

First experimental confirmation of Dirac cones in borophene

Graphene has, in just a few short years, captured the fancy of materials scientists and physicists because of its unique properties and the potential for tailoring them to obtain desired behaviors. Graphene has linear (as opposed to the usual parabolic ones) electron bands near the Fermi energy known as Dirac cones. Branching out from graphene, researchers have looked for analogous behavior in monolayers of other elements. A joint Japanese-Chinese-United States collaboration headed by Iwao Matsuda of The University of Tokyo has now provided the first experimental confirmation of the existence of Dirac cones in monolayer boron (or borophene). Moreover, they discovered a way to split the cones and possibly enlarge the spectrum of possible properties. “Our work not only suggests borophene could be a platform for developing new quantum devices but also opens a door to atomic-scale engineering in lattices with large unit cells to produce materials with novel properties,” says Baojie Feng, the first author of the report in *Physical Review Letters* (doi:10.1103/PhysRevLett.118.096401).

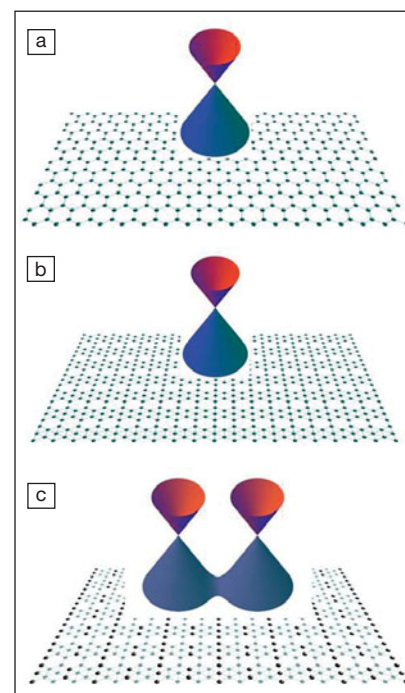
The Dirac cones in graphene are a consequence of the atomic structure of carbon and the resulting two-dimensional (2D) hexagonal or honeycomb lattice with two atoms per unit cell. The cones are primarily π and π^* bands derived from p_z orbitals. Researchers have sought Dirac cones in other monolayer materials with the same kind of honeycomb lattice, such as silicene, germanene, and stanene. Borophene, says Feng, was predicted to exist about 10 years ago but was only recently synthesized. One form of borophene on a silver substrate was observed to have a modified honeycomb lattice known as a β_{12} sheet, whose rows of honeycombs are alternately filled with an extra boron atom. Boron has one fewer electron than carbon, and the extra boron atoms are needed to stabilize the lattice.

Matsuda’s group set out to explore the electronic properties of borophene, combining tight-binding and first-principles

calculations (density functional theory) of electronic structure with angle-resolved photoemission spectroscopy (ARPES) studies at the Photon Factory synchrotron radiation facility at the KEK Laboratory in Tsukuba, Japan. With a simple tight-binding model involving only p_z orbitals, the group was able to show the existence of Dirac cones, despite the apparent absence of a honeycomb lattice.

When it comes to electronic structure, details of the quantum wave functions play an important role. Analyzing the p_z wave function amplitudes at the boron atoms, the researchers showed that the β_{12} sheet could be decomposed into two sublattices. The extra boron atom sites were the only ones with zero amplitude in both sublattices. Superimposing the two resulted in an effective honeycomb lattice with nonzero amplitudes at its lattice sites. “From the tight-binding calculations, we know that the Dirac bands originate from an equivalent honeycomb lattice,” says Feng, “so the tight-binding calculations are very important.” The more complete first-principles calculations not only verified these conclusions, but also revealed additional information, such as the placement of the Dirac point (where the upper and lower cones intersect) at about 2 eV above the Fermi energy level, as compared to graphene where they intersect at the Fermi energy. One thing the calculations did not show was whether there was an energy gap at the Dirac point, because spin-orbit interactions were not included in the calculations. This is an important requirement for semiconductor-type applications.

Experimentally, borophene samples were prepared by molecular beam epitaxy on an Ag(111) substrate. Though weak, there is interaction between the borophene and the substrate that affects the electronic structure, including the Dirac cones. Matsuda’s group ascribed this interaction to a lattice mismatch that gives rise to a long-range modulated charge distribution on the surface that is observable as a Moiré pattern with scanning tunneling microscopy. One consequence of the periodic perturbation is the splitting of the Dirac cones. ARPES measurements provided a



Dirac cones for three lattices. (a) Honeycomb structure characteristic of graphene with a single cone; (b) β_{12} sheet characteristic of unperturbed borophene, also with a single cone; and (c) the β_{12} sheet with a periodic perturbation due to a weak interaction with the silver substrate that modifies the electronic structure and splits the cone—the blue and green balls represent the boron atoms with different on-site energies due to the perturbation in a tight-binding analysis. Note that the Dirac cones are in momentum space (energy versus momentum in x and y directions), whereas the lattices are in real space. Credit: Baojie Feng, The University of Tokyo.

detailed catalog of these and other band-structure properties, including the observation that the Dirac point was now 0.25 eV below the Fermi energy because of hybridization between silver orbitals and the boron p_z orbitals. The energy resolution of the measurements was not sufficient to detect a gap at the Dirac point. Applying first-principles calculations to the borophene-silver system yielded good agreement between experiment and theory.

“There are not that many two-dimensional materials that show a Dirac cone, so there is a lot of excitement when a new one is found, and it is important to investigate them thoroughly,” says graphene researcher Eli Rotenberg of the Lawrence Berkeley National Laboratory. The next step in investigating borophene, or indeed any of the 2D materials that may

be produced, is tight integration of sample synthesis and characterization. “A difficulty with working with borophene films on silver is that the borophene exhibits

multiple grain orientations, so ARPES sees an average of the different grain types,” Rotenberg says. “Up-and-coming nano-ARPES instruments with state-of-the-art

sample synthesis and preparation tools chambers may become useful to probe individual borophene grains in the future.”

Arthur L. Robinson

Nano Focus

DNA-coated nanoparticles programmed to assemble into clathrates

A collaboration between Chad Mirkin of Northwestern University and Sharon Glotzer of the University of Michigan has led to the creation of the most complex colloidal crystal synthesized to date, as reported recently in *Science* (doi:10.1126/science.aam7927). Their combined work, for which Mirkin’s group provided the nanocrystals and Glotzer’s group performed the thermodynamic simulations, demonstrates that researchers may soon be able to predict and control the formation of exotic crystals at the nanometer level.

Since 1996, Mirkin’s group has been leading the field in DNA-functionalized nanoparticle assembly. In this technique,

a monodisperse sample of nanoparticles is coated with strands of DNA. The tip of each DNA ligand is single-stranded, and these tips can be made complementary to each other, causing the particles to bind. According to Mirkin, “You can begin to think of particles as atoms, and DNA and variants of it as chemical bonds.” In atoms, the valence shell describes the number of bonds an atom can form. Here, Glotzer says the “[nanoparticle’s] shape imparts a valence” determining the DNA bonding interactions. This has led to a versatile way to form colloidal crystals; Mirkin’s group has created over 500 different crystals spanning over 35 different symmetries.

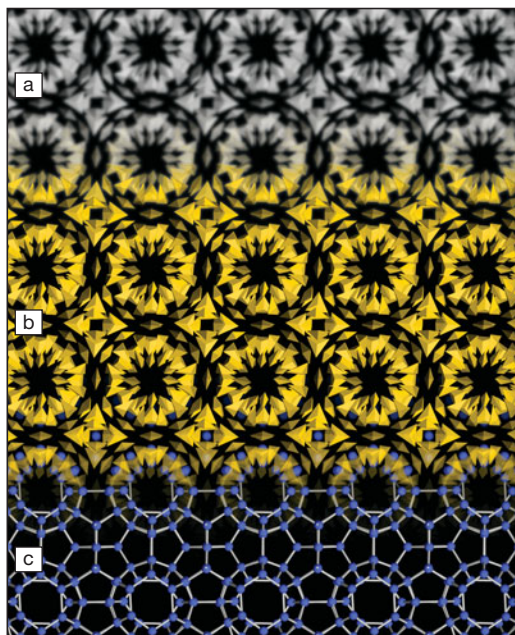
To produce the clathrate crystals—that is, “structures consisting of polyhedral cages with large pores that can be used for host–guest chemistry”—Mirkin’s group coated triangular bipyramid gold nanoparticles with a dense layer of self-complementary DNA. The angles of the bipyramid ($\sim 110^\circ$) closely matched the bonding angles observed in molecular clathrates ($100\text{--}125^\circ$), causing these cage-like structures to form when the surfaces of the particles were functionalized with DNA. “These structures are significantly more complex than structures that have been created previously with this technique,” says John Crocker, a professor at the University of Pennsylvania who works on similar DNA-functionalized nanoparticle assemblies, but was not involved with this work.

The researchers in Mirkin’s group found that they could control the type of clathrate formed with the help of the Glotzer group’s simulations by adjusting the size of the DNA shell. Experimentally, the

length of the DNA shell was increased, giving rise to a series of slightly different structures. The longer DNA shell gives the nanoparticles more freedom during assembly, which leads them to optimize into different clathrates. The simulations were able to reproduce each of these structures. Glotzer and Mirkin attribute this to an interplay between geometry and interactions that maximize binding between the nanoparticles. As the coatings get thicker, the sharp triangular bipyramids become more rounded, which allows the particles to explore a range of different bonding angles. Glotzer thinks of the DNA as “a string between the nanoparticles” and that lengthening the string means the nanoparticles “have more thermal motion to find their optimal position.” This flexibility in bonding angle led to higher quality clathrates with larger internal cages.

This flexibility afforded by changing the DNA ligand length could be the next step in crystal engineering and more exciting than finding a use for the clathrate cages themselves. Applications for complex clathrate structures abound: molecular clathrates encapsulate gases such as methane, and these mesoscale cages produced by Mirkin could potentially hold biological units such as cells. More importantly, Glotzer’s model demonstrates that for a given nanoparticle shape, a class of crystal architectures may be predictable by simply varying the DNA length. This could lead to what Mirkin describes as a “reliable set of design rules for engineering crystal structures.” His excitement is shared by others in the field. According to Crocker, Glotzer has been “making predictions of incredibly complicated structures formed from polyhedra for several years” (see *Nature Materials*, doi:10.1038/nmat4152) and this work demonstrates that these structures are “accessible and realizable with DNA.”

Lauren Borja



(a) Colloidal clathrate crystal; (b) the computer model; and (c) the atomistic equivalent. Credit: Sangmin Lee, Glotzer group, University of Michigan.