

Force Measurements on Nanorod - enriched Sintered Colloidosomes

Onyinye Ofoegbu
College of Engineering
Morgan State University
Baltimore, Maryland

Harvard University
Research Experience for Undergraduates
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Experimental Soft Condensed Matter group
Gordon McKay Laboratories
Harvard University
Mentor: Vernita Gordon

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Abstract

We present a method of breaking colloidosome shells using a magnetic field. Nickel nanorods were incorporated into Colloidosome shells. A magnetic field was then applied using magnetic tweezers in order to detach the rods from the colloidosomes. We have determined that the force required to break a five – minute sintered colloidosomes should be at least 50nN. Furthermore the tweezers were calibrated to get a force-distance relationship.

1. Introduction

Fabrication of capsules for encapsulation and controlled release of various materials is a growing area of research. Colloidosomes are one of such capsules developed for encapsulation of various materials such as drugs, dyes, cosmetic, biomaterials, as fillers in catalysis and waste removal^[1,2]. An efficient encapsulation technique should provide effective regulation of size, for versatility in choice of materials for encapsulation; permeability, to facilitate timed and controlled release; mechanical strength, to enable release defined by shear rates and compatibility, so that the techniques accommodates encapsulation of sensitive materials¹. These capsules thus have various potential applications in industry and Medicine. However, how to release the contents of these delivery vehicles is a prime concern. Although colloidosomes can be broken primarily by mechanical means, increase the physical anisotropy of these structures has helped in exploring other avenues in which they could be broken¹. In particular, the introduction of metallic nanostructures into the colloidosome shells has opened the doors for electromagnetic interaction.

2. Materials and Methods

2.1 *General Fabrication process of Colloidosomes*

Colloidosomes were made from the self-assembly of polystyrene beads on the interface of an oil-in water emulsion and then sintered for 5 minutes to stabilize the structures. Below is schematic illustration of the assembly process.

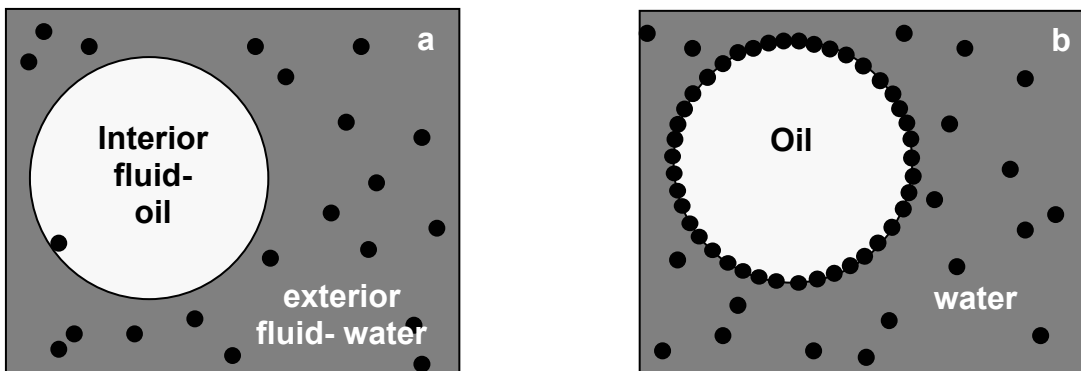


Figure 1

Schematic illustration of self-assembly process (Courtesy Ming Hsu)

(A) Emulsion droplets are introduced to particles in the immiscible exterior fluid

(B) Particles assemble on the interface to minimize the total surface energy

A. D. Dinsmore et al., Science 298, 2002.

The bead solution by was made by diluting one part 1.1 micron-diameter polystyrene beads (Interfacial Dynamics Corporation) in 20 parts water and vortexing up the mixture to disperse the beads. The dispersed phase contained a mixture of equal volumes of toluene and filtered vegetable oil (Wesson). Glycerol solution was prepared by from 70% glycerol (99% pure) and 30% de-ionized water. Sample chambers were made for the colloidosome by sticking coverslips to microscopes slides. The colloidosomes samples are pipetted into the gap between the two surfaces and held in place by capillary action.

