1. PRF#: 57452-DNI9
2. Project Title: Realizing an Electric Ferrofluid through Rational Nanoparticle Design
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NARRATIVE PROGRESS REPORT
9/1/2017 to 8/31/2018

OVERVIEW

The goal of this project is the incorporation of rationally designed nanoparticle constructs into fluids in a manner that endows the fluid with emergent properties. In order to achieve this, there are three facets that must be addressed: (1) Bulk properties of colloidal suspensions must be interrogated in a robust fashion. (2) An understanding of how nanoparticle properties lead to emergent properties of a fluid must be realized. (3) New methods must be developed for fabricating or synthesizing nanoparticles with controlled properties. In the current performance period, we have made advancements in all three of these facets. As an evaluation of this paradigm for optimizing an emergent fluid property, we developed a method for evaluating the mechanical properties of liquid marbles and elucidated how the emergent elastic and failure mechanics of marbles depend on particle properties. We also report progress on a synthesis scheme to realize particles with custom shapes. In the context of realizing ferroelectric fluids, we have developed a method for evaluating fluid properties by observing the formation of floating water bridges and made initial progress on the synthesis of ferroelectric nanoparticles through ball milling. In the subsequent sections, we detail our specific achievements in these areas.

EMERGENT MECHANICAL PARTICLES THROUGH PARTICLES ON INTERFACES

When drops of fluid are coated with non-wetting particles then can become 'liquid marbles' which adopt several solid like characteristics such as the ability to float on liquid, roll without wetting, and elasticity. We sought to understand the manner in which the mechanical properties of such marbles were influenced by the properties of the particles that make up their coating (Figure 1). Thus, we designed a process for compressing the marbles in an apparatus in which the force and displacement could be measured while the marbles were optically observed to determine the morphology of the coating. This process, along with a novel doubly truncated oblate spheroid model to parameterize the shape of marbles, was used to relate the energy and surface area of the marbles during compression. Through these experiments, we learned that the particles had no influence on the elastic mechanics of the marble. In particular, the energy required to deform a marble is given solely by the product of the surface tension of the core fluid and the change in area of the marble. In contrast with the elastic mechanics, the failure mechanics of the marbles strongly depended on the particles. In particular, by testing two particle types, a non-interacting powder consisting of lycopodium spores and a strongly interacting powder consisting of Teflon particles, we found that more strongly interacting particles result in more brittle marbles which can accommodate smaller deformations prior to catastrophic failure. In order to prove this, we defined a new marble property in ductility, or the areal change in the marble prior to rupture. The observation that weaker interparticle

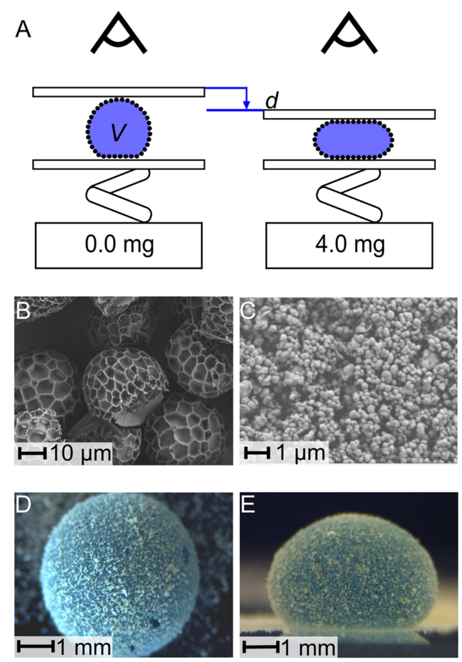

Figure 1. (A) Schematic of apparatus to relate liquid marble mechanics to particle properties. Electron micrographs showing coating particles including (B) lycopodium and (C) Teflon particles. (D) Top and (E) side views of a liquid marble.

interactions lead to more ductile marbles has an interesting analogy in bulk solid mechanics where metals, which generally have weaker interatomic interactions than ceramics, fail in a more ductile manner due to microscopic plastic deformation.

