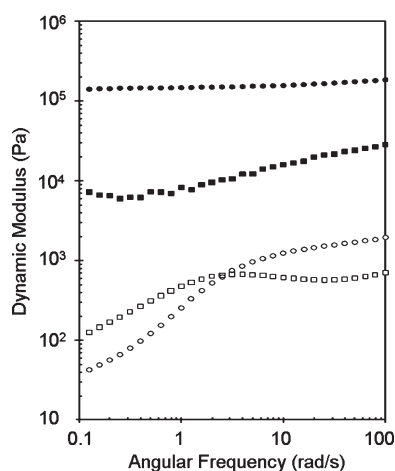

Figure 3. Dynamic loss (squares) and storage (circles) moduli for uncured (open symbols) and cured (solid symbols) SA. Samples were tested in a linear viscoelastic regime with strains of 10% (open symbols) and 0.1% (solid symbols).

number of trials, we found the following scheme for building an effective surfactant, which yields an effective SA for organic microfabrication.

Synthesis of the Sacrificial Agent

The continuous phase of our colloidal emulsion (Figure 2a, b) is a perfluorinated compound, perfluorotripentylamine (FC-70, 3M). However, the suspended oil-phase compound contains multiple acrylates, UV absorbers, and a trace amount of photoinitiator. The droplets were stabilized by a synthesized surfactant, which is a block copolymer of three segments: lipophilic segments of poly(propylene glycol) (PPG, MW $\sim$900), fluorophilic segments of perfluorinated poly(propylene glycol) (PFPPG, MW $\sim$6500), and an acrylate group (located at the lipophilic end) that cross links with the emulsion droplets upon polymerization (Figure 2e). The ratio between the lengths of PFPPG and PPG segments is roughly 7 to 1, thus it is thermodynamically preferable that the amphiphilic molecules self-assemble to form submicrometer droplets of lipophilic cores ($\sim$500 nm in diameter).[10] The amphiphilic molecules were proven to be capable of casing the monomer droplet at a high volumetric ratio of 85:15 (oil/organofluorine). Details about the surfactant synthesis and the emulsification process are available in the Supporting Information.
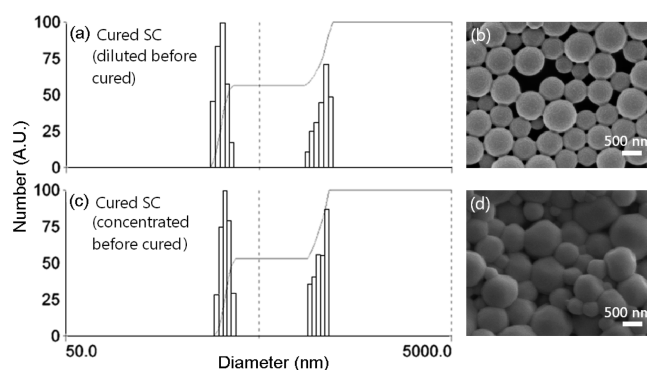

Figure 4. Distribution of the particle size of diluted (a, b) and close-packed (c, d) submicrometer droplets after photopolymerization.

Characterization of the SA

The fluorinated emulsion solidified in response to an exposure of light ($\sim$400 nm wavelength). The postexposure bulk (Figure 2c) was nondissolvable in ordinary solvents such as water, acrylates, chloroform, acetone, alcohols, ethyl ether, and dichloromethane but can be dissolved by perfluorinated agents such as perfluorohexane (C_6F_{14}) and methoxyperfluorobutane ($C_4F_9OCH_3$) in which the particles were readily redispersed (Figure 2d).

Dynamic mechanical spectroscopic analysis was performed to characterize the emulsion response to light exposure. Figure 3 shows the dynamic storage (G') and loss (G'') moduli as a function of oscillatory frequency in the linear viscoelastic region (i.e., the measured properties are independent of the magnitude of the applied deformation or strain). The uncured sample exhibits classic viscoelastic fluid behavior with a crossover in G' and G'' at 2.5 rad/s and a viscosity that is higher than that of either component individually.[11] The viscoelastic character of the uncured sample, which is composed of two Newtonian fluids, arises from the fact that the dispersed droplets are near the close-packed sphere limit and the thin liquid film separating them must deform with the droplets for the sample to flow.[11,12] As a result, surface tension forces contribute heavily to the viscoelastic properties. These characteristics are consistent with other colloids with $\sim$1 μm dispersed liquid particles near the close-packed limit including oil-in-water and water-in-oil emulsions.[12–14] Upon