5 μ L of the oil mixture were introduced into 500 μ L of the bead solution. Gentle shearing was applied for several seconds to disperse the oil and create emulsion droplets. Initially the dispersion was done by vortexing but that method produced small emulsion droplets resulting in smaller colloidosomes, thus shearing was adopted. The beads then assemble on the interface of the emulsion driven by interfacial energy minimization Glycerol solution containing 30% water and 70% glycerol by volume was then added to raise the boiling point of water in order to prevent the water from boiling off during sintering. The sample was then sintered at 105 °C for five minutes. Sintering helps stabilize the colloidosome structure as well as to improve the resilience of the shell during the interior fluid removal. Finally, the interior fluid was removed by immersing the colloidosome samples overnight in ethanol.

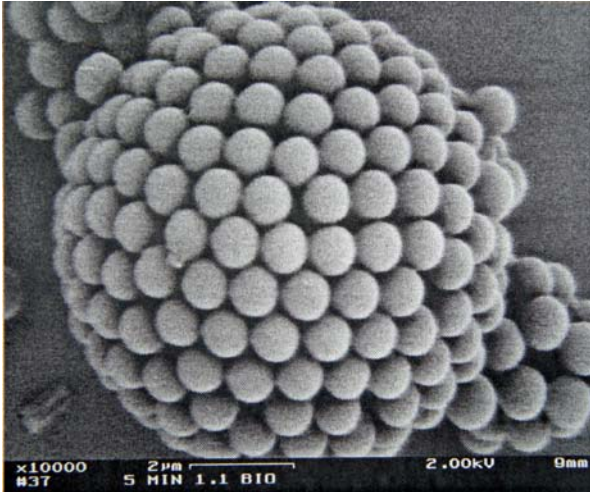


Figure 2

Scanning electron microscope image of dried 10µm-diameter colloidosome composed of 0.9µm-diameter polystyrene spheres sintered for 5 minutes at 105 °C
courtesy Weitz laboratory, Harvard university.

2.2 Synthesis of Nanorods

Synthesis of nanoparticles is an area of growing research motivated by the interest in producing complex superstructures by self-assembly⁷. Research on magnetic nanomaterials is driven by their expected application in high-density magnetic recording or magnetic sensors⁴. Although most of the work has been carried out using spherical or isotropic particles, anisotropic particles are now being studied because of their optical and electrical application⁷.

Pioneered by Martin and Moskovits⁷, the general principle involves the electrochemical deposition of a metal on a porous membrane. Although a variety of membranes exist, 'Track-etch' polymeric membranes and the porous alumina membranes are most frequently used. The main difference between the two membranes is that unlike the track-etched membranes, alumina membranes have an isolating non-connecting structure because of the absence pore tilt with respect to the surface normal⁹. Electrochemical deposition of the metal within the pores involves first coating the membrane with a metal film through sputtering or thermal evaporation. The sputtered metal serves as the cathode electrode. The diameter of the wire is controlled by the pore size of the membrane while the length of the rod is controlled by the deposition time. A summary of the Nanorod synthesis is depicted in **Figure 3**.

