Study reveals new insights into how hybrid perovskite solar cells work

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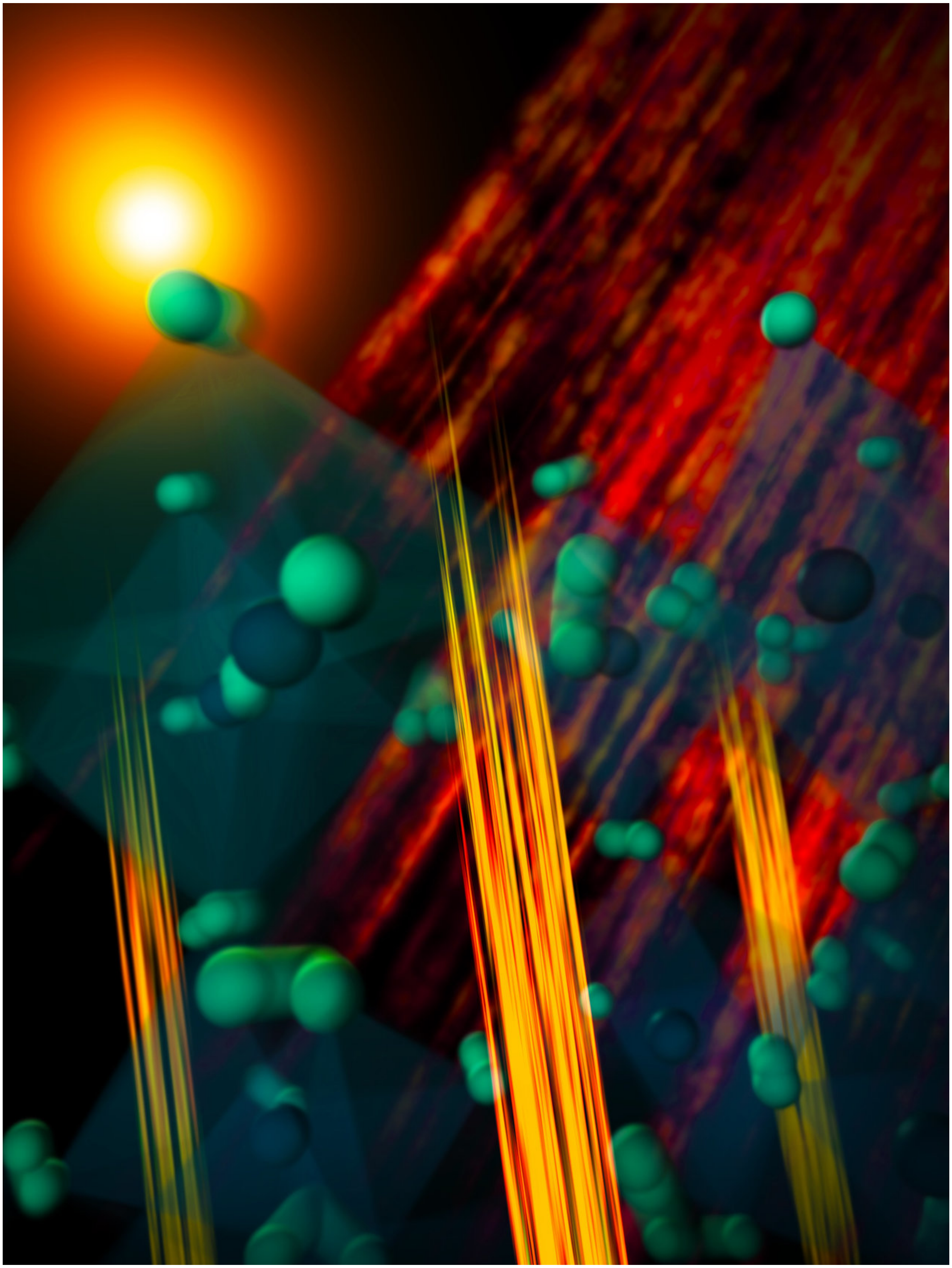

This illustration depicts what happens inside a hybrid perovskite material in the first few trillionths of a second after it's hit with simulated sunlight (upper left). The blue and green spheres are atoms, arranged in double pyramids as shown at left. When light hits, electrons start to separate from positively charged “holes,” the first step in creating an electrical current (yellow streaks). Meanwhile, atoms begin to vibrate within the perovskite’s lattice-like structure. Scientists detected these processes by analyzing the terahertz radiation (red streaks) the processes released. Credit: Greg Stewart/SLAC National Accelerator Laboratory

Scientists have gained new insights into a fundamental mystery about hybrid perovskites, low-cost materials that could enhance or even replace conventional solar cells made of silicon.

Under a microscope, a slice of perovskite looks like an abstract mosaic of random grains of crystal. The mystery is how this patchwork of tiny, imperfect grains can transform sunlight into electricity as efficiently as a single crystal of pure silicon.

A recent study by scientists at Stanford University and the Department of Energy's SLAC National Accelerator Laboratory offers new clues. Writing in the March 15th issue of *Advanced Materials*, the scientists provide a new understanding of how electric charges separate in perovskites a few billionths of a second following the absorption of light, the crucial first step in generating an electric current.