Having elucidated the manner in which particles determine the mechanics of liquid marbles, we sought to employ rational design to realize custom particles that lead to programmed marble behaviors. In particular, we developed a process for using photolithography to pattern particles of programmed shape by transferring a profile from photoresist to an underlying hydrophobic polymer (Figure 2A). This process allowed us to pattern arrays of particles with programmed cross sections on a 4 inch wafer (Figure 2B). A major challenge of this process is reliably releasing the particles from the surface, which we were able to achieve by employing a water-soluble adhesive layer to peel the particles off the surface (Figure 2C). These particles will subsequently be used to explore the mechanics of liquid marbles.

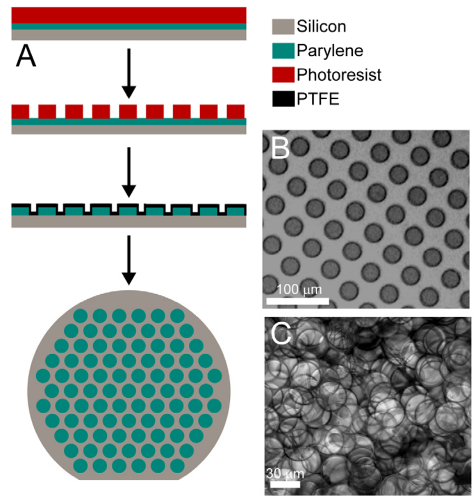

Figure 2. (A) Process for realizing custom particles. Micrograph of particles (B) on a wafer and (C) after release.

ELECTROHYDRODYNAMIC PROPERTIES OF COLLOIDAL SUSPENSIONS

In order to understand the relationship between nanoparticle properties and the emergent electrohydrodynamic couplings in fluids, we adopted a two pronged approach. In particular, we sought to produce ferroelectric nanoparticles through a ball-milling process wherein barium titanate microparticles were milled for a number of hours to produce nanoparticles of controlled size (Figures 3A,B). In particular, 22 hours of ball milling did not produce a substantial change in average particle diameter, as measured by electron microscopy, which we attribute to reattachment in suspension during milling. Future work will focus on bottom-up methods of synthesizing particles and novel surfactants to prevent reattachment.

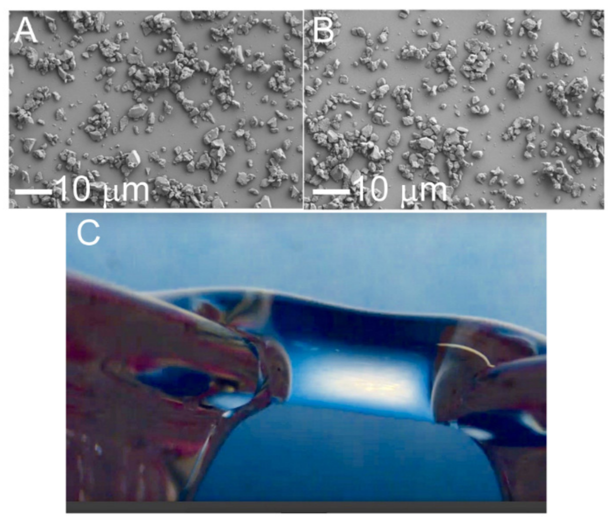

Figure 3. Electron micrographs of barium titanate particles (A) before and (B) after 22 hours of ball milling. (C) Floating water bridge.

In parallel with efforts to produce ferroelectric nanoparticles, we sought to determine connections between properties of the particle and electrohydrodynamic effects. To this end, we have been performing experiments on floating water bridges (Figure 3C), in which solutions form stable bridges between two containers upon the application of a high voltage potential difference between the containers. While the precise mechanism of bridge formation and stability has come under debate in recent years, this process represents the balance of electrostatic stresses, surface tension, and gravity.

CAREER IMPACT

Support for this work has provided an empowering series of career opportunities for the PI, a graduate student, an undergraduate, and even a high school student. In particular, this support has provided the resources for the PI to embark on a new research direction which has led to one published paper, one paper in review, and two more in advanced preparation. Additionally, this work has already resulting in the PI being invited for an invited talk at a conference and given the PhD student the opportunity to present twice in large national meetings.