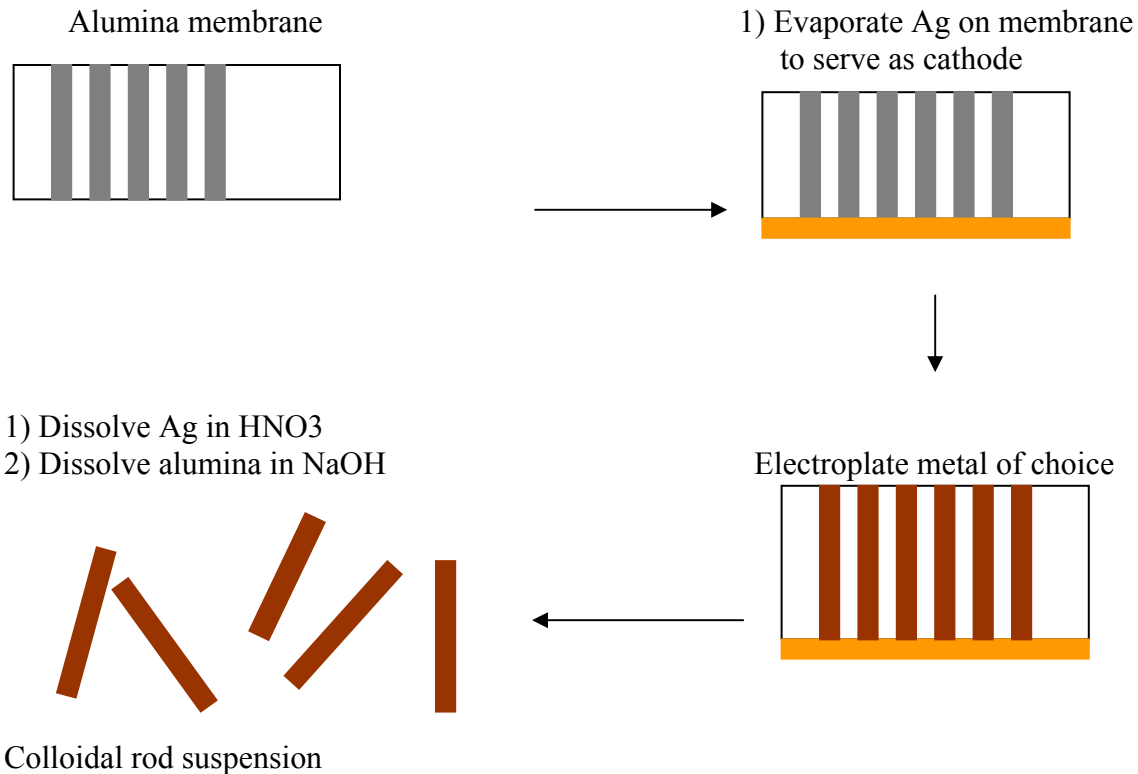


Figure 3

Schematic illustration of the Electrochemical synthesis of nanorods
Benjamin R. Martin et al *Advance Materials*, 11, No. 12

The rods we used were supplied by Chris Love of the Whitesides Group and were made based on the technique above. These Nickel rods were 80nm in diameter and 2-3 microns long.

2.3 Incorporation of Nanorods

The nanorods are incorporated into the colloidosome by adding a small quantity of rod sample taken from the bottom of the vial to the mixture of the oil and bead solution before shearing. Initially the rod solution was vortexed before being added but this produced low incorporation success rate. Consequently, the rod solution was allowed to sediment and rods were picked from the bottom of the vial to increase rod concentration. During shearing the rods also move to the interface of the emulsion and become randomly distributed on the colloidosome structures. Sintering also helps to lock the rods in place as some of them get trapped in the crevices as the beads melt.

2.4 *Magnetic Tweezers*

The tweezers were made by taping a steel nail to a magnet thus creating a magnetic field gradient. The micromanipulator setup on the inverting microscope was then used to navigate the tweezers in the colloidosome sample.

3. Experiment

3.1 *Setup*

The setup for the experiment is shown in the figure below:

