Macro-scale Bubbles for Aligning Carbon Nanotubes

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Single-wall carbon nanotubes (SWCNTs) exhibit high aspect ratios that can lead to extreme anisotropic mechanical and electrical properties if macroscopically aligned SWCNT ensembles can be made. Here, we used simple macro-scale bubble structures to align SWCNTs in larger quantities and in less time compared to pre-existing methods. We mixed SWCNTs, surfactant, and water to make the macro-scale bubbles that were composed of three layers with a total thickness of around 1 μm. The inner and outer surfaces of these bubbles were made up of surfactant and the middle layer was composed of SWCNTs and water. After using a pipette to create a 5 to 25 mm diameter bubble, pressing a glass substrate against a living bubble garnered a flat sample for testing. We demonstrated the bubble's aligning qualities from this two-dimensional imprint via polarized Raman microscopy. Since SWCNT's Raman G-bands intensities are dependent on the polarization of light, the alignment direction and intensity were determined by using a half-wave plate and light polarizer. Our results show that SWCNTs can be aligned in bubbles oriented towards the peak apex of the bubble structure. We also have evidence that SWCNTs are aligned tangent to the curvature of the bubble near the boundary. Possible reasons for these behaviors include water molecule runoff down the side of the bubble and surface tension forces pulling the SWCNTs into thin spaces where they are forced to align. Our method is promising for a wide range of applications that include nanoelectronics, sensors, and photonic devices.

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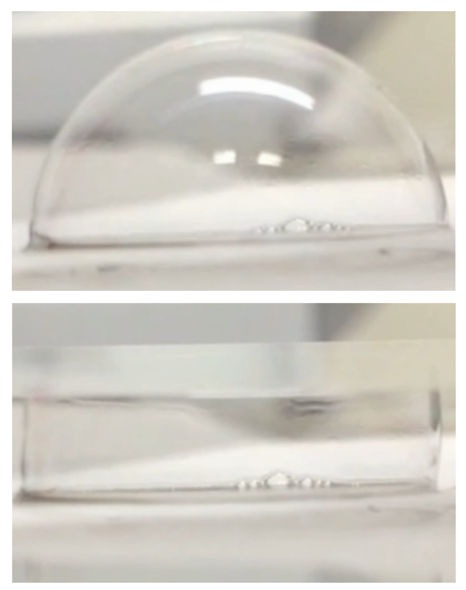
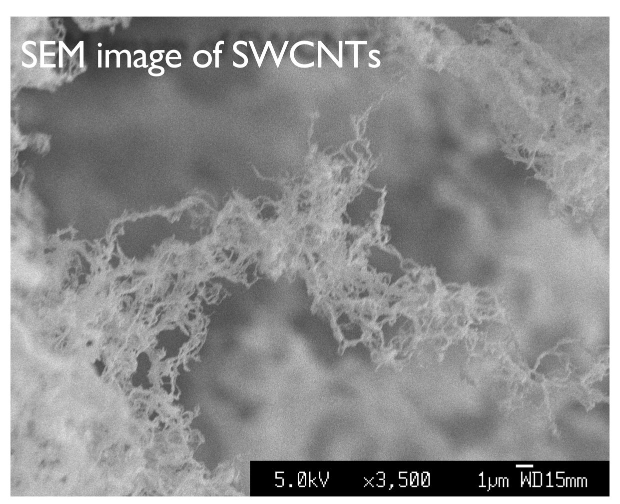
Bubble for Carbon Nanotube Alignment

Photo of SWCNT bubble



Since bubbles are macroscopic in nature, being able to manipulate micro-scale materials with them would serve as a convenient and cost effective method for interacting between macro-scale objects and nanoscale dependent qualities. Bubbles, having a wall thickness between 400 nm and 1300 nm and a diameter between 5mm-25mm, could prove to be a useful tool for future research.

