Stop-Flow Lithography for Complex Particle Synthesis and Application in Directed Assembly

Priyadarshi Panda

Department of Chemical Engineering,

Massachusetts Institute of Technology, Cambridge, MA

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Abstract

The synthesis of complex microparticles is an important objective. These particles can find use in a number of applications ranging from tissue engineering to ceramics and assembly. Tuned assembly of anisotropic particles can give rise to macrostructures with complex morphologies. Externally applied fields like electric or magnetic fields are useful ways to tune the assembly of anisotropic particles. This thesis begins with an understanding of the flow conditions in stop-flow lithography (SFL), the technique used for anisotropic microparticle synthesis, followed by the demonstration of the versatility of SFL by synthesizing soft cell-laden microgels, hard ceramic microcomponents and 3D curved microparticles. The thesis ends with the study of the assembly of anisotropic magnetic hydrogels synthesized using SFL.

In the first section of the thesis, we introduce SFL and identify optimal conditions for particle synthesis using SFL. We do so by analyzing the dynamic response of a retracting PDMS wall after the removal of an external stress. We realized that for small deformations the problem lends itself to a regular perturbation analysis that is analytically solvable at zeroth-order. We compared the zeroth-order solution to the numerically solved full solution and to trends seen in experiments.

In the second section we demonstrate the ability to synthesize complex particles using SFL. We generated anisotropic cell-laden microgels with reasonable cell viability. This work required the use of careful, benign conditions to ensure good cell viability and precise stop of the flow to ensure good resolution of cell-laden hydrogels. We determined an optimal cell density in a mixture of the cell suspension with the oligomer and photoinitiator. Then, we varied the concentrations of the oligomer and photoinitiator in the mixture to achieve reasonable polymerization times while simultaneously ensuring the desired cell viability. In a different work, we demonstrated the ability to make colloidal glass and silicon microcomponents using SFL. We flew a shear thinning colloidal silica suspension mixed with oligomer and photoinitiator through a microchannel and flashed UV light through a photomask to synthesize polymeric microcomponents of desired shape. In order to enhance their structural integrity, these colloidal microgears were transformed into fully dense, glassy silica microparticles by sintering at 1150 °C for 3 - 10 hours. SFL has traditionally been used to synthesize 2D extruded particles. We demonstrated the ability to synthesize 3D curved particles using SFL by introducing curvature in the direction orthogonal to the projection of UV light. We achieved this by co-flowing two streams which we called the polymerization and tuning fluid respectively, through a microchannel. On stopping the fluids, curvature developed at the
interface of the fluids to minimize the surface energy. The quiescent fluids were exposed to a flash of UV light through a photomask which resulted in the gelling of the region within the polymerization fluid. The resulting microparticle had a shape in the plane of projection of light dictated by the mask and curvature in the plane orthogonal to the projection of light determined by the surface properties of the fluids used. The chemical programmability of this technique was demonstrated by synthesizing Janus, patched and capped polymeric microparticles.

In the final part of this thesis we present a framework for the study of the directed assembly of H-shaped magnetic hydrogels. We synthesized non-Brownian H-shaped microparticles with encapsulated nanometer sized magnetic beads for assembly studies. Directed assembly at low surface coverage involves two time steps: i) rotation to attain an equilibrium orientation, followed by ii) translation to form assembled structures. Hence, as a first step to understanding the assembly of these particles, we studied their rotation. We developed a Finite Element Integration (FEI) method to identify the preferred particle orientation (relative to the applied field) at different values of the geometric parameters defining H shapes and constructed a phase diagram to generalize the results. We validated the theoretical predictions by comparing with experiments performed using magnetic hydrogels synthesized using SFL. These results aided in the choice of H-shaped particles for further assembly studies wherein we demonstrated the ability of these particles to widen chains and induce branching orthogonal to the applied field.