Engineering Carbon Nanotube Microdrops Using Microfluidic Devices

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Abstract:

Since the discovery of carbon nanotubes (CNTs) by Sumio Iijima in 1991 [1], they have been of great interest to the nanotechnology community. In this work, we explored microfluidic drop generators to fabricate CNT microdrops with a controlled geometry and fast throughput. On the one hand, CNT microdrops were assembled using CNTs water suspensions in oil. On the other hand, we explored the fabrication of CNT shells according to the Pickering emulsion principle. These CNT microdrops were first validated using shear mixing in vials and then transferred to microfluidic drop generators.

Introduction:

Graphene is a planar sheet of sp2-hybridized carbon atoms in a honeycomb structure; and CNTs are essentially graphene sheets rolled into cylindrical structures. There are two types of CNTs. First, single sheet of graphene rolled in to a cylinder is referred to as single-walled carbon nanotubes (SWNT), and multiple layers of graphene rolled are known as multi-walled carbon nanotubes (MWNT). The diameter of CNTs can range from less than 1 nm to more than 100 nm depending on the size and number of graphene shells; and the length of the nanotubes varies from tens of nanometers up to several centimeters, hereby truly bridging nanometer and macroscopic length scales [2].

CNTs attract interest in the nanotechnology community due to their unique characteristics. For instance, their mechanical properties include high tensile strength (~ 37 GPa), and Young's modulus (1 TPa). The electrical conductivity can be as high as 10^9 A/cm^2, and the measured room temperature thermal conductivity for an individual MWNT is around 3000 W/m•K, which is greater than that of natural diamond [3].

In this work, we looked into new shaping methods of these nanomaterials.

Experimental Procedure:

Materials. CNTs used in this work were MWNTs with the diameter of nine nanometers and length of approximately 0.5 to 3 μm. These were acquired from NanoCyl, product type NC7000. Carboxyl functionalized CNT were fabricated by hot nitric acid treatment while refluxing at 60°C. CNT-water suspensions were made by sonication and subsequent centrifugation of carboxylic CNTs as well as CNT-surfactant. Typically, suspensions of a few weight percent Span 80, SDBS, SDS, Tween, and F127, and ABIL were sonicated for a few hours at low energy, followed by a one hour centrifugation at 5000 g. Also for the continuous phase, various fluids were tested including water, mineral oils, and kerosene.

Droplet Formation by Shear Mixing. CNT suspension was inserted to a vial containing an oil phase and the vial was shaken to generate CNT microdrops. Calibrated microscopes, as well as scanning electron microscopy (SEM) was used to characterize the droplets.

Droplet Formation by Microfluidic Devices. Glass capillary microfluidic devices were fabricated as follows. First, two round capillaries were tapered by a micropipette puller. The capillary surfaces were treated with *n*-octadecyltrimethoxyl silane, making them hydrophobic, thereby preventing the water-based drops to collapse to the glass. Then as shown in Figure 1, the tapered capillaries are aligned co-axially and

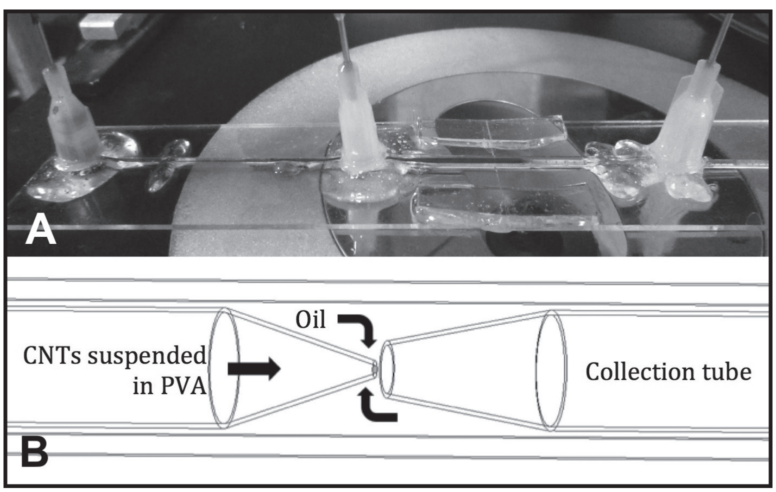

Figure 1: A) Microfluidic glass capillary device. B) Close up schematic diagram of the device.