The study is the first to probe the inner workings of hybrid perovskites at the atomic scale using laser pulses that match the intensity of solar radiation, and thus mimic natural sunlight. The authors say their discovery could lead to improvements in the performance of perovskite solar cells and a new way to probe their functionality.

Perovskites and Silicon

Most solar cells today are made of purified silicon manufactured at temperatures above 3,000 degrees Fahrenheit (1,600 degrees Celsius). These rigid silicon panels can last for decades in all kinds of weather conditions.

Perovskite solar cells, although far less durable, are thinner and more flexible than silicon cells and can be produced near room temperature from a hybrid mixture of cheap organic and inorganic materials, like iodine, lead and methylammonium.

Researchers, including Stanford co-author Michael McGehee, have shown that perovskite solar cells are as efficient at converting light to electricity as commercially available silicon cells and can even outperform them. This combination of efficiency, flexibility and easy synthesis has fueled a worldwide race to develop commercial-grade perovskites that can withstand long-term exposure to heat and precipitation.

"Perovskites are very promising materials for photovoltaics," said lead author Burak Guzelturk, a postdoctoral scholar at Stanford and SLAC. "But people wonder how they can achieve such high efficiencies."

Electrons and Holes

All solar cells operate on the same principle. Photons of sunlight absorbed by the crystalline material kick negatively charged electrons into an excited state. The freed electrons leave behind positively charged spaces or "holes" that separate from one another. This separation gives rise to an electric current.

Pure silicon, with its highly ordered atomic structure, provides a direct path for electrons and holes to travel through the solar cell. But with perovskites, the road is far from smooth.

"Perovskites are typically filled with defects," said co-author Aaron Lindenberg, an associate professor at SLAC and Stanford and investigator with the Stanford Institute of Materials and Energy Sciences (SIMES). "They're not even close to being perfect crystals, yet somehow the electric currents don't see the defects."

Terahertz Emission

For the study, the research team used laser pulses to simulate waves of sunlight from both ends of the visible light spectrum – high-energy violet light and low-energy infrared light. The results were measured at the picosecond timescale. One picosecond is one trillionth of a second.

"In the first picoseconds after sunlight hits the perovskite, the electrons and holes in the crystalline lattice start to split," Lindenberg explained. "The separation was uncovered by measuring the emission of high-frequency terahertz light pulses oscillating a trillion times per second from the perovskite thin film. This is the first time anyone has observed terahertz emission from hybrid perovskites."

The terahertz emission also revealed that electrons and holes closely interact with lattice vibrations in the crystalline material. This interaction, which occurs on a femtosecond timescale, could help explain how electric currents navigate through the patchwork of crystal grains in hybrid perovskites.

"As the electric charges separate, we observe a sharp spike in the terahertz emission, matching a vibrational mode of the material," Guzelturk said. "That gives us clear evidence that the electrons and holes are strongly coupling with the atomic vibrations in the material."

This finding raises the possibility that coupling to the lattice vibration could protect the electrons and holes from charged defects in the perovskite, shielding the electric current as it travels through the solar cell. Similar scenarios have been proposed by other research teams.

"This is one of the first observations of how the local atomic structure of a hybrid perovskite material responds in the first trillionths of a second after absorbing sunlight," Lindenberg said. "Our technique could open up a new way of probing a solar cell right when the photon is absorbed, which is really important if you want to understand and build better materials. The conventional way is to put electrodes on the device and measure the current, but that essentially blurs out all of the microscopic processes that are key. Our all-optical, electrode-less approach with femtosecond time resolution avoids that problem."

Hot Electrons

The researchers also found that terahertz light fields are much stronger when perovskite is hit with high-energy light waves.

"We found that radiated terahertz light is orders of magnitudes more intense when you excite the electrons with violet light versus low-energy infrared light," Lindenberg said. "That was an unexpected result."

This discovery could provide new insights on high-energy "hot" electrons, Guzelturk said.

"Violet light imparts electrons with excess kinetic energy, creating hot electrons that move much faster than other electrons," he said. "However, these hot electrons lose their excess energy very rapidly."

Harnessing the energy from hot electrons could lead to a new generation of high-efficiency solar cells, added Lindenberg.

"One of the grand challenges is finding a way to capture the excess energy from a hot electron before it relaxes," he said. "The idea is that if you could extract the current associated with hot electrons before the energy dissipates, you could increase the efficiency of the solar cell. People have argued that it's possible to create hot electrons in perovskites that live much longer than they do in silicon. That's part of the excitement around perovskites."

The study revealed that in hybrid perovskites, hot electrons separate from holes faster and more efficiently than electrons excited by infrared light.

"For the first time we can measure how fast this separation occurs," Lindenberg said. "This will provide important new information on how to design solar cells that use hot electrons."

Toxicity and Stability

The ability to measure terahertz emissions could also lead to new research on non-toxic alternatives to conventional lead-based perovskites, said Guzelturk.

"Most of the alternative materials being considered are not as efficient at generating electricity as lead," he said. "Our findings might allow us to understand why lead composition works so well while other materials don't, and to investigate the degradation of these devices by looking directly at the atomic structure and how it changes."

More information: Burak Guzelturk et al. Terahertz Emission from Hybrid Perovskites Driven by Ultrafast Charge Separation and Strong

Electron-Phonon Coupling, *Advanced Materials* (2018). DOI: 10.1002/adma.201704737

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