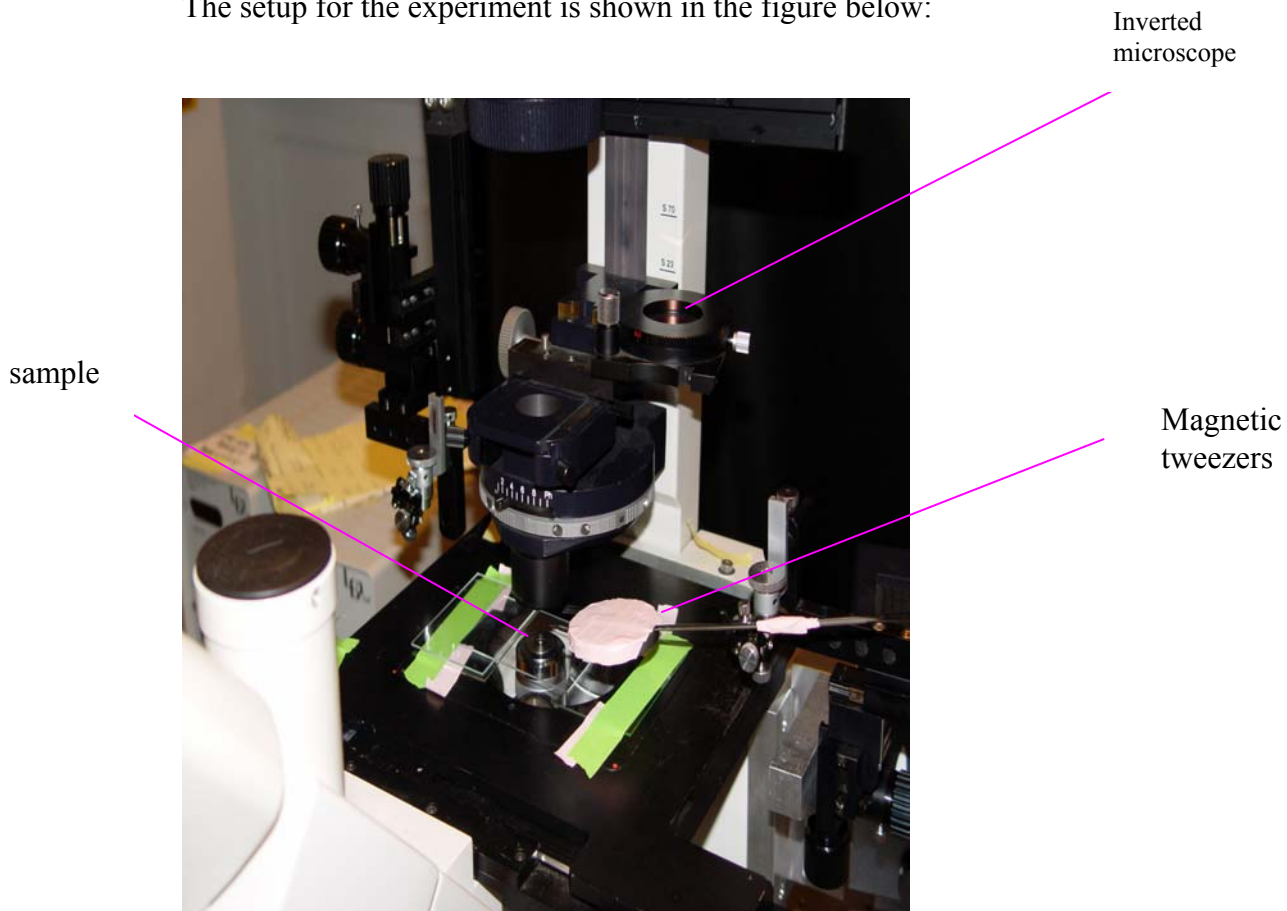


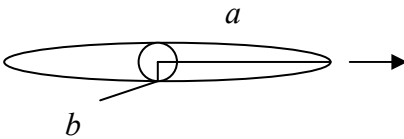
Figure 4: experimental setup showing inverting microscope, magnetic tweezers

The sample is placed on the microscope stage and the 10X objective is used to scan the sample for colloidosome. Then, the 63X objective is used to determine if the colloidosome has rods in the shell. Before this stage we ensure that the tweezers is centralized on the imaging screen. The microcantilever is used to move the tweezers' tip as close as possible to the colloidosome as close as possible without actually puncturing the shell.

3.2 Calibration of force on the rods

The next step was to calibrate the force on the rods. This was done by calculating the Stokes' drag on the rods in glycerol with the magnetic tweezers at the same position it was when we had the colloidosome sample. The rods were also imaged using the 10X objective. A movie is taken of the rods in glycerol being pulled to the tweezers tip. An average of 50 frames was taken at a frame rate of 200ms. Then we determined the velocity of the rods in glycerol. This was done using particle tracking in which the coordinates of the position of the rods are noted at each time interval. The distance moved by the particle during each frame is calculated using Pythagorean rule. Since this distance is in pixels it has to be multiplied by the average pixel length which we determined to be 42.6microns for the camera we used. The value obtained divided by the interval of travel gives the velocity of the rods.

We obtained the Stokes' drag using the equation below :

$$F = \frac{4\pi\eta aV}{\ln \frac{2a}{b} - \frac{1}{2}}$$


Where: a = radius of the rod, b = half the length of the rods, η = viscosity of glycerol, V = velocity of rods in glycerol, F = force on the rod

Note: For simplicity, we approximated the rods as an ellipsoid.

4. Results

The graph in Figure 5 was obtained from the results of the particle tracking. We were able to determine the maximum force on the rods using our magnetic tweezers.

