Zhan-Ting Li of Shanghai Institute of Organic Chemistry and Fudan University, China, and his collaborators used a combination of self-assembling tripods and macrocycle rings to form a porous framework with honeycomb periodicity, similar to that of a MOF, but which remains rigid in solution. Equipping the tripods with bulky hydrophilic groups that resist stacking preserved the solubility and single-layer 2D architecture of the framework.

"That our framework is held together by reversible, noncovalent supramolecular interactions ensures good solubility in water," Li said. "The precise dimensional control of our solution-based processing facilitates the structural and chemical customization of our frameworks."

The tripods of these SOFs were made from aromatic bipyridine molecules whose trio of struts or arms was interlocked with the struts of their neighboring molecules through the macrocycles, which were made from cucurbituril molecules. The molecules used in this study were proof-of-principle starters. Other molecules for the struts could be employed in the future for the design of similar or more complex architectures.

Liu and his collaborators at the Molecular Foundry and in Shanghai are now working to create soluble SOFs in three dimensions.

Lynn Yarris

Nano Focus

Iron catalyst reservoir doubles CNT growth on alumina

The most common way to synthesize tall carpets of vertically aligned carbon nanotubes (CNTs) is to heat samples with thin films of iron (catalyst) on top of alumina (underlayer) in the presence of hydrocarbon gases at temperatures between 700°C and 800°C. Now researchers at Bar Ilan University (BIU) in Israel have shown how a thin film of iron positioned *below* the alumina underlayer can substantially affect the growth of CNTs. The results may also help solve the long-standing puzzle: what makes CNTs grow?

"The idea came after attending a presentation at a Materials Research Society Fall Meeting 2011, when Dr. Benji Maruyama explained how iron catalyst diffusion into the alumina underlayer was a factor in CNT growth termination. I thought that if the disappearance of iron on the top surface through porosity in the alumina is the cause for CNT termination, then we can replenish its supply from the bottom by using a reservoir of iron. We indeed doubled the growth but the underlying mechanism was very different from what we expected," said Gilbert Daniel Nessim, principal investigator of this research, which was published in the February 7 issue of *Nanoscale* (DOI: 10.1039/C3NR05240K; p. 1545).

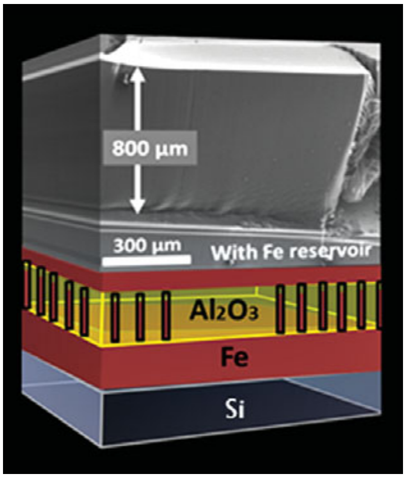
The researchers on Nessim's team used the standard iron/alumina system as a benchmark. From the very first experiment, the new iron/alumina/iron reservoir system led to taller CNTs, with heights up to two times that of the iron/alumina system.

"From the start, the good results showed that we were onto something, but we started questioning the mechanism at play when we noticed that even very short growth experiments—30 seconds—led to taller CNTs on the sample with the iron reservoir," said Efrat Shawat, a PhD candidate in the Nessim laboratory and lead author of their article. "It is only after extensive annealing experiments to observe the catalyst surface dewetting that we understood that the iron reservoir affected the morphology of the top surface," she said.

Annealing experiments performed using samples with increasing thicknesses of the alumina layer gave the research team the clue to understanding this mechanism. As thicker alumina layers did not show the height enhancement factor, it appeared that pinholes in the alumina underlayer were key to understanding the mechanism at play.

"Only a few years back, observation of morphological size evolution of catalyst nanoparticles during CNT growth provided a significant hurdle to the realization of growing infinitely long, continuous CNTs," said Cary Pint, an assistant professor of mechanical engineering at Vanderbilt University who, along with graduate student Landon Oakes, collaborated with the Bar Ilan researchers on this study. "Our work demonstrates that materials once neglected in playing any role in this process could be the key to overcome this hurdle."

Shawat said that with the understanding of this new mechanism, the research team now wants to study the effects of different reservoir materials on CNT growth. "For instance, we used a different non-catalytic metal and obtained interesting carpets with uniformly dispersed pores that we plan to use for battery electrode applications," she said.



Schematic illustrating the migration of iron from the thin-film catalytic reservoir (iron) to the top surface of alumina through pinholes in the alumina layer. The resulting carbon nanotube carpets obtained are up to two times taller compared to the samples without the reservoir.

"By achieving taller CNT carpets, the throughput of the manufacturing process increases, and CNTs are more useful in applications that require longer CNTs and taller carpets," said John Hart, associate professor at the Massachusetts Institute of Technology who was not involved in this research. "I look forward to potential future work integrating this method into applications," he said.

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