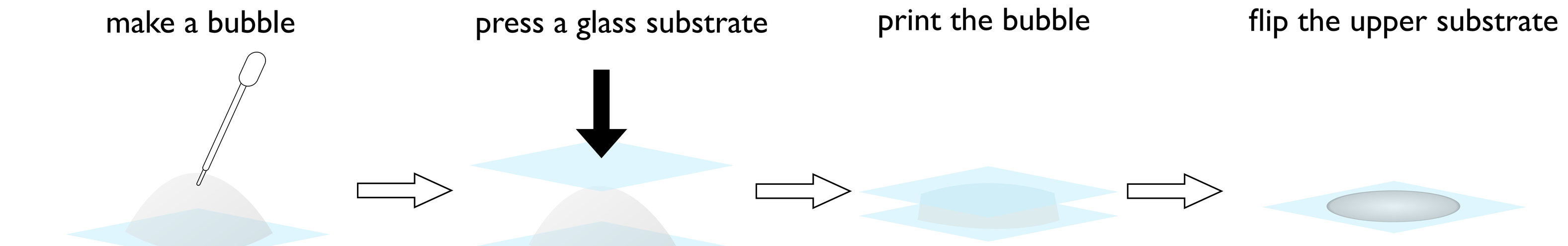


Single wall carbon nanotubes (SWCNTs) possess extreme aspect ratios (about 1nm diameter and 1μm in length) that lead to highly anisotropic properties that make alignment crucial for harnessing certain unique characteristics. Here, we investigated how simple, macro-scale bubbles align SWCNTs.

Bubble to Substrate Printing Process

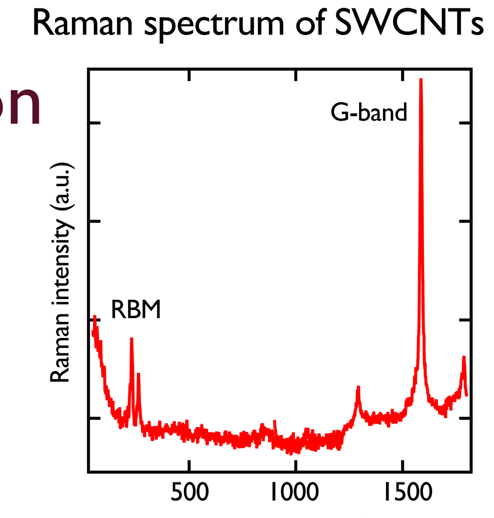
1 wt% of SWCNTs provided by Rice University was loaded into water with SDBS surfactant and then the solution was sonicated for 1 hr. Then bundled SWCNTs were removed by centrifugation (173,600 g, 10 min).

A glass substrate is pressed against the bubble before it pops in order to catch a permanent picture of the CNTs. This substrate is then used for analysis using Raman microscopy.



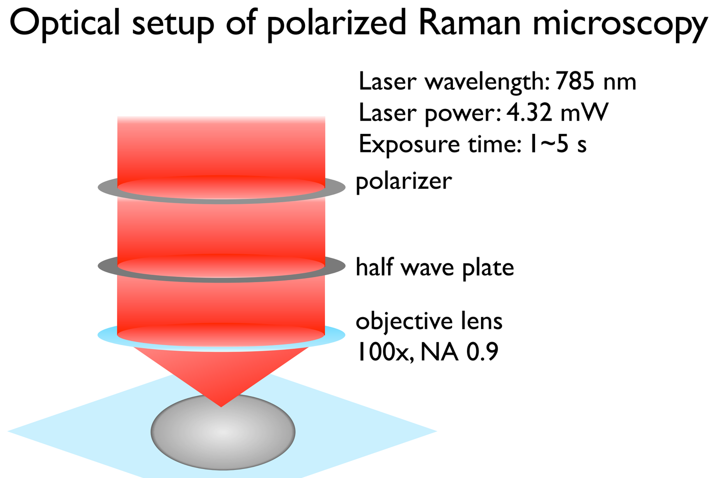
Light Polarization Dependence is Used to Determine CNT Orientation

Raman spectrum of SWCNTs



CNTs that are parallel to the polarization of light exhibit greater G-band intensities than perpendicular CNTs.
By manipulating light polarization angles and measuring the G-band heights, we were able to determine the alignment orientation of CNTs.

Optical setup of polarized Raman microscopy



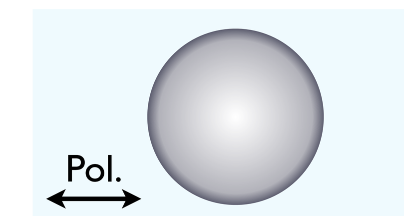
Light becomes polarized horizontally at the polarizer. The half-wave plate manipulates the angle from 0 -180 degrees. Raman scattering takes place and sends light back up through the lens and wave plates to be measured.

