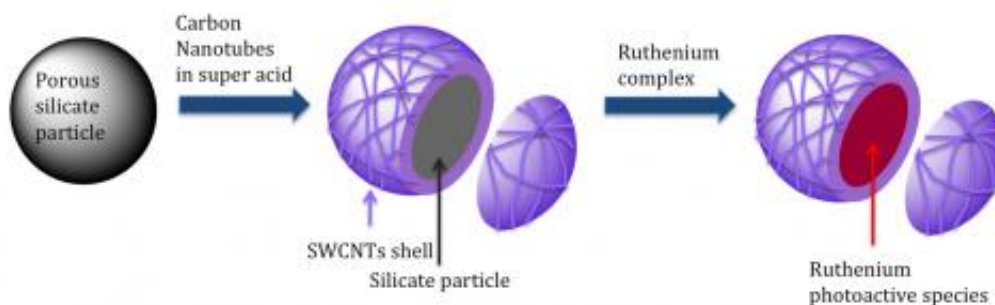


Supramolecules get time to shine

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Rice University researchers have found a way to bind carbon nanotubes to a porous silicate particles to create supramolecules. The new material allows researchers to test interactions between nanotubes and photoluminescent materials. (Credit: Martí Lab/Rice University)

(PhysOrg.com) -- What looks like a spongy ball wrapped in strands of yarn -- but a lot smaller -- could be key to unlocking better methods for catalysis, artificial photosynthesis or splitting water into hydrogen, according to Rice University chemists who have created a platform to analyze interactions between carbon nanotubes and a wide range of photoluminescent materials.

The [microscopic particles](#) assembled in the lab of Angel Martí, an assistant professor of chemistry and bioengineering, combine single-walled carbon nanotubes with porous silicate materials that can absorb various molecules -- in this case, a ruthenium complex.

Martí, graduate student and lead author Avishek Saha and their colleagues reported their results today in the Royal Society of Chemistry journal *Chemical Science*.

The ability to immobilize individual carbon nanotubes on a solid surface is interesting enough, but combining supramolecular systems with nanomaterials to produce hybrids is unique, they said.

"This can be used as a general platform to study the interaction of not only ruthenium complexes, but most photoactive molecules can be encapsulated within these porous silicates in a very simple way without chemical modification, without anything," Marti said.

Saha endured trial and error at every step in bringing the new particles to fruition, first figuring out the best way to keep long, single-walled carbon nanotubes produced by the Rice-born HiPco process from aggregating into bundles while allowing them to adhere to the particles.

The solution suggested by co-author Matteo Pasquali, a Rice professor in chemical and biomolecular engineering and in chemistry, involved dissolving the bundles in chlorosulfonic acid, which added protons -- and thus a positive charge -- to each nanotube.

That was the key to making nanotubes attractive to the three types of silicate particles tested: a commercial version of MCM-41, a mesoporous material used as a molecular sieve; another version of MCM-41 synthesized at Rice by Saha, and microporous Zeolyte-Y.

"We don't fully understand the mechanism, but the truth is they have a very strong affinity to silicon oxide networks," said Marti, describing the nanotube-wrapped particles. "Once they're protonated, they just bind."

But that wasn't enough to create a proper platform because protonated

nanoparticles are no longer photoluminescent, a quality the researchers required to "see" such tiny structures under a spectroscope. "Protonated nanotubes are cool, but we want to have pristine nanotubes," Martí said.

"We were stuck there for a while. We tried a lot of things," he said. Acetone, ammonia, chloroform and other substances would deprotonate the nanotubes, but would also release them from the silicate sponges and allow them to clump. But vinylpyrrolidone (VP) did the trick by giving the nanotubes a polymer-like coating while returning them to their pristine states.

"This becomes interesting not only from the standpoint of getting individualized nanotubes on top of a surface, but also because we got fluorescence of nanotubes not from a solution, but from a solid material," Martí said.

The experiment went one critical step further when the researchers introduced ruthenium molecules to the mix. The silicates absorbed the ruthenium molecules, putting them into close proximity with an array of nanotubes. Under a spectroscope, the ruthenium complexes would photoluminesce, but they saw something unexpected in the interaction.

"Basically, we found out that if you put a photoactive species (ruthenium) there and excite it with light, two different processes happen. If it has carbon nanotubes close by, it will transfer an electron to the nanotubes. There's a charge transfer, and we knew that would happen," Martí said. "What we didn't expect when we analyzed the spectrum was seeing two different species of ruthenium complexes, one with a very short photoluminescence lifetime and one very long."

The researchers theorized that ruthenium in the center of the sponge was too far from the nanotubes to transfer electrons, so it retained its standard luminescence.

The research leads to some interesting possibilities for materials science, Saha said. "MCM itself has many applications (as a mesoporous sieve in fuel refineries, for instance), and carbon nanotubes are wonderful materials that many people are interested in. We're just combining these two into a hybrid material that might have the virtues of both."

While pore sizes in zeolites are locked by their crystalline structure at 0.7 nanometers, pores in MCM can be customized, as Saha has done, to absorb specific materials. "There are many things we can do to tune the system that we haven't explored," he said; combining metal molecules or even quantum dots with MCM and nanotubes might lead to interesting results.

Martí said putting charged nanotubes on the surface of a solid also opens the door to use them as catalysts in solar-energy conversion. "You need that driving force, that charge separation, for [artificial photosynthesis](#)," he said.

More information: Single-walled carbon nanotubes shell decorating porous silicate materials: A general platform for studying the interaction of carbon nanotubes with photoactive molecules, Avishek Saha, Saunab Ghosh, Natnael Behabtu, Matteo Pasquali and Angel A. Martí, Chem. Sci., 2011, Advance Article, [DOI:10.1039/C1SC00323B](https://doi.org/10.1039/C1SC00323B)

Abstract

Single-walled carbon nanotubes (SWCNTs) have been deposited onto the external surface of porous silicate materials by deposition from a solution of individualized, protonated SWCNTs in chlorosulfonic acid. It is demonstrated that the deposited SWCNTs can be deprotonated on the silicate surface, yielding a microporous or mesoporous material with individual or small bundles of SWCNTs. These carbon nanotubes present all the spectral characteristics of pristine SWCNTs, including van Hove transitions, Raman and NIR photoluminescence. Furthermore,

it is shown that these materials can be used as scaffolds to study the interaction of SWCNTs with photoactive molecules loaded in the cavities of the porous silicate materials. As a proof-of-concept, we showed that the photoluminescence of tris(2,2'-bipyridine)ruthenium(II) can be quenched by protonated SWCNTs in the nearby surface decreasing its lifetime by nearly two orders of magnitude. This represents a novel application for these materials, especially considering the large amount of different molecules that can be immobilized in the internal cavities of these porous silicates.

Provided by Rice University

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