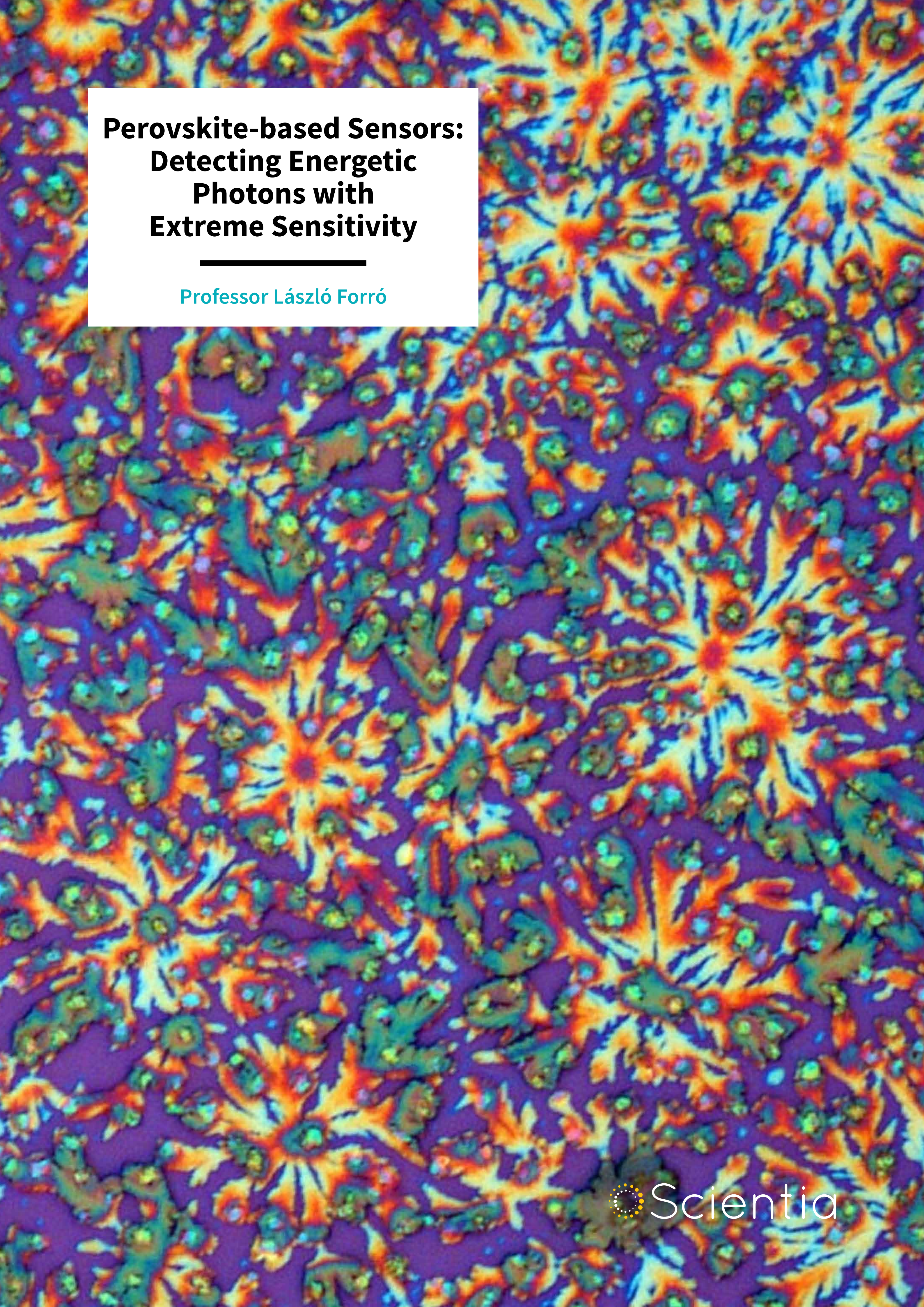


Perovskite-based Sensors: Detecting Energetic Photons with Extreme Sensitivity

Professor László Forró

Scientia

PEROVSKITE-BASED SENSORS: DETECTING ENERGETIC PHOTONS WITH EXTREME SENSITIVITY

Organo-metallic perovskite crystals are widely known for their ability to boost the performance of solar cells, with efficiencies reaching 25% and beyond. This is because photons of light can mobilise electrons in these materials with very high efficiency. **Professor László Forró** and his team at Ecole Polytechnique Fédérale de Lausanne have realised that this same ability could be harnessed in the development of high-performance sensors that detect photons of various energies. By integrating perovskite with graphene or carbon nanotubes, the team's detectors show outstanding sensitivity, with the ability to detect single photons. Their technologies are leading to new applications ranging from more sensitive medical diagnostics, to safer nuclear reactors.

