Charged-Molecule Physics

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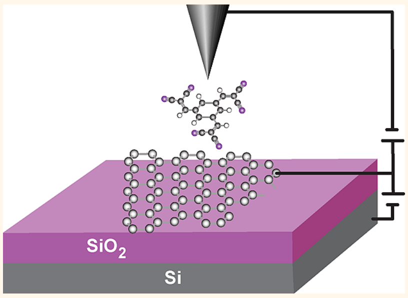
ABSTRACT Commonly, chemical modification is considered to be the ultimate way to tune properties of graphene for new devices. The work of Riss and colleagues reported in this issue of *ACS Nano* demonstrates a reverse approach that enables tuning of molecular properties with graphene. When a back-gate voltage is used, the Fermi level of graphene is shifted with respect to the electronic states of the molecules. This extra electric field opens fascinating new routes toward ultimate sensitive sensors or experimental devices for studying new molecular physics.



Graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms, is often considered to be the nanomaterial of the future. Because of its unique electronic properties, it has attracted substantial attention.[1] Tuning the properties, however, remains a challenge. A common tuning method lies in chemical and structural alteration of graphene which, in turn, tunes the properties of the complete carbon sheet.[2] Hence, the combination of molecules with graphene provides a good opportunity for new hybrid devices with tailored properties. It has been shown, for example, that molecular adsorption can tune electronic, optical, and magnetic properties of graphene hybrid devices.[3]

While a majority of "graphene engineers" focus on studying its properties after chemical modification, in this issue of *ACS Nano*, Riss *et al.* present the inverse approach, namely, influencing the electronic state of a molecule by using graphene in a hybrid device as an electrode material.[4] Graphene serves as a template for molecular adsorption as well as an electrode material in order to tune the chemical properties of molecules by changing their charge state in an electric field. With the use of a scanning tunneling microscope (STM), this approach is extended to the single-molecule level, which opens new possibilities for studying chemistry and molecular physics of charged molecules at the nanoscale.

Scanning tunneling microscopy (STM) is based on electron tunneling between a sharp tip and a surface and stands as *the* method that actually initiated the fields of nanoscience and nanotechnology. The distance between tip and surface is controlled with an accuracy of a few picometers by clever electronics that use the tunneling current as a distance-sensitive parameter. A STM image results from scanning the tip over the surface; however, the STM-surface system can also be used as a spectrometer, probing the electronic states of surface systems with lateral resolution at the atomic level.[5] This makes STM the ultimate tool to study physical properties of nanostructures on surfaces as well as single molecules. Consequently, this technique has become the most powerful tool in surface science and has unraveled long-standing problems in the field. In addition to the ability to use its ultimate spatial resolution as a microscope, STM also enables the manipulation of single atoms and molecules in order to study the physics of artificial nanostructures.[6] Researchers have also used STM manipulation to control the properties of single molecules, for example, by changing molecular conformation,[7] or by performing single-molecule chemistry.[8] To induce molecular dynamics in single molecules, energy is usually deposited into the molecule by inelastic electron tunneling (IET), exciting molecular vibrational modes.[9,10] Either the inelastic tunneling event is then identified by minute changes occurring in the tunneling current or by statistical analysis of molecular dynamics

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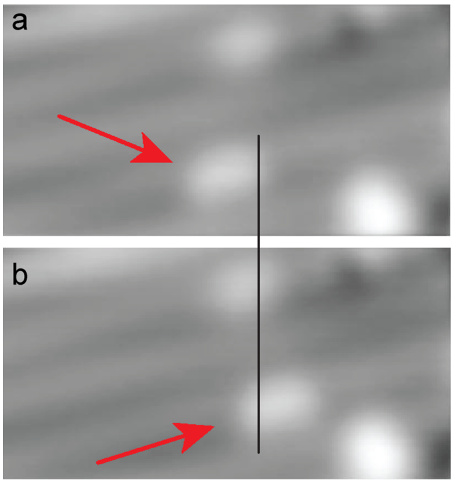

Figure 1. Hopping induced by inelastic electron tunneling. (a) A single molecule (indicated by the red arrow) is probed with increasing bias voltage until an action mode—in this case hopping to a new location—is observed (b). The threshold voltage of the action enables conclusions such as the vibrational mode that was first excited before action occurs. In praxis, many manipulations are required to achieve sufficient statistical resolution. The black line shows that the molecule hopped to a new location. Reproduced from ref 11. Copyright 2011 American Chemical Society.

following the excitation event (see example discussed in Figure 1). Both ways, however, require ultimate thermal and mechanical stability of the STM setup or numerous experiments. By making use of their graphene hybrid device, Riss *et al.* have now found a way to address and to control vibrational states of single molecules without the detour of vibronic excitation by inelastic electron tunneling.[4] In this issue of *ACS Nano*, Riss *et al.* influence the electronic state of a molecule by using graphene in a hybrid device as an electrode material.

