

If We Could Talk to the Animals

Humans have long sought ways to communicate with animals for various purposes, including research and training. However, humans and many other species of interest suffer from a sound frequency band mismatch. Whereas humans can hear sound frequencies between 20 Hz and 20 kHz, other animals often communicate over significantly larger frequency ranges, including ultrasonic frequencies far beyond 20 kHz. Current earphones designed for human use only produce sounds in the human hearing frequency range, stymieing the application of these tools for human–animal communication.

In a new study, Tian *et al.* (DOI: 10.1021/nn5009353) demonstrate the use of graphene earphones using a laser-scribed method.

Using a graphene oxide (GO) film as the starting material, the researchers use a laser to reduce GO into graphene in a desired pattern, reducing resistance in this region by almost 5 orders of magnitude. After attaching electrical inputs to this graphene film, the researchers used it to replace the voice coil speaker in conventional earphones. Tests showed that, compared to conventional earphones, the graphene earphones could produce sound over a much wider frequency range, from 100 Hz to 50 kHz. Calculations showed that these novel earphones could potentially produce sound up to 1 MHz. Using these headphones, the researchers trained a dog to respond to ultrasonic commands. The authors suggest that graphene earphones

could offer a way to make use of the hearing ranges of both humans and various animals of interest.



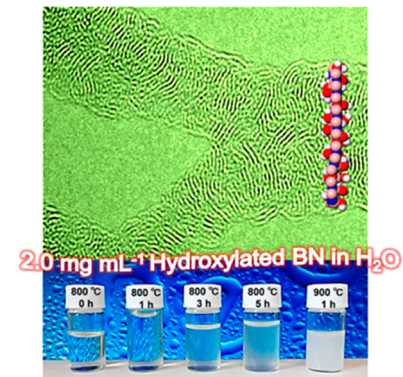
Fighting Cancer with Boron Nitrides

Researchers have investigated several different nanocarbons, including carbon nanotubes and graphene oxide, for biological applications. However, numerous assays in animal models and cultures have shown these carbon-based materials to have dose-, time-, and shape-dependent toxicity. In contrast, boron nitrides (BNs), structural analogues of carbon nanotubes whose C atoms have been replaced by B and N atoms, have been shown to have better biocompatibility and lower cytotoxicity than their carbon-based counterparts. Although these materials offer a promising alternative for biological applications, their use for this purpose has remained largely unexplored due to their extremely poor solubility/suspension in physiological solutions.

Seeking a way around this dilemma, Weng *et al.* (DOI: 10.1021/nn5014808) developed a novel solid reaction that directly fabricates

BNs by thermally substituting C atoms with boric acid substructures in graphitic carbon nitrides. Tests showed that BN samples prepared at 800 °C for up to 3 h displayed excellent solubility in water. Both energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy demonstrate high degrees of hydroxylation for the more soluble samples, which also displayed a highly porous construction. These characteristics made the fabricated BN materials good candidates for serving as vehicles for pharmaceuticals. Testing this possibility, the researchers showed that one sample in particular demonstrated a high loading capacity for the cancer drug doxorubicin (DOX), with pH-dependent release. *In vitro* tests showed that DOX-loaded hydroxylated BNs killed cancer cells more effectively than free DOX. The authors suggest that these novel

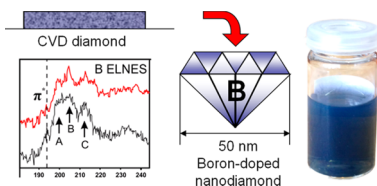
materials hold promise for a variety of biological and medical applications.



Boron Is a Diamond's Best Friend

Blue diamonds colored from boron doping have gained fame as gemstones, most notably the Hope and the Blue Wittelsbach diamonds. However, B-doped diamonds have also attracted interest for their interesting fundamental properties and potential applications. For example, B-doped chemical vapor deposition (CVD) diamond films have the widest known electric potential window, suggesting an ideal material for electrochemical electrodes. Nanocrystalline diamond particles with homogeneous boron doping have been suggested for a variety of other intriguing applications. However, researchers have yet to report the fabrication of this material.

In a new study, Heyer *et al.* (DOI: 10.1021/nn500573x) present a multistep process to generate highly boron-doped diamond nanoparticles. Using boron-doped CVD diamond film as a starting material, the researchers crushed the film using a vibration mill and grinding balls made of tempered steel, using a multistep milling process to avoid heating the



material and causing subsequent graphitization. They purified the resulting powder to remove steel components and extraneous carbonaceous material, resulting in a deep blue colloidal solution of boron-doped diamond particles in water. Subsequent analysis showed that the particles ranged in size from 10 to 60 nm with B content of about $2.3 \times 10^{21} \text{ cm}^{-3}$. Using aberration-corrected high-resolution transmission electron microscopy, the researchers found the presence of defects within individual particles and a thin carbon nondiamond layer at the surface. Showcasing their potential, the researchers demonstrated that the boron-doped diamond nanoparticles

could seed the growth of a boron-doped diamond film by CVD. The authors suggest that these particles could be used for a variety of applications in electrochemistry, thermal management, and fundamental studies.