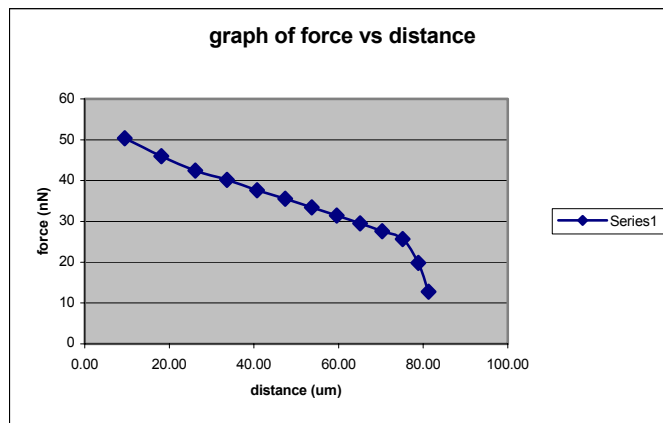


Figure 5: Graph illustrating the relationship between the force on the rods and the distance from the tweezers tip.

No noticeable deformation was observed on the colloidosome shell. However, it was observed that when the tip of the tweezers was close enough to some colloidosomes, they stuck to the tip. The maximum force on the rods using our tweezers was about 50nN. We believe this information will be useful in controlled diffusive release of colloidosomes contents in which case the magnetic field will be used as a steering mechanism to maneuver the colloidosome to its site of action where the encapsulated materials will be allowed to diffuse over a time period.

5. Conclusions

We concluded that the field generated by the magnetic tweezers is not large enough to pull the rods off the 5 minute sintered colloidosome. We determined that the minimum force required to pull the rods off five-minute sintered colloidosomes is about 50nN. Also we determined that the tweezers could be used as a steering mechanism to explore other alternative release methods. Finally we decided that an electromagnet should be made to torque the rods instead of pulling them from them colloidosomes' shell. We hope that the twisting motion of the rods will dislodge the beads and break the colloidosomes.

6. Future work

6.1 Electromagnet

We are in the process of making the electromagnet that we hope will generate a larger magnetic field, thus provide a torque the rods. The design consists of two pairs of solenoids on a microscope stage, one oriented parallel to the sample and the other orthogonal to the sample depicted in Figure 5. The pair of solenoids orthogonal to the sample magnetizes the rods when a current passes through the coil while the other pair exerts a torque on the rods as they try to align with the magnetic field. We hope that the twisting motions of the rods will cause them to detach from the colloidosome shell, thus breaking the colloidosome.

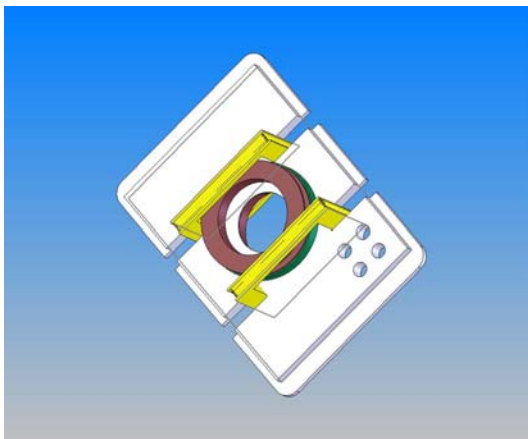


Figure 5: Electromagnet design to torque nickel nanorods

7.2 *Variation of rod properties*

We also plan to incorporate the colloidosome with composite rods that are made up of alternate layers of metals. These rods will have the properties of both metals and ultimately we can manipulate the colloidosomes using external forces as well as chemically. For example, a nanorod made of up alternate layers of Nickel and gold will have the magnetic properties of Nickel but the gold part can be functionalized to direct the colloidosome based on the affinity of the attached functional group for the molecules in the site of release.

7.3 *Pumping: an alternative method of controlled release?*

Finally, we hope to use our tweezers set up on a different type of shell that is more elastic and is stabilized chemically using poly-l-lysine. Nanorods will also be incorporated into these shells and magnetic tweezers will also be used to manipulate them. In this setup however, the tweezers will be mounted on opposite ends of the colloidosome. By manipulating the rods with the tweezers, we hope to create a kind of pumping action, which we believe is a possible avenue for the discharge of encapsulated materials.

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