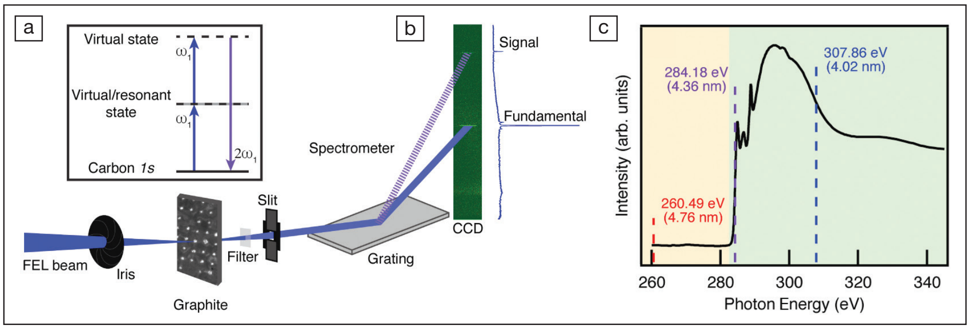


The experimental design of soft x-ray second-harmonic generation (SHG). (a) Schematic showing the energy diagram of the SHG process; (b) experimental setup showing the SHG signal generation from the transmitted free-electron beam on a graphite sample; (c) x-ray absorption SHG spectrum of the graphite sample. FEL is free-electron laser. Credit: *Physical Review Letters*.

rigorous interfacial specificity. This limitation is usually associated with the optics, laser source, and experimental techniques. Recent developments in nonlinear optics with coherent x-ray free-electron laser sources now make it possible to probe buried interfaces with elemental specificity.

In a recent issue of *Physical Review Letters* (doi:10.1103/PhysRevLett.120.023901), a research team, led by Craig Schwartz, Richard Saykally, and Royce Lam at Lawrence Berkeley National Laboratory and the University of California, Berkeley, reports the first observation of soft x-ray second-harmonic generation (SHG) in graphite thin films. "This [technique] effectively combines the surface/interface specificity optical second-order spectroscopy with the elemental specificity of soft x-ray spectroscopy," says Lam, the lead author of this work, "with signal originating primarily from the topmost molecular layer." The interfacial specificity comes from the enhancement of the second-order nonlinear response to a high-energy, coherent photon beam, which distinguishes itself from surface-specific x-ray spectroscopy that is restricted by the inelastic mean free paths of the photoionized electrons or by the penetration depth of the incident x-rays.

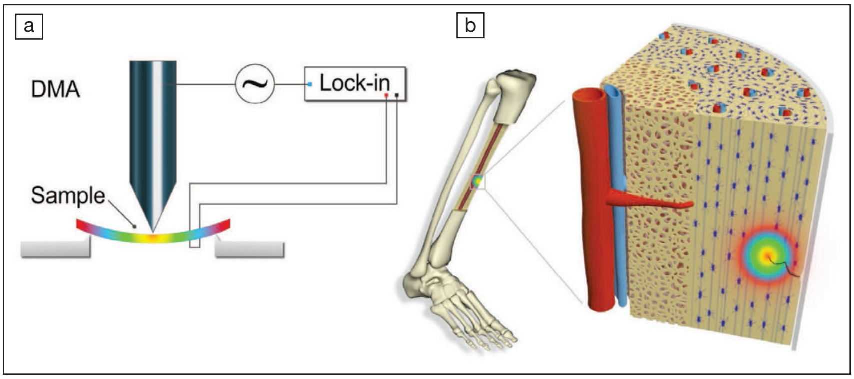
The researchers also developed a first-principles electronic structure framework with a density-function-theory-based supercell approach that matches the experimental spectrum with a calculated linear spectrum for an eight-layer slab of graphite. "This technique should be broadly applicable to a wide variety of materials systems," Lam says. "Additionally, as the pulses remain coherent in the SHG process, we expect it to be possible to combine soft x-ray SHG with lensless coherent imaging techniques that allow for simultaneous spectroscopic and spatial resolution of materials systems."

"This work is one of the first to study second-harmonic generation using soft x-ray pulses from a free-electron laser, which could be widely applied to study the interfacial chemical reaction that may be hidden in the materials," says Liang Zhang, a postdoctoral researcher with expertise in soft x-ray spectroscopy at the Advanced Light Source at Lawrence Berkeley National Laboratory.

YuHao Liu

Bio Focus

Flexoelectricity found in bone



(a) Schematic of the experimental setup for measuring flexoelectricity; (b) strain gradients, and thus flexoelectricity, apparent at crack tips in bone mineral. DMA is dynamic mechanical analyzer. Credit: *Advanced Materials*.

Bones generate electricity and it has been known for a while that this plays a critical role in their regeneration. However, it was not clear where the electricity came from or how it choreographed the healing of a broken bone. An international group of researchers from Catalonia, Costa Rica, Iran, and Switzerland have identified a phenomenon called flexoelectricity, most commonly found in ceramics, to be an important actor in this process.

Bones are composed of living cells, biopolymers, and minerals. The most common bone mineral is hydroxyapatite, a phosphate of calcium, which provides most of the load-bearing strength. These minerals are bound together by a tough protein called collagen that allows a bone to be more flexible. Collagen, it turns out, is piezoelectric; it is able to convert an applied mechanical stress to electric signals, for example when the bone is bent. Besides collagen's piezoelectricity, streaming ions also produce movement of charges, leading researchers to believe

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that this is the source of bone electricity. However, it was discovered that new bone-forming cells or osteoblasts accumulate on the surface of pure hydroxyapatite, which has neither collagen nor streaming ions. The researchers wondered what was attracting these osteoblasts to a pure mineral.

