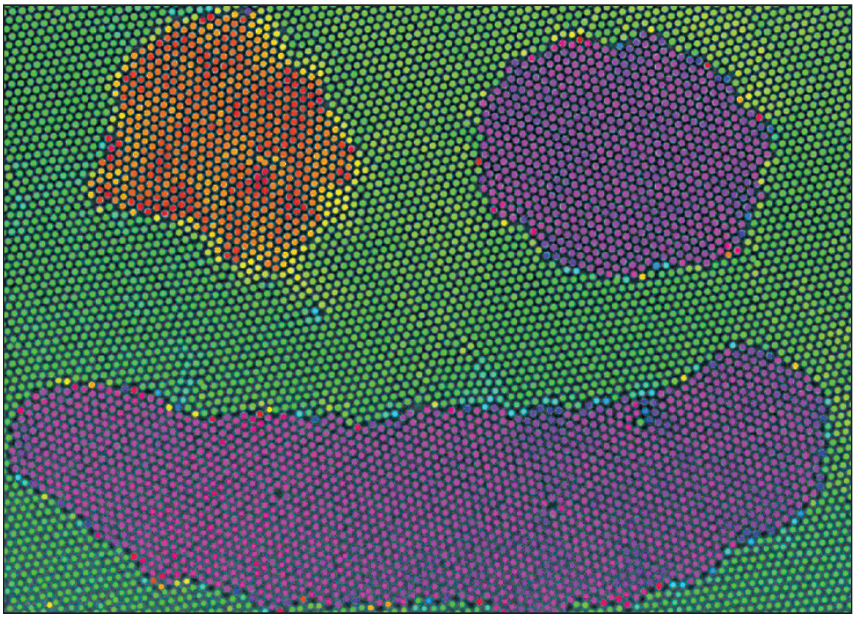
Optical blasting of polycrystals manipulates grain boundaries

In the realm of materials science and beyond, grain boundaries play a central role in defining the optoelectronic, magnetic, thermal, mechanical, and other properties of materials. Materials scientists are concerned about grain boundaries owing largely to their stochastic nature. The boundaries usually scatter charge carriers inhibiting transport, disrupt long-range crystallinity, and lead to brittleness, rendering the materials less attractive for applications. This might, however, change with a discovery made by the research group of Sharon Gerbode of Harvey Mudd College, and published recently in *Physical Review Letters* (doi:10.1103/PhysRevLett.120.018002).

Gerbode's group, consisting solely of undergraduates, has developed "optical blasting" as a unique tool to maneuver and control grain boundaries in two-dimensional (2D) polycrystal monolayer assemblies. Optical blasting is an analogue of the well-known "optical tweezers" initially reported in 1970. Whereas optical tweezers have been successfully employed to bring together and trap nanoscale and sub-nanoscale objects, as the name implies, optical blasting repels particles. It has so far only been explored by the Gerbode group.

The research team locally rastered a laser beam across silica microcrystals assembled in a liquid medium. Aided by a mismatch between the refractive indices of the microcrystals and the medium, the laser induced a repulsive force between adjacent microcrystals, locally melting the grain boundaries. Upon recrystallization, the grain boundaries were found to have moved from their original positions.



A smiley face experimentally fabricated using optical blasting. Particles are colored by the phase of the local orientational order parameter, showing grain orientation. Credit: *Physical Review Letters*.

"The boundaries can be made permanently distorted for longer laser interaction timescales," Gerbode says. Using the technique, the group was able to sculpt a variety of artificial grain shapes in the polycrystal assembly. "Interestingly, if the liquid medium is then evaporated, you can lock the crystals into a new grain boundary geometry," she says.

The researchers use light to locally melt a colloidal crystal and then watch as the grain boundaries reform in a new configuration. They also speculate that it may be possible to use this sort of method to perturb actual three-dimensional solid-state crystals. "The challenge there would be to image the grain boundary of the crystal in the first place, and then be able to make an intelligent local perturbation to that boundary," says Eric Weeks, an expert in colloidal glasses and a professor in the Department of Physics at Emory University.