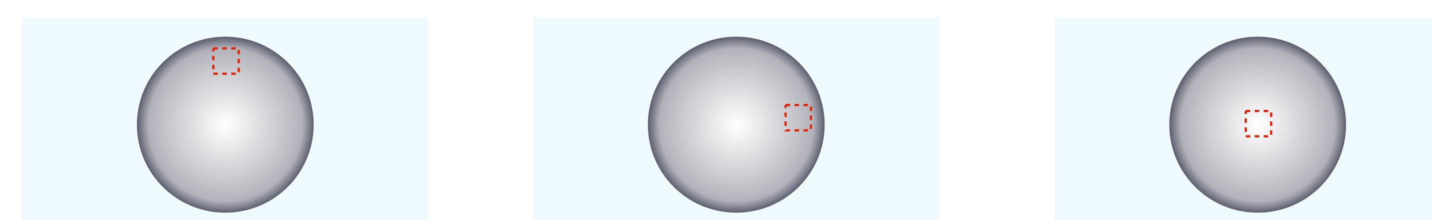
G-band Dependence Upon Light Polarization Angle Shows CNT Alignment in Bubble Structures

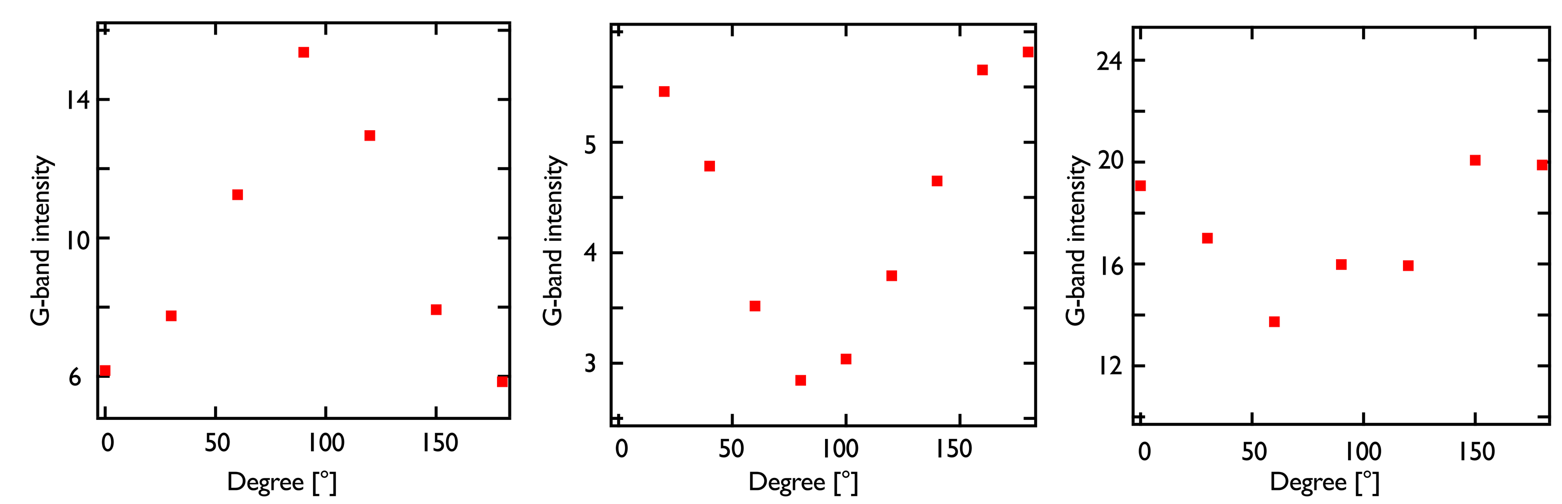
Peaks at 90 degrees represent vertical alignment at the selected scanning area. 0 and 180 represent horizontal alignment at this locations.

Near the top boundary, CNTs are aligned vertically, pointed radially towards the center of the circle. At the left boundary, CNTs are pointed horizontally, also radially aligned. At the center, CNTs are randomly aligned.

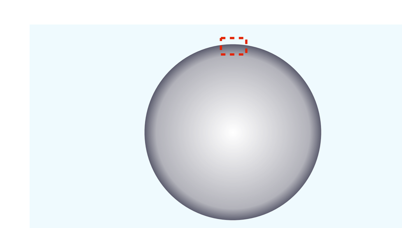
Top view of coffee ring



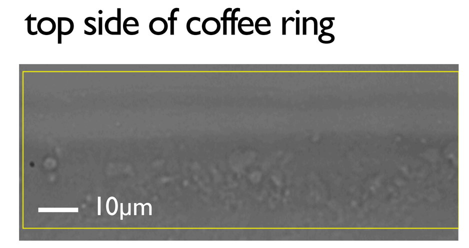




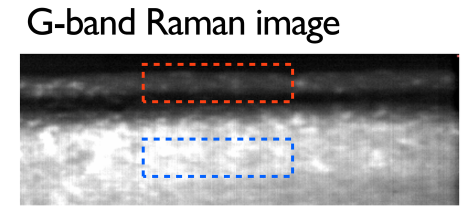
Azimuthal alignment is seen on the coffee ring boundary of the bubble. The Raman intensity reached its peak around 0 degrees, showing that the CNTs were aligned horizontally along the boundary. In the thinner outer edge of the coffee ring, a 9:1 peak intensity height to minimum intensity height is exhibited.