As reported in a recent issue of *Advanced Materials* (doi:10.1002/adma.201705316), G. Catalan of the Barcelona Institute of Science and Technology and colleagues first looked at whether hydroxyapatite itself was piezoelectric. This is still a contentious issue; piezoelectricity originates from a fundamental asymmetry in the distribution of charges in a mineral, and structural studies disagree about whether the symmetry of hydroxyapatite is consistent with piezoelectricity. Laboratory measurements of the piezoelectric properties of hydroxyapatite by the team, however, revealed that the mineral is not piezoelectric.

However, even if a material is microscopically symmetric, a differential strain acting on the body can cause an asymmetry. This is called flexoelectricity, which is a coupling between a strain gradient in a body (flexure) and the amount of charge generated on the surface. As the name suggests, "flexure" leads to electricity. Tiny hairs in the inner ear, for example, have evolved to use this phenomenon for converting air waves to neural signals, thereby making flexoelectricity fundamentally important in auditory functioning. The researchers then set out to carefully flex natural bone and synthetic hydroxyapatite in the laboratory, measuring the bending-induced current using a lock-in amplifier. The flexure-induced current in synthetic hydroxyapatite and natural bone were remarkably similar, suggesting that flexoelectricity does indeed play a major role in generating electricity in bones. Moreover, because synthetic hydroxyapatite has no collagen, the quantitative similarity between the results rules out collagen piezoelectricity as a relevant contributor to the flexoelectricity of bone.

To fully understand the extent that flexoelectricity plays in bone regeneration, the researchers calculated the flexoelectric potential at a micro-crack in a bone. They found that even a small stress can be magnified at the apex of a crack tip, generating very high flexoelectric potentials. These flexoelectric potentials were compared with the electric fields that biologists had previously established to be sufficient to "electrostimulate" the beginning of the process of healing. As the crack starts healing, the apex shifts thereby serving as a beacon in directing the flow of healing cells. Thus flexoelectricity allows a micro-crack to call for help without the need for collagen piezoelectricity or streaming ions.

Brian Rodriguez at the University College Dublin, who is not connected to this research, says, "This work underscores the significance and ubiquity of flexoelectricity and clarifies several nagging and, until now, unresolved issues related to our understanding of bone remodeling."

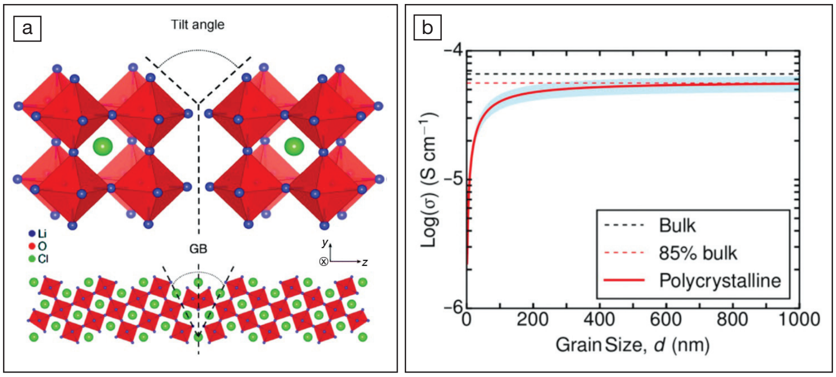
Vineet Venugopal

Energy Focus

Influence of grain boundaries on Li-ion conductivity characterized at atomic scale

A research team led by M. Saiful Islam of the University of Bath, UK, has investigated how the grain boundaries of solid electrolytes in Li-ion batteries influence Li-ion conduction at the atomic scale. The researchers performed a set of large-scale molecular dynamics simulations that analyzed the Li-ion conductivity at stable grain boundaries of Li_3OCl, a promising anti-perovskite solid electrolyte for Li-ion batteries. Their findings were published in a recent issue of the *Journal of the American Chemical Society* (doi: 10.1021/jacs.7b10593).

Solid electrolytes such as Li_3OCl enable the manufacture of all-solid-state batteries with improved duration and safety, mainly due to their nonvolatility and nonflammability. Since electrolytes shuttle Li ions during battery operation, their ion conductivities are of critical importance. "However, the influence of grain boundaries is rarely quantified or characterized in detail especially at the atomic scale," Islam says. "There is also debate concerning the precise Li-ion migration barriers and ionic conductivity of Li_3OCl." Specifically, the migration barriers estimated by *ab initio* computational studies are consistently lower than those characterized by experimental work that employs electrochemical impedance spectroscopy.



(a) Schematic illustration of a grain boundary (GB) in Li_3OCl. A grain boundary is the surface between two crystallites (grains) of different orientations, as represented by the dashed lines. (b) The plot of Li-ion conductivity versus grain size. The red curve represents the simulation results of a polycrystalline Li_3OCl at 300 K (where the blue band highlights the upper and lower limits). The black and red dashed lines are the calculated conductivity of a grain-boundary-free bulk material and the maximum average conductivity of a polycrystalline sample, respectively. Reproduced with permission from *J. Am. Chem. Soc.* **140** (2018), the American Chemical Society.

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