

Encapsulation of Single-Walled Carbon Nanotubes in Microgels

In the past, the cytotoxicity (toxicity to cells) of carbon nanotubes (CNTs), hollow cylinders of carbon atoms that are 1/10,000th the width of a human hair, has rendered impossible proposed biological applications for CNTs—such as biosensors, targeted cancer treatment, drug delivery into individual cells, extendable appendages for nanobots in the bloodstream, and regrowth of broken or severed nerve endings.¹⁻² Encapsulation of CNTs in a biologically compatible material would render CNTs harmless, surmount a long-standing barrier to applications within the human body, and suggest that all these ideas may soon become possibilities. Since Fall 2005, I have sought an answer to this problem by conducting research in the laboratory of Dr. Zhibing Hu, Department of Physics, University of North Texas. Hydrogels (macromolecular networks that can retain a high percentage of water within their structure), and especially the special class of hydrogels called "smart hydrogels"—which can respond to environmental stimuli such as temperature, pH, light, pressure, presence/absence of water, electricity, and even magnetic field—have been used for years in the human body, where their biological compatibility makes them ideal biosensors and agents for targeted drug release.³⁻⁵ Our research team has developed a method of encapsulating single-walled carbon nanotubes in microgels, roughly spherical hydrogels several hundred nanometers across. I am contributing to the research effort by synthesizing the encapsulated CNTs, testing the properties of the encapsulated CNTs, and modifying the procedure based on my past research experience working with CNTs. Our research creates a novel hybrid material from hydrogels and CNTs, two materials with a host of unique properties and applications. Most importantly, the method presented in our research is a significant step towards safe introduction of CNTs into the human body and towards making such applications as nanobots and selective cancer cell destruction reality.

I used the "smart hydrogel" poly(N-isopropylacrylamide) (PNIPAAm) to form microgels. Normally, PNIPAAm microgels are composed of PNIPAAm polymer strands, which are linked together like the two sides of a ladder by a crosslinking agent, N,N'-Methylene-bis-acrylamide (BIS) that becomes embedded inside the microgel during formation. BIS terminates at both ends in vinyl groups; this end structure is what allows BIS to perform its specialized function. Hence, we replaced the crosslinking agent BIS with CNTs functionalized with vinyl groups on the ends. Since BIS and the functionalized CNTs had matching end structure, the CNTs reacted in a similar fashion with the PNIPAAm polymer strands, resulting in encapsulation of the nanotubes within the microgel.

I treated single-walled CNTs with sulfuric acid and nitric acid, sonicated the mixture for 30 minutes, and heated it for 24 hours at 80°C. During this time, H₂SO₄ and HNO₃, both oxidizing acids, cut cleanly through the walls of the CNTs. This process both shortened the CNTs and removed the fullerene endcaps, converting the original CNTs into short, open-ended segments functionalized with carboxylic acid groups.⁶ I dialyzed the mixture in deionized water to remove any remaining acids. In a flask, I vacuum-dried the mixture, sublimating and removing the liquid contents to leave only the functionalized CNTs. I added N-(3-Aminopropyl)methacrylamide hydrochloride (NMH), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), and deionized water to the CNTs. On each CNT, EDC reacted with the carboxylic acid group and formed an active intermediate. NMH was attracted by the partial positive charge on the carbon atom in the carboxylic acid group and bonded with the CNT. The carbon atom, now unstable with 5 bonds, released EDC. After removing unreacted EDC and NMH, the resultant CNTs terminated at the ends in NMH molecules, which in turn terminated in vinyl groups. Hence, this process converted CNTs functionalized with carboxylic acid groups into CNTs functionalized with vinyl groups. I carried out the reaction for formation of PNIPAAm microgels, substituting CNTs for BIS as a crosslinking agent. After purification in an ultra-high-speed centrifuge, the resultant microgels were composed of NIPA monomer and functionalized CNTs.

The procedure yielded yellow-green, opalescent microgels composed of NIPA monomer and CNTs (Fig. 1). For PNIPAAm microgels to form, a crosslinking agent must be present to link the PNIPAAm polymer strands together. Normally, BIS is utilized as a crosslinking agent, but in this procedure no BIS was added and no other reactants had the necessary chemical end structures to function as crosslinking

agents. Hence, the very fact that microgels successfully formed is proof that the CNTs functioned as crosslinking agents and must have been successfully functionalized with vinyl groups and encapsulated as intended.

Using a laser light scattering (LLS) machine, I measured the change in radius of the microgels containing CNTs against change in temperature (Fig. 2). The data taken verified that even with the substitution of CNTs for BIS, the smart hydrogels had retained their most valuable and useful property: their capacity to respond to their environment. This feature is what gives smart hydrogels the ability to be used as drug delivery systems and biosensors in the human body and the potential to be used in many more biomedical and biotechnological applications, which is what makes them such ideal agents for the introduction of CNTs into the human body.

Finally, future investigations may include encapsulation of materials other than CNTs in microgels. The ability of microgels to serve as safe transportation as they have for years in drug delivery suggests that they have potential in encapsulation of many other materials that would find application in the human body. The encapsulation of CNTs, for which cytotoxicity has been a seemingly insurmountable obstacle, is a promising indication of the bridge into biological applications that microgels can provide to a host of other materials.



Figure 1. Microgels composed of NIPA monomer and functionalized CNTs. CNTs are encapsulated within the microgels.

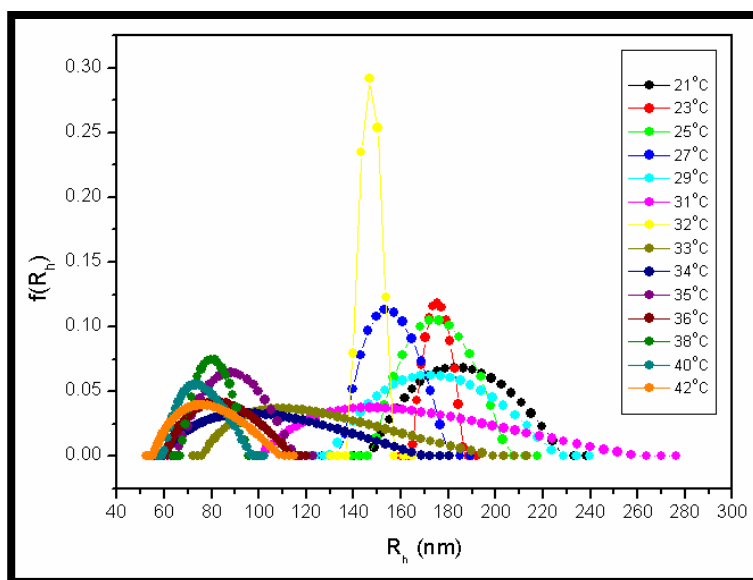


Figure 2. Though the size distribution of the microgels (height and width of each curve) varies, notice that as temperature increases, average microgel radius decreases (the curves shift to the left).

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