Perovskites

Solar cells have made their way to the forefront of public discussion in recent years. With its ability to convert the energy contained in photons of sunlight into useable electrical currents, the technology promises to play an increasingly important role in renewable energy generation in the coming years. However, even the most advanced solar cells available today continue to face shortcomings relating to their efficiency. Although physical processes limit the efficiency of solar cells to 33.7% – with some energy inevitably being converted into unusable heat – the light-to-electricity conversion efficiencies of solar cells have remained particularly low, until recently.

Today, rapid improvements are being made to solar cell efficiencies, thanks to a special family of minerals named 'perovskites'. Featuring particular arrangements of atoms in orderly crystal lattices, these materials are both easy and inexpensive to manufacture, and are known to strongly absorb light across a broad range of frequencies contained within sunlight. As a result, they have enabled researchers to increase the efficiencies of some commercially available solar cells by over 25% in the past decade – promising a bright future for the industry. For Professor László Forró at the Swiss Federal Institute of Technology Lausanne, these exciting advances are only the beginning of perovskite's full potential.

Growing Sensitive Nanowires

While perovskite is already a highly advanced material, Professor Forró and his colleagues proposed in their earlier research that its efficiency could be raised even further if it were manufactured in the form of wires just a few nanometres in width. At first, they manufactured these so-

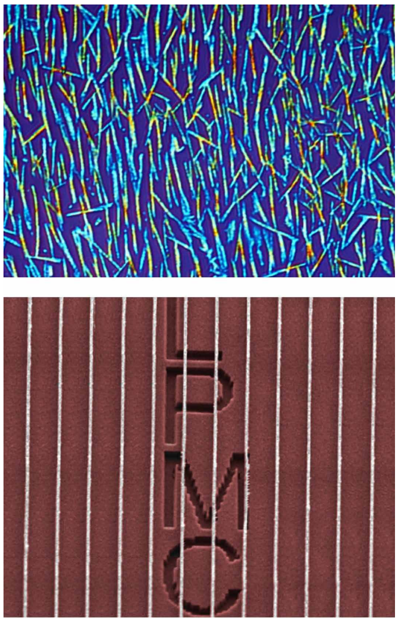
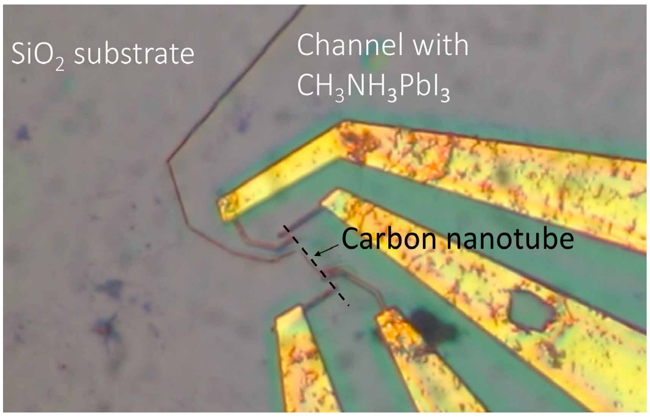


Figure 1: Nanowires grown by slip-coating (top) and in lithographic channels (bottom). Typical lateral dimensions are in the 10–500 nm range.

called nanowires using a 'slip-coating' method, whereby a perovskite solution is confined between two surfaces which slide in opposite directions.



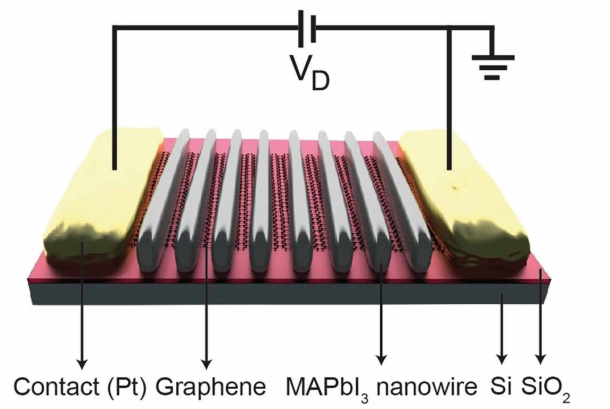


Figure 2: Photon detector comprising single carbon nanotubes and perovskite nanowires (left). Supersensitive photon detector based on graphene and perovskite nanowires (right).