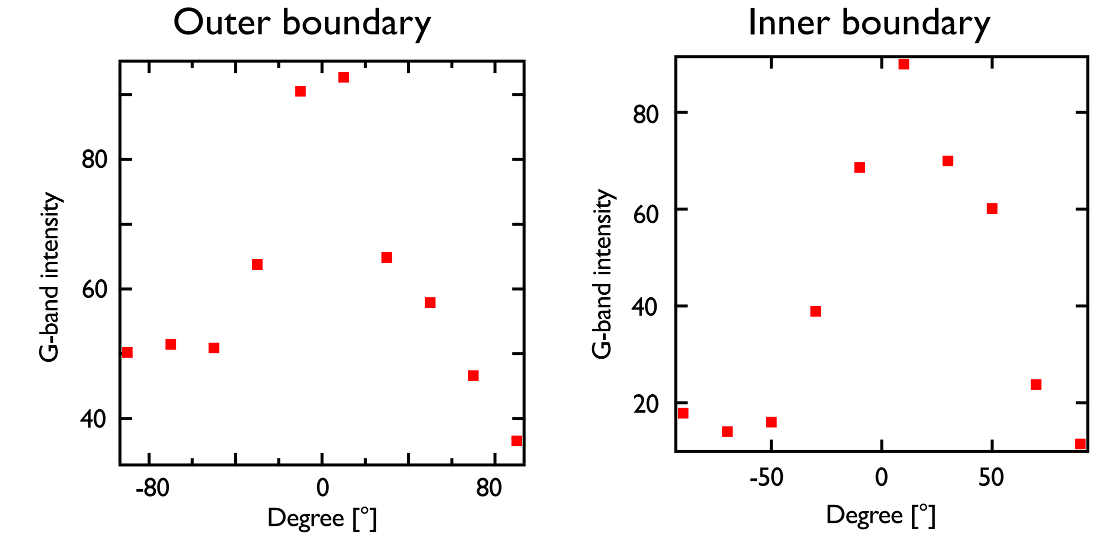


Bright field image of top side of coffee ring



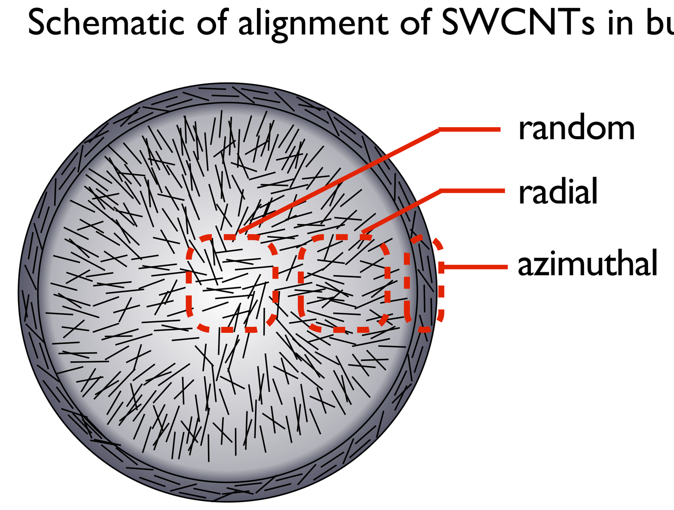
G-band Raman image





CNT alignment in the coffee ring

Schematic of alignment of SWCNTs in bubble



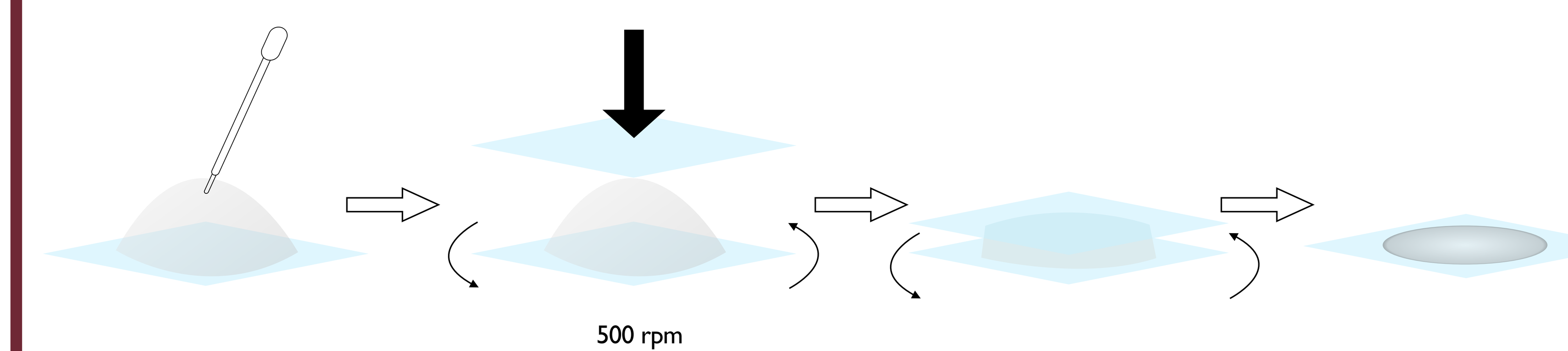
Center: random CNT orientation

Side walls: radial alignment

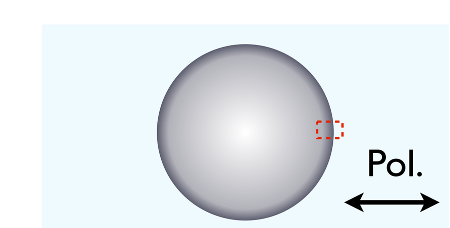
Coffee ring boundary: azimuthal

Spinning Bubble During Substrate Transfer Offers Radially Aligned CNTs along the boundary

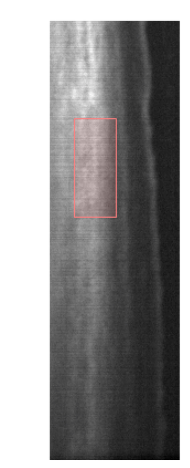
While the bubble is being spun at 500 rpm, the glass substrate is pressed down as far as possible onto the spinning bubble. This substrate is held until the bubble pops and is then used for testing under Raman microscopy.



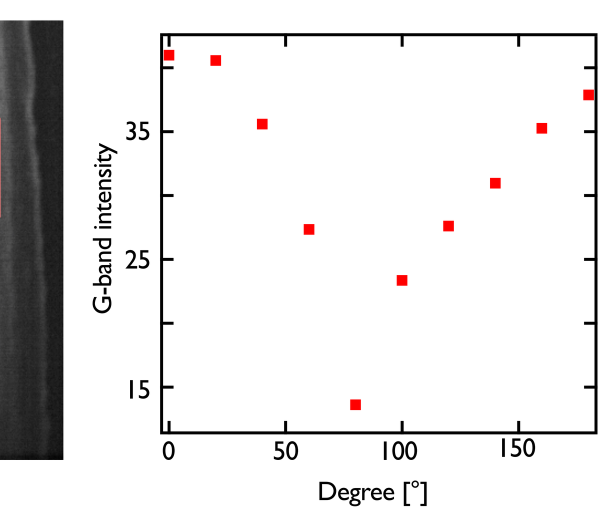
CNTs in the boundary are aligned radially in spun bubbles. This is shown by the peak at 0 degrees when the polarization of light is horizontal. This is opposite to usual CNT behavior that takes place in the coffee ring.



G-band Raman image



Right Boundary



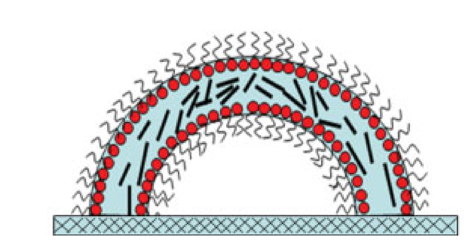
Mechanisms for Alignment

Water molecule runoff contacting CNTs

Surface tension pulling CNTs into a thin area

The popping dynamics

Centripetal forces



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Conclusion

Macro-scale bubbles cause SWCNTs to align naturally in the membrane of the bubble and azimuthally along the boundary. When bubbles are spun, they exhibit radially aligned CNTs in the coffee ring of the substrate.

Acknowledgments

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- KIP students for introducing NanoJapan students into Japan
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