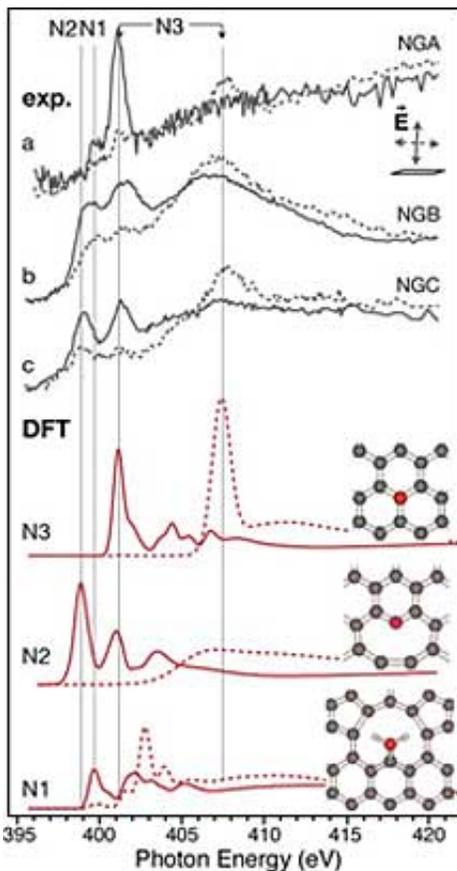


X-rays illuminate nitrogen's role in single-layer graphene

November 29 2012, by Laura Mgrdichian



Top: Experimental x-ray absorption spectroscopy data for three nitrogen-doped graphene (NG) samples (a,b,c). Bottom: Theoretical (computer-generated) data for three types of nitrogen-carbon bonds (N1, N2, N3). Red dots indicate nitrogen atoms.

(Phys.org)—Researchers using x-rays to study a single-atom-thick layer

of carbon, called graphene, have learned new information about its atomic bonding and electronic properties when the material is "doped" with nitrogen atoms. They show that synchrotron x-ray techniques can be excellent tools to study and better understand the behavior of doped graphene, which is being eyed for use as a promising contact material in electronic devices due to its many desirable traits, including a high conductivity and, most notably, tunable electronic properties.

Doping graphene with small amounts of another element, such as nitrogen or boron, turns it into either an "n-type" material (having excess negative [charge carriers](#), i.e. electrons) or a "p-type" material (having excess positive charge carriers, i.e. electron vacancies called "holes"). In this way, doping allows scientists to "tune" its properties, including the types of bonds between the atoms and how charge carriers are distributed. This kind of control is key when developing a material with specific applications in mind. A similar example is the doping of silicon used in silicon-based photovoltaics; indeed, doped graphene is being examined for its potential use as a contact material in [solar cells](#) (among its many suitable qualities for such a role is its transparency to visible light, a necessary feature for a solar-cell [electrical contact](#)).

In this work, the researchers discovered that several bond types may be present between carbon and [nitrogen atoms](#), even within the same [graphene sheet](#). This results in profoundly different effects on the charge carrier concentration across the sheet, which is not ideal.

"Our findings indicate that controlling the bond types in chemically doped graphene will be a crucial part of tailoring its properties for a particular application and advancing graphene-based electronics in general," said Theanne Schiros, the study's corresponding scientist, who is a researcher at the Energy Frontier Research Center at Columbia University. She is also the lead author on the corresponding published paper in *Nano Letters*.

The paper's co-authors include colleagues at Columbia University as well as the Stanford Synchrotron Radiation Lightsource (SSRL), CNR-Nanoscience Institute (Italy), Sejong University (Korea), the National Institute of Standards and Technology, Stockholm University (Sweden), and Brookhaven National Laboratory.

The group's x-ray data show that while it is possible to create n-type graphene – in which a single nitrogen atom substitutes for a single carbon atom, called a graphitic bond – up to three bond types may be observed in a single sheet depending on processing and growth conditions. These correspond to the three ways in which a nitrogen atom and a carbon atom can share electrons.

The effects of each type on the graphene's electronic structure are quite different. For example, nitrogen atoms that form a "graphitic" bond with carbon atoms, meaning the nitrogen and the carbon share two electrons, tend to increase the number of charge carriers in the material. "Pyridinic" and "nitrilic" bonds, on the other hand, tend to withdraw charge carriers from the carbon lattice.

At NSLS beamline U7A and SSRL beamlines 10-1 and 13-2, Schiros and her group employed three x-ray techniques to study their graphene samples: x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and x-ray emission spectroscopy (XES). Each works by taking advantage of one way in which x-rays can interact with a sample, therefore each provides unique information about that sample.

XPS measures the number and energies of the electrons that escape the surface of a sample when it is illuminated with [x-rays](#), and therefore provides information on the elemental concentration and binding energies, which reflect the local chemical bond environment. XAS provides direct information about the type of bond between the nitrogen and carbon atoms, the orientation of that bond, and the unoccupied

molecular orbitals formed between dopant and host atoms. XES provides complementary, atom-specific information about the occupied electron energy levels near the "Fermi level," which plays a key role in graphene's electronic behavior.

When combined with theoretical calculations, the three techniques yield a clear picture of the dopants' role in the graphene's electronic behavior.

This research is published in the June 29, 2012, online edition of *Nano Letters*.

More information: [www.bnl.gov/ps/eNews/files/pdf ...
ry3-SummarySlide.pdf](http://www.bnl.gov/ps/eNews/files/pdf...ry3-SummarySlide.pdf)

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