As the liquid evaporated, the crystal grew out of groups of bonded atoms named 'nucleation centres'. The result was a network of solid wires, which spread out in patterns resembling the seeds of a dandelion (Figure 1; top). The material used by the researchers was a 'lead halide' perovskite – where each unit of the crystal lattice features an atom of lead, and three atoms of a halogen element, such as bromine. Lead halide perovskites are widely known for their excellent ability to convert light into electrical current, meaning each of the team's nanowires could function as a microscopic, highly efficient solar cell.

Following on from their initial studies, Professor Forró and his team members, Pavao Andričević, Endre Horváth, Márton Kollár, Bálint Náfrádi, Gábor Náfrádi and Massimo Spina, showed how nanowire fabrication could be improved further. They did so by etching a series of nano-sized channels into layers of silicon, and then depositing a lead halide solution inside them. Since the liquid could move to fill the channels through the process of capillary action, this gave the researchers far more control over the lengths, widths, and orientations of their nanowires (Figure 1; bottom). This technology already promised to improve the capabilities of perovskite solar cells – but the team's nanowires would soon be surpassed by even more advanced structures.

Boosting Performance with Carbon Nanotubes and Graphene

As research into perovskites was gathering pace, another material that was increasingly grabbing the attention of physicists was graphene. Featuring atom-thick layers of carbon arranged in a honeycomb pattern, the structure of graphene makes it an excellent electrical conductor. By introducing other materials to the carbon honeycomb, its electrical properties can be improved even further. In addition, graphene can be 'rolled' into thin cylinders, creating structures named carbon nanotubes – which possess their own unique electrical properties.

Professor Forró's team showed how lead halide perovskite nanowires could be grown directly on the surfaces of carbon nanotubes or graphene (Figure 2). As photons of light interact with the perovskite, the electrons they contained jumped into higher energy levels, leaving behind positively-charged 'holes', which behave like particles in themselves. Afterwards, these holes and electrons could be rapidly transferred to the carbon nanotubes or graphene – amplifying the electrical signal produced by the perovskite.

Working together, the perovskite material with nanotubes or graphene can convert the energy contained in photons into electrical current with extremely high efficiency. Their combined properties make them around ten-million times more responsive to light – producing detectable currents from a single photon. In addition, the setup could operate over a wide region of the electromagnetic spectrum: from ultraviolet to red light. Immediately, the benefits of these materials to detector technologies were clear.

In a similar study, the team grew perovskite onto the surfaces of vertically-aligned 'forests' of carbon nanotubes (Figure 3). 'The perovskite engulfs the carbon nanotubes, providing an excellent interface between these two materials,' explains Professor Forró.

His team now hopes to investigate whether their carbon nanotube forests could be used to create high-performing solar cells. 'For photodetectors this technology works perfectly, and it remains to be seen whether it could be expanded to solar panels,' says Professor Forró.

Harvesting Energy from X-rays

X-rays carry far more energy in their photons than visible light, which could in theory produce stronger electrical currents if successfully absorbed by perovskite materials. Unfortunately, however, these photons cannot be easily harvested using existing solar cells. After prolonged exposure to x-rays, the crystal structures of these materials will instead become

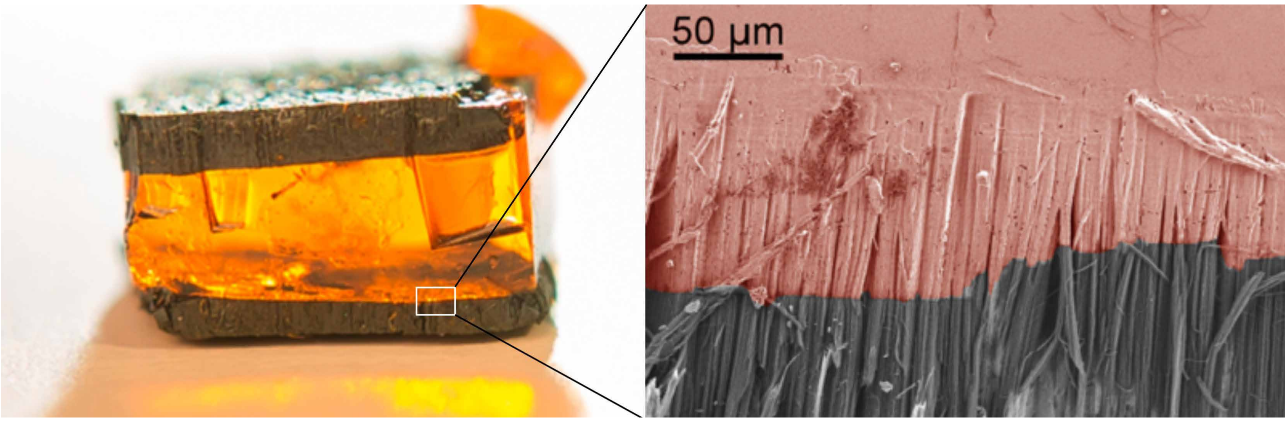


Figure 3: Perovskite crystal with carbon nanotube 'forest' electrodes at both sides (left). Magnification of the interface, showing that the perovskite material (coloured) engulfs the vertically aligned forest of carbon nanotubes, creating a perfect contact (right).

damaged, diminishing their ability to convert further incoming photons. So far, this has meant that x-rays needed to be prevented from reaching solar cells, restricting access to a large fraction of the energy radiated by the Sun. Through their research, Professor Forró and his colleagues aimed to alleviate this issue.

This time, the team assessed the properties of a lead halide containing iodine – the heaviest of the four stable halogen elements. Not only does this perovskite possess a high light-to-electricity conversion efficiency – the heavy atomic nuclei it contains can also readily absorb x-ray photons, without sustaining significant damage. Furthermore, the material remains stable over long periods of time, even when exposed to high doses of x-ray radiation.

These properties were clearly promising, but the material alone cannot generate useful electrical currents. Through their latest research, the team has developed a new approach to achieve this goal.

Aerosol-jet Printing

In this study, the researchers used a novel 3D-printing technique named 'aerosol-jet' printing. In this method, a solution containing perovskite in the form of tiny droplets is focused onto specific places on a surface using a jet of nitrogen gas. After being fired from a fine nozzle, the solvent within these droplets will mostly evaporate during flight, and perovskite crystals grow, before being deposited onto the surface of a material called a substrate. This technique enables researchers to deposit materials in highly intricate patterns, such as networks of spirals and pillars (Figure 4; top), onto a wide variety of different substrates. In their study, Professor Forró's team used aerosol-jet printing to deposit their perovskite material in a specific pattern on a graphene substrate.

To maximise the performance of the perovskite, the team printed it out in a grid-like pattern of straight, interlocking lines, featuring tall pillars of material where the lines met. Like with the carbon nanotubes used in their previous studies, the holes produced when electrons were excited by x-rays could then rapidly transfer to the graphene substrate, amplifying the perovskite's electrical signal. Through their experiments, Professor Forró and his colleagues demonstrated an x-ray sensitivity over 10,000 times greater than current state-of-the-art devices. One particularly important application for this technology lies in medical diagnostics.

Safer X-ray Doses

X-rays have long been widely used in medicine, owing to their ability to pass straight through many lower-density materials, including biological tissues, without being absorbed. Crucially, they enable doctors to view higher-density regions inside the body, particularly bone, without the need for invasive operations.

Today, x-rays are used in diagnostic techniques including radiography, fluoroscopy, and CT scans. Unfortunately, however, these processes can expose patients to high amounts of ionising radiation, inducing DNA damage and increasing their risk of developing cancer.

Through access to technologies that are more sensitive to x-rays, doctors would be able to obtain the information they need with far smaller x-ray doses, greatly reducing this risk. Using an aerosol-jet printed perovskite pattern with a highly sensitive detector, x-rays could simply be detected by photocurrent measurements, without the need for a complex electronic set-up.

By encapsulating perovskite layers within a specialised polymer, the researchers demonstrated an advanced detector (Figure 4; bottom), which produced reliable electrical signals from far lower x-ray intensities than those currently used in medicine. At the same time, the device remained stable for over nine months, with no degradation in performance. The