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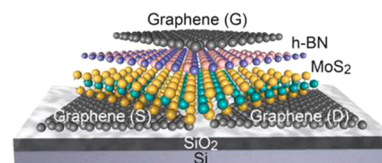
Transistors Go Completely Two-Dimensional

■ The possibility of making two-dimensional (2D) transistors has attracted increasing attention due to the potential for obtaining uniform thickness down to a monolayer without dangling bonds. Graphene has several qualities that could be advantageous in such materials systems, such as its small quantum capacitance and extremely high carrier mobilities. However, these are overshadowed by its lack of an intrinsic band gap. Transition metal dichalcogenides (TMDCs), with inherent band gaps that are tunable by composition and number of layers, offer promising alternatives. Ideally, a 2D transistor would be composed of a TMDC material, with a layered insulator as the gate dielectric and layered metallic source/drain and gate contacts. Such a

transistor made completely from 2D materials has yet to be reported.

In a new study, Roy *et al.* (DOI: 10.1021/nn501723y) accomplish this feat. Using few-layer MoS₂ crystals as the channel, the researchers use large area chemical vapor deposited graphene as the source/drain. Exfoliated hexagonal boron nitride acted as the layered gate dielectric, and exfoliated graphene served as the top-gate contact. All interfaces were based on van der Waals bonding, eliminating possible lattice parameter constraints. Tests show that this transistor exhibits n-type behavior, with high ON/OFF ratios and electron mobility. This mobility does not degrade at high gate voltages, a significant advantage over conventional

Si transistors. Continuing the theme, the researchers also demonstrate a WSe₂–MoS₂ diode with graphene contacts. The authors suggest that future work will focus on reducing the thicknesses of individual components down to a monolayer.



Power Shirts Are the New Power Suits

■ Wearable electronics are a growing area of multidisciplinary research, with a variety of applications for health and medicine. Sensing garments for monitoring physiological and biomechanical signals from the human body have already been invented. However, these “smart” garments typically require bulky battery packs or need to be plugged in to operate, limiting their widespread use. Some researchers have suggested harvesting biomechanical energy to power wearable devices, using strategies including electromagnetic fields, the piezoelectric effect, the electrostatic effect, and the triboelectric effect. Ideally, to create the most comfortable, flexible, and breathable garments, built-in energy harvesters would be implemented as textile-fiber structures.



fiber-based generator (FBG) that can be woven into a self-powered smart garment. To create the FBG, the researchers coated cotton threads with carbon nanotubes. They coated a subset of these carbon nanotube-coated threads with polytetrafluoroethylene, one of the representative electret materials

for power generators that can theoretically retain electrostatic charges on its surfaces for years. Entangling these two thread types formed the FBG. When the FBG was stretched and released, it produced an alternating current. Tests showed that the average output power density of this novel device was about 0.1 $\mu\text{W}/\text{cm}^2$. Placing a single FBG on a volunteer's finger and weaving a patch into a lab coat, the researchers showed that flexing the threads generated enough energy to power a liquid crystal display and a body temperature monitoring system. The authors suggest that this FBG could lead to a new generation of smart textiles.

In a step toward this goal, Zhong *et al.* (DOI: 10.1021/nn501732z) created a metal-free

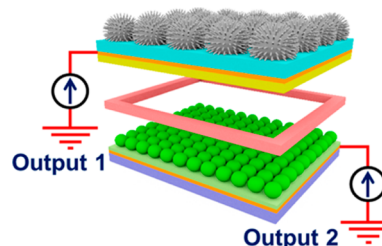
Harvesting Energy Straight from the Tap

■ Self-powered nanosensors have a variety of advantages over those requiring power from an outside source, such as smaller sizes and avoiding use of the environmentally unfriendly materials that are found in batteries. These positive attributes have driven an increasing amount of research toward this area. Thus far, researchers have developed self-powered nanosensors for pH, temperature, and toxic pollutants, among other uses. Among energy sources, mechanical energy holds particular promise because it is not dependent on the variability of sunlight. Triboelectric nanogenerators (TENGs), which rely on triboelectric and electrostatic effects to scavenge energy, have proven effective in harvesting mechanical energy under dry conditions. However, although previous research suggests that water droplets falling from the

sky or flowing through an insulated tube can generate triboelectricity, this effect has yet to be harnessed for harvesting mechanical energy or powering nanosensors.

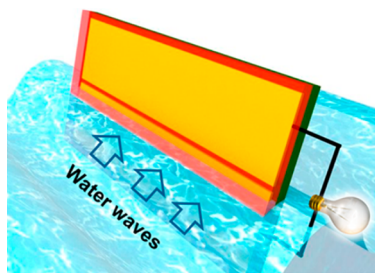
In a new study, Lin *et al.* (DOI: 10.1021/nn501983s) use this effect to collect energy from water flowing through a household tap. The researchers constructed a hybrid TENG that simultaneously harvests electrostatic and mechanical energies of flowing water. To collect electrostatic charges, they relied on a superhydrophobic layer of TiO₂ with hierarchical micro/nanostructures to enhance the electrostatic induction effect. To collect mechanical energy, they constructed a polytetraethylene film and a layer of assembled SiO₂ nanoparticles. This hybrid TENG was able to power light-emitting diodes and charge commercial capacitors. Additionally, a modified

version of the electrostatic charge collector could serve as a self-powered ethanol detector. The authors suggest that TENGs could be a viable option for harvesting the energy of flowing water.