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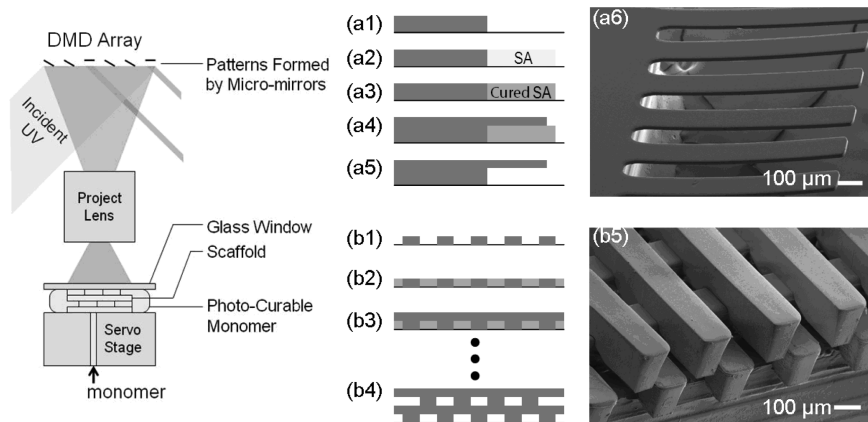
Figure 5. Fabrication of organic microstructures using the synthesized SA as a temporary support.

polymerization of the dispersed monomer particles, the dynamic properties change substantially. The curing of the monomer droplets results in a higher overall modulus and transforms the material into a very elastic solid with G' being an order of magnitude higher than G''. This behavior is consistent with the fact that curing the monomer particles reduces their ability to deform, yielding dynamic properties that resemble those of a highly concentrated particulate gel.[11]

Dynamic light scattering (DLS) measurements (Figure 4a,c) were performed to compare the size distribution of postcuring droplets in a dense emulsion with that in a diluted emulsion (two size groups, about 300 and 800 nm). The DLS results of the close-packed sample showed a negligible difference in the distribution of particle size after the polymerization process, indicating negligible particle binding or clustering during the photo-cross-linking process. The size of the particles was also investigated via SEM (Figure 4b,d). Note the polyhedral geometry of the cured, close-packed particles (Figure 4d), which likely hinders the particles' mobility and enhances hardening after photopolymerization.

Three-Dimensional Microstructures Fabrication Using SA

We have developed a digital-micromirror-device- (DMD-) based microfabrication apparatus for rapidly prototyping 3D microstructures (Figure 5). The system fabricates 3D architectures through dynamically masked photolithography in which microstructures are developed layer-by-layer from a photopolymerizable monomer. Details about this DMD microfabrication system were reported in our previous publication.[5] In brief, a digital light processing (DLP) chip set (XGA Discover 1000, Texas Instrument) was used to create active, reflective photomasks. These photomask patterns are cross-sectional images of a 3D microstructure. Uniform UV light illuminates the photomask to form UV patterns, and a UV-grade optical lens projects the UV patterns onto a fabrication stage, which is located at the focus of the projection lens. The 3D microstructure was fabricated from a photopolymerizable monomer (PPM, see Supporting Information) that cures in response to UV illumination. On the fabrication stage, the UV images from the optical lens solidify the PPM injected from a monomer outlet and create layers of thin, cross-sectional structures to form the 3D microstructure. After the fabrication of each layer, the fabrication stage was repositioned to create a new layer. A glass coverslide was placed above the microstructure to control the flatness of each microstructure layer. The bottom surface of the coverslide was coated with a nonstick layer (about 5 μm thick) formed by 5% agarose gel (Fisher Scientific), which readily releases the postcured microstructure.

The SA was used after the fabrication of each construction layer and was solidified by light (Figure 5a,b). The cured SA covered the cavities in the microstructure underneath and became the temporary support for the following construction. Before applying the SA, the microstructure was rinsed with isopropanol and then methoxyperfluorobutane (MPFB) to remove uncured PPM. After all of the cross-sectional microstructures were built, the finished 3D microstructure was dismounted from the stage and was rinsed in 50/50 (v/v) acetone/MPFB to dissolve the cured SA. Figure 5a6,b5 shows SEM pictures of two organic 3D microstructures fabricated using SA, revealing the layer-by-layer constructions for each microstructure. Figure 5a6 shows an array of cantilevers with a uniform, controllable thickness of 10 μm; the SA is shown to be capable of assisting in the building of uniform, thin organic microstructures. Note that both the cantilever and woodpile microstructures are common architectures for 3D microsystems; applications of these architectures include photonic devices, chemical and biological sensors, microchemical reactors, and tissue engineering scaffolds.[1−4,15]

Conclusions

We synthesized a close-packed, photosensitive, fluorinated colloidal emulsion that undergoes a significant rheological change upon light exposure. The emulsion presents the following qualities of a sacrificial agent for organic microfabrication: (i) it is a liquid under standard ambient conditions and is effective at filling a supported microstructure; (ii) it is chemically and physically separable from organic microstructures; and (iii) it solidifies and can be removed afterwards without damaging the supported microstructures. We applied this colloidal emulsion to support the 3D microfabrication of organic materials and successfully constructed several microstructures.

Supporting Information Available: Experiment details for surfactant synthesis and the emulsification of an organofluorine colloid. This material is available free of charge via the Internet at http://pubs.acs.org.

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