The possibility of locally melting and manipulating grains and defects in materials will equip researchers with hitherto unachievable control over grain boundaries. The biggest advantage of the finding, Gerbode says, is the opportunity to internally tune various materials properties by grain manipulation. One can now envisage converting the routine, isotropic crystals into materials that exhibit direction-dependent properties, such as charge transport or elasticity. It could become possible, for example, to realize crystals with mechanical softness in a particular direction and stiffness in the other.

This discovery opens a vibrant chapter in materials research, and suggests that some of the simplest materials systems could become home to phenomena that can challenge conventional logic.

Ahmad R. Kirmani

Probing the buried interface between graphite layers

The secrets of the first few molecular layers near the surface of a material, or adjacent to buried interfaces is an underexplored area of science. Interfaces in rechargeable battery catalysts, semiconductor dielectrics, and two-dimensional materials play important roles in determining energy-conversion efficiency, device performance, and chemical and physical reactivity. X-rays with high photon energies are commonly used to "see" into materials due to their penetrating ability and small wavelength that approximates to the size of molecules and atoms. However, while most soft x-ray spectroscopy techniques can achieve chemical and elemental specificity, they are not able to offer

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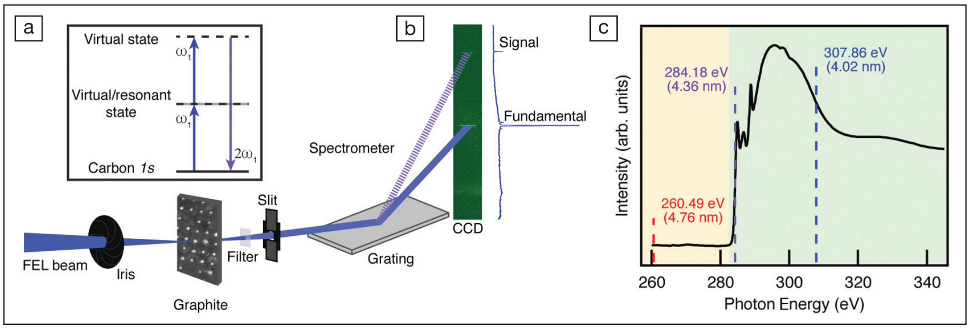
rigorous interfacial specificity. This limitation is usually associated with the optics, laser source, and experimental techniques. Recent developments in nonlinear optics with coherent x-ray free-electron laser sources now make it possible to probe buried interfaces with elemental specificity.

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 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*.

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."

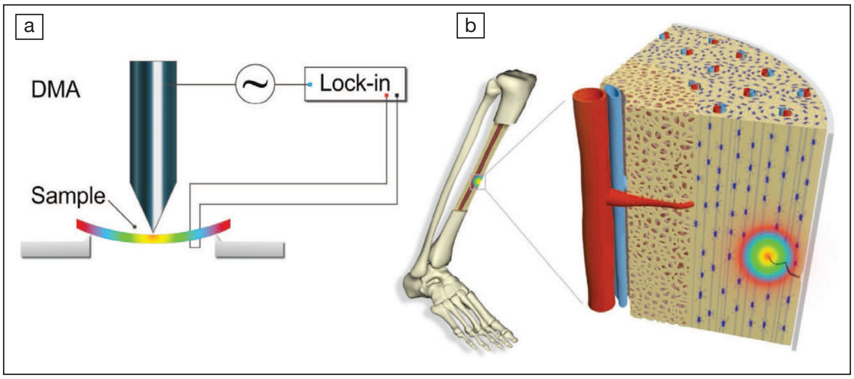
"This work is one of the first to study second-harmonic generation using soft x-ray pulses from a free-electron laser, which could be widely applied to study the interfacial chemical reaction that may be hidden in the materials," says Liang Zhang, a postdoctoral researcher with expertise in soft x-ray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

YuHao Liu

Bio Focus

Flexoelectricity found in bone

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.



(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 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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