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Beyond the primary tip–surface setup, STM has been further developed into a multiprobe tool by integrating more electrodes into the experiment. Two early examples are shown in Figure 2. Ballistic electron emission microscopy (BEEM), as introduced by Bell and Kaiser in 1988,[12] uses ballistic charge carrier transport through a Schottky-type device in order to study scattering processes in injection, propagation, and transmission in thin film systems (Figure 2a).[13] In 1986, Muralt and Pohl introduced a setup for studying the lateral variation of the electrochemical potential across a surface (Figure 2b).[14] At the same time, the first STM results from the liquid–solid interface were presented,[15] and more recently STM has been upgraded for studying electrochemistry at electrode surfaces immersed in liquid electrolytes.[16]

By making use of graphene exfoliation technology, researchers have previously shown the feasibility of studying electronic transport properties of graphene on a thin silicon oxide film with STM while simultaneously applying a gate voltage.[17] Moreover, single Co atoms have been charged this way.[18] Now, Riss *et al.* present a similar, but improved, setup for studying molecular electronic states in an electric field arising from voltage gating (Figure 3). The improvement is based on using a boron nitride (BN) flake underneath the graphene layer. This trick guarantees a perfectly flat graphene layer above the BN flake, making it much easier to study molecular films with the STM. Riss *et al.* adsorbed organic molecules (1,3,5-tris(2,2-dicyanovinyl)-benzene, CVB, Figure 3) from the gas phase onto the graphene surface in ultrahigh vacuum (UHV) and studied their electronic states with STM and spectroscopy. When the bias voltage is swept between graphene and the STM tip from sufficient negative to positive values, electrons tunnel either from the occupied molecular states into the metallic STM tip or from the tip into unoccupied states of the molecules, giving rise to pronounced resonances. With such local spectroscopy, the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), for example, can be located on the accessible voltage scale. When scanned with bias voltages corresponding exactly to these levels, the spatial distributions of these orbitals can be visualized, because they dominate the STM image contrast under these conditions. When scanned at positive sample bias, the LUMO level of CVB is identified at 1.86 eV above the Fermi level of the substrate, which is, for graphene, the so-called Dirac point. Surprisingly, strong satellites of the LUMO level were also observed in the tunneling spectrum, representing vibronic states of the CVB molecule. This observation indicates a strong electron–phonon coupling between certain vibronic states and the LUMO electronic state. So far, single-molecule vibronic levels have only been observed with the STM in the above-mentioned inelastic electron tunneling process. Scanning tunneling microscopy at bias voltages corresponding to these vibronic levels, in turn, displays the locality of these vibrational modes in the molecule. Supported by density functional theory calculations, out-of-plane C–H group vibrations of the molecule

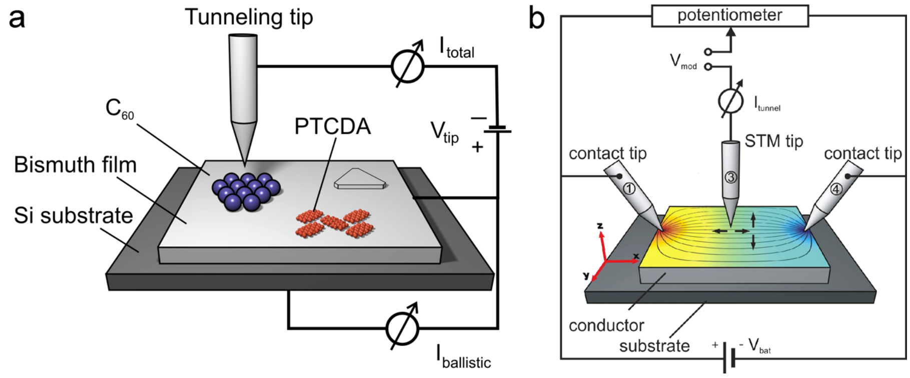

Figure 2. Examples for additional electric field gradients in a scanning tunneling microscope (STM) experiment. (a) In a typical ballistic electron emission microscopy (BEEM) setup, the tip of an STM injects electrons (I_{total}) into a metal layer, either directly or through an adsorbate. Because the metal layer and the silicon substrate are in contact, the ballistic fraction in the tunneling current ($I_{ballistic}$) can be determined. (b) Scheme of measuring and influencing the electrochemical potential under an STM tip. Two contact tips introduce a current across a surface. The resulting lateral potential distribution and the morphology can be then mapped by the normal STM tip.[13] Adapted with permission from ref 13. Copyright 2012 the Swiss Chemical Society.

