Quantitatively deposit silica onto nanotubes

Mandakini Kanungo, Hugh Isaacs, and Stanislaus Wong

An electrochemical, solution-phase process deposits a controlled thickness, non-covalent layer of silica dielectric on carbon nanotubes.

Using carbon nanotubes in applications ranging from molecular circuits to switches requires heterostructures that combine nanotubes with an insulator. Silica (SiO$_2$) has exceptional insulating properties that make heterostructures with carbon nanotubes particularly intriguing.

A thin SiO$_2$/ SiO$_x$ layer is transparent, and silica is well known for its biomolecular compatibility, so a thin silica coating on carbon nanotubes would enable applications in biomedical optics. A protective silica coating on carbon nanotubes would also help to avoid tube-tube contact, bundle formation, as well as tube oxidation, which pose barriers to the use of chemically functionalized carbon nanotubes as individualized gate dielectric materials in field-effect transistors (FETs).

Chemical functionalization$^{2-5}$ aims to rationally tailor single-walled carbon nanotubes (SWNTs) for use in functional devices and circuits. Coating SWNTs with insulating materials to fabricate nanotube-based devices such as FETs, single-electron transistors, and gas sensors$^{1,6,7}$ is a particularly promising but relatively unexplored way to achieve this functionalization.

Two general strategies have been pursued for coating SWNTs with silica. One involves covalent bonding of silica onto carbon nanotube sidewalls using a range of either silyl or silane derivatives.$^{8-12}$ Though covalent bonding is a robust, well-controlled process, it also seriously compromises or otherwise degrades the desirable electronic and optical properties of the carbon nanotubes.

An alternative strategy is to coat carbon nanotubes with silica using a noncovalent methodology. A recent theoretical study has shown that a non-bonded, protective layer of silica only weakly perturbs the electronic structure of SWNTs.$^{13}$ Therefore, a protective layer of silica on the carbon nanotubes should not only preserve their desirable electronic, mechanical, and optical properties, but also simultaneously and non-destructively functionalize these nanoscale species for a variety of applications.

Although several groups have successfully prepared silica coatings on carbon nanotubes, controlling the thickness of the deposited film remains challenging. Published experimental conditions for silica deposition tend to involve harshly acidic or basic conditions, long reaction times, and a multistep synthesis procedure with resulting byproducts. Ultimately, these techniques provide little or no control over the thickness of the silica coating. In fact, the only reported method for the quantitative tuning of silica thickness is varying the deposition time during pulsed laser deposition, but this technique requires sophisticated, expensive instrumentation and lacks the versatility and flexibility of solution-phase chemistry.

We developed methods to coat SWNTs with various reproducible thicknesses of silica by means of an electrochemical sol-gel process. We used two different experimental protocols. In one procedure, a SWNT mat was the working electrode for direct deposition of silica. In the second procedure, nanotubes were dispersed in solution and silica was deposited on these solubilized nanotubes in the presence of a platinum working electrode. Applying a negative potential resulted in the condensation of silica onto the carbon nanotube surface. The thickness of the silica coating was controlled by varying the potential of the working electrode as well as the concentration of the sol solution.

The electrochemical methodology has several advantages. First, the silica appears to be coated on the nanotubes in a noncovalent and therefore nondestructive fashion, as suggested by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), as
well as UV, visible, and near infrared spectroscopy. Second, the procedure is fairly mild and environmentally friendly requiring a minimum amount of reactants and reaction conditions that are neither harshly acidic nor basic. Third, the reaction time for electrodeposition is about 5 to 10 minutes, much shorter than the reaction times for other methods. Moreover, all of these experiments can be carried out at ambient conditions.

To the best of our knowledge, our study is the first report of the formation of a sol-gel coating of silica on SWNTs through electrodeposition. This is also the first controllable methodology aimed at fine tuning of the silica film thickness on carbon nanotube surfaces through a solution-phase methodology involving a rational and systematic variation of reaction parameters. We are currently working to optimize the quality of silica film deposition.

Author Information

Mandakini Kanungo and Hugh Isaacs
Brookhaven National Laboratory
Upton, NY

Stanislaus Wong
Stony Brook University
Stony Brook, NY
Brookhaven National Laboratory
Upton, NY

Stanislaus S. Wong earned a B.Sc. (First Class Honours) from McGill University in 1994 and subsequently completed his Ph.D. thesis from Harvard University in 1999 under the tutelage of Professor Charles M. Lieber. After finishing a postdoctoral fellowship at Columbia University with Professor Louis E. Brus, he initially held the position of Assistant Professor (2000-2006), and was subsequently promoted to Associate Professor (September 2006 – present) in Chemistry at the State University of New York at Stony Brook with a joint appointment at Brookhaven National Laboratory. He and his group have wide-ranging interests in nanoscience, including the rational chemical functionalization of carbon nanotubes, the synthesis and characterization of metal oxide nanostructures (such as titanates, ferrites, and zirconates), the development of synchrotron-based techniques for nanoscale characterization, and the use of probe microscopy to initiate localized chemistry. Professor Wong has earned a National Science Foundation CAREER award, commencing in 2004, as well as an Alfred P. Sloan Foundation Faculty Fellowship (2006-2008).

References