Riding the Renewable Energy Wave

■ The ebb and flow of ocean or river waves, and even the trickle of raindrops, contain a vast reserve of renewable energy. Finding ways to harvest this energy could lessen dependence on fossil fuels as well as provide energy to self-powered autonomous systems. Thus far, devices to harvest power from water motions have typically consisted of electromagnetic generators that are bulky and heavy. These systems also often required other components, such as an absorber, to collect ambient water motions and a turbine to drive the generator, adding to each system's size, complexity, and cost. Developing a small, lightweight, cost-effective, and all-in-one approach for harvesting water's mechanical energy could solve these problems.



Toward this goal, Zhu *et al.* (DOI: 10.1021/nn5012732) crafted a liquid–solid electrification-enabled generator (LSEG) based on a fluorinated ethylene propylene (FEP) thin film to capture triboelectric charges. The film, embedded with vertically aligned nanowires

to increase hydrophobicity and surface area, covered an array of electrodes on one side of the device. These components were applied to a substrate. When water contacts the FEP surface, it retains a layer of lingering negative surface charges. Interacting with the positive charges in repeated waves or droplets of water generates a current. Using the device in simulated waves or in the spray of a sprinkler generated enough electricity to power tens of LED bulbs. Further investigation showed that shrinking the LSEG's width could improve performance. The authors suggest that this LSEG holds promise for gathering energy in oceans, rivers, or even rainy settings.

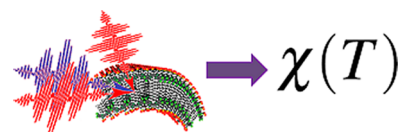
New Excitement over Excitons

■ Several recent reports have detailed the detection of long-lived coherent dynamics in natural light-harvesting photosynthetic complexes using two-dimensional spectroscopies. These findings have ignited interest and debate about the roles of this long-lived coherence in the efficient design of light harvesters and exciton transport in biological and artificial systems. At the crux of these discussions is the importance of correctly interpreting the spectroscopic data in terms of the materials of interest's microscopic dynamics. Exciton dynamics and vibrational dynamics can interact to produce complex and sometimes ambiguous spectroscopic data, making it a challenge to dissect out information about only exciton transport. Developing more stringent

tests to probe exciton transport could resolve these questions.

In a new study, Yuen-Zhou *et al.* (DOI: 10.1021/nn406107q) use a novel strategy—ultrafast quantum process tomography (QPT)—to characterize the room-temperature dynamics of excitons originating from the inner and outer walls of supramolecular light-harvesting nanotubes that self-assemble in solution from an amphiphilic cyanine dye monomer. The absorption spectrum of these nanotubes has been well studied, but their excited state dynamics are not fully understood, making them ideal candidates for studying using ultrafast QPT. Findings show an absence of nonsecular processes, a unidirectional energy transfer from the outer to

inner wall exciton states, and coherence between those states lasting about 150 fs. Together, these results suggest weak electronic coupling between the walls. The authors suggest that this QPT approach could be applied to a variety of other systems to provide new insights into their excited-state dynamics.



Making the Smallest Switch

■ Driven by the push to miniaturize electronics, researchers have created single-molecule transistors, rectifiers, and switches. To realize very large scale integration of molecular circuits, researchers must find ways to minimize heat generation through dissipative channels that may accompany the function of a circuit element. Controlling electron transport across a junction through conductance switching is a way to accomplish this goal. Manipulating conductance through the movement of a single atom has already been reported. However, to miniaturize molecular electronics even further, researchers must control conductance instead by the function of a single electron on a single molecule, effectively suppressing dissipation by eliminating the need for moving parts.

In a new study, Lee *et al.* (DOI: 10.1021/nn501875m) show that this scenario is indeed feasible. Their novel switch consists of a single Zn-etio porphyrin molecule isolated in the double-barrier junction of a cryogenic ultra-high vacuum scanning tunneling microscope (STM) and reduced to a radical anion by injecting an electron. The researchers interrogated this switch by recording time traces of tunneling current and photon counts over a grid to map its function spatially. Their findings show that the junction current of the switch is modulated by the injected electron's spin-flip bistability. Using the functional images they gathered, they created wiring diagrams for controlling the switch's frequency, amplitude, polarity, and duty cycle. Further examination suggests that this switch

relies on the quantum mechanical effect produced by spin-aligned electrons interacting with a singularity, the single adsorbed molecule. The authors suggest that future research might allow them to take full advantage of this effect through spin-polarized STM to manipulate the quantum bit of information stored in the switch.