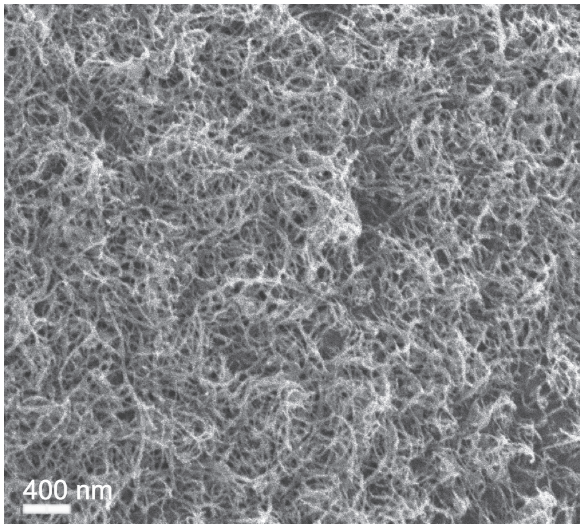

Figure 2: Close up SEM image of the CNT microdrop surface revealing the CNTs.

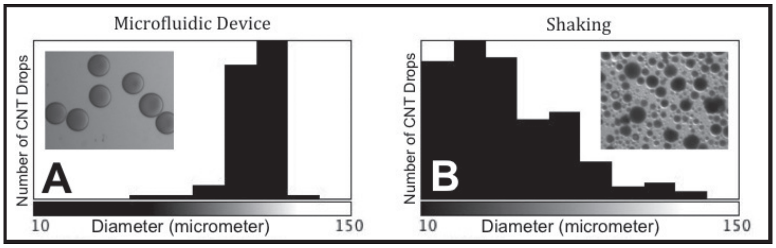

Figure 3: A) Microdrops generated by the microfluidic device and diameter distribution. B) Microdrops generated by shaking a vial and diameter distribution.

inserted into a square capillary. Epoxy was used to glue them together.

Next, plastic syringes containing CNT suspension and the continuous oil phase were connected to syringe pumps. The pump flowed liquids to the microfluidic device at a constant flow rate and therefore, the device made monodispersed CNT microdrops. The device was also connected to a hydrophobic collection vial for further research. SEM was used to take images.

Pickering Emulsions. CNT shells were fabricated based on the Pickering emulsion principle. This principle relies on particles that sit astride the oil-water interface, to reduce the total surface energy. The particle refers to a solid object or a small liquid droplet with a size ranging anywhere from two nanometers to a few millimeters. In this work, we formed hollow particles using carboxyl functionalized CNTs adsorbed in a water-cyclohexane interface. This process was in accordance with prior work found in literature. Chen, et al., prepared CNT microcapsules by using plasma treated CNTs and cyclohexane [4].

Results and Conclusions:

As shown in Figure 3, stable CNT microdrops were generated using both the shaking and the microfluidic device. Using image analysis, the diameter of the drops was determined. The diameter distribution of solid CNT microdrops from the microfluidic device was concentrated around 100 μm. However, the diameter distribution from the shaking method ranged from 10 μm to 120 μm. Also, changing the flow rates, the diameter of the drops made by the microfluidic device can be controlled.

Future Work:

Coalescence was a problem throughout the project. Especially the fact that the Pickering emulsion CNT microdrops coalesced inside the plastic tubing while traveling to the collection vial. Also, the other CNT microdrops coalesced, particularly when their diameter exceeded 100 μm. Some approaches to the problem this summer were the following; to provide more time for stabilization, longer plastic tubing was used in the microfluidic device, and also, the tubing was sonicated for Pickering emulsions, in accordance to a procedure found in literature. Further work is needed in order to stabilize these drops.

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