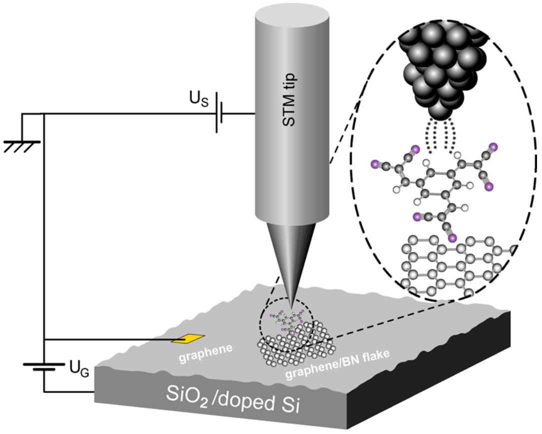

Figure 3. Setup for investigating single molecules in an electric field. Exfoliation and deposition of boron nitride flakes followed by graphene deposition *via* the same method onto an insulating silicon oxide film on doped silicon allows gate voltages (U_G) to be applied after proper electrical contacts have been made. When the voltage is swept between the scanning tunneling microscope tip and the graphene surface (U_S), the effect of different electric fields on molecular electronic states can be studied.

are identified as the origin. The fact that pronounced and well-resolved vibronic states of molecules can be observed is due to the special property of the graphene/molecule system: the molecule electronically decouples from the rather inert graphene layer. With the application of a gate voltage of 60 V, all molecular states are shifted 0.2 eV, *i.e.*, to lower tip−sample biases by 0.2 V.

The work by Riss *et al.* promises exciting potential implications in molecular physics and chemistry. Toward applications, we note the desire for ultimate sensitivity in chemical detectors and sensors. Being able to study vibronic levels at the single-molecule level provides not only selectivity but also the utmost sensitivity. So far, such sensitivity has been beyond the feasibility of practical sensors or has required unrealistic scanning probe approaches. A back-gated device, however, would not necessarily include a scanning tip, but rather a static tip electrode without losing much of its sensitivity. For various molecular species in question, different gate voltages would then deliver the selectivity needed. By making use of their graphene hybrid device, Riss *et al.* have now found a way to address and to control vibrational states of single molecules without the detour of vibronic excitation by inelastic electron tunneling.

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The fascinating application of electrochemistry without electrolytes now also seems close to realization. When an electrode surface is charged in vacuum with respect to a reference counter electrode, the result is essentially a shift of the electrical potential of the vacuum level with respect to the Fermi level, leading to a linear change in work function with respect to the applied electrode potential.[19] In that case, however, the electrical potential of an adsorbed molecule does not change with respect to the electric potential of the underlying conducting surface. That is, the HOMO and LUMO levels, as well as all other molecular states, are not changed in energy with respect to the Fermi

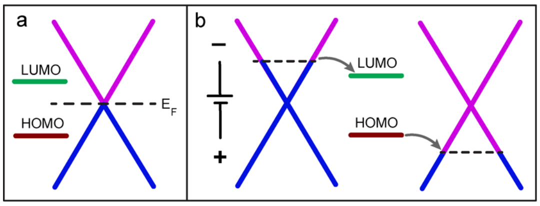

Figure 4. Charging molecules by back-gating. (a) Relative positions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels with respect to the Dirac cone (or Fermi level E_F) of graphene. (b) When a back-gate voltage is used, the Fermi level is shifted such that it reaches the LUMO or HOMO level, with the consequence of charge transfer to or from the molecule that effectively negatively or positively charges the molecule.

level of the conducting sample underneath. The molecule/graphene hybrid device used here, however, now allows relative shifts of molecular states by leaving the Fermi level pinned (or *vice versa*, depending on which level is taken as reference). One can imagine that different species with different polarizabilities act differently under the electric field, enabling, for example, switching of long-range ordered structures in two-component self-assembly. Likewise, field-induced conformational changes in molecules could provide actuators at the monomolecular film level. For the CVB molecules used by Riss *et al.*, the 0.2 eV shift was not sufficient to push the LUMO level all the way down to the Dirac point of graphene. Yet, for a molecular system with a HOMO or LUMO level much closer to the graphene Fermi level, negative or positive molecular charging seems possible (Figure 4). This opens the door to true electrochemistry between molecules, *i.e.*, two-dimensional polymerization that would otherwise require high temperature, light, or activation by additional catalysts. However, adding metals or metal clusters, in case additional catalysts are required, is still an additional option for this graphene/molecule hybrid device and offers electrocatalysis at the nanoscale level, again without electrolytes.

Finally, a fascinating option for new devices will be to trigger superconductivity of organic molecular films. To induce strong electron–phonon coupling, often an additional charge has to be introduced into the molecule by chemical doping with strong electron donors, like alkali or alkaline earth metals. In particular, for buckminsterfullerene (C_{60}) and its fragment derivatives (so-called buckybowls), doping has been found to be crucial in order to achieve higher transition temperatures. For example, transition temperatures as high as 66 K have been predicted for monoanionic corannulene ($C_{20}H_{10}^{-}$), the simplest buckybowl.[20] However, because that molecule acts as a strong electron acceptor, favoring multiple charged states,[21] careful doping would be required. In general, poor control of doping is often identified as the source of the lack of reproducibility in such systems. With the use of controlled charging/decharging with the back-gate technique of such molecules on graphene, superconducting states can be virtually switched on and off without changing the temperature or applying magnetic fields. Again, such back-gated devices suggest excellent perspectives of new molecular devices and open exciting possibilities for exploration into new molecular physics.

Conflict of Interest: The authors declare no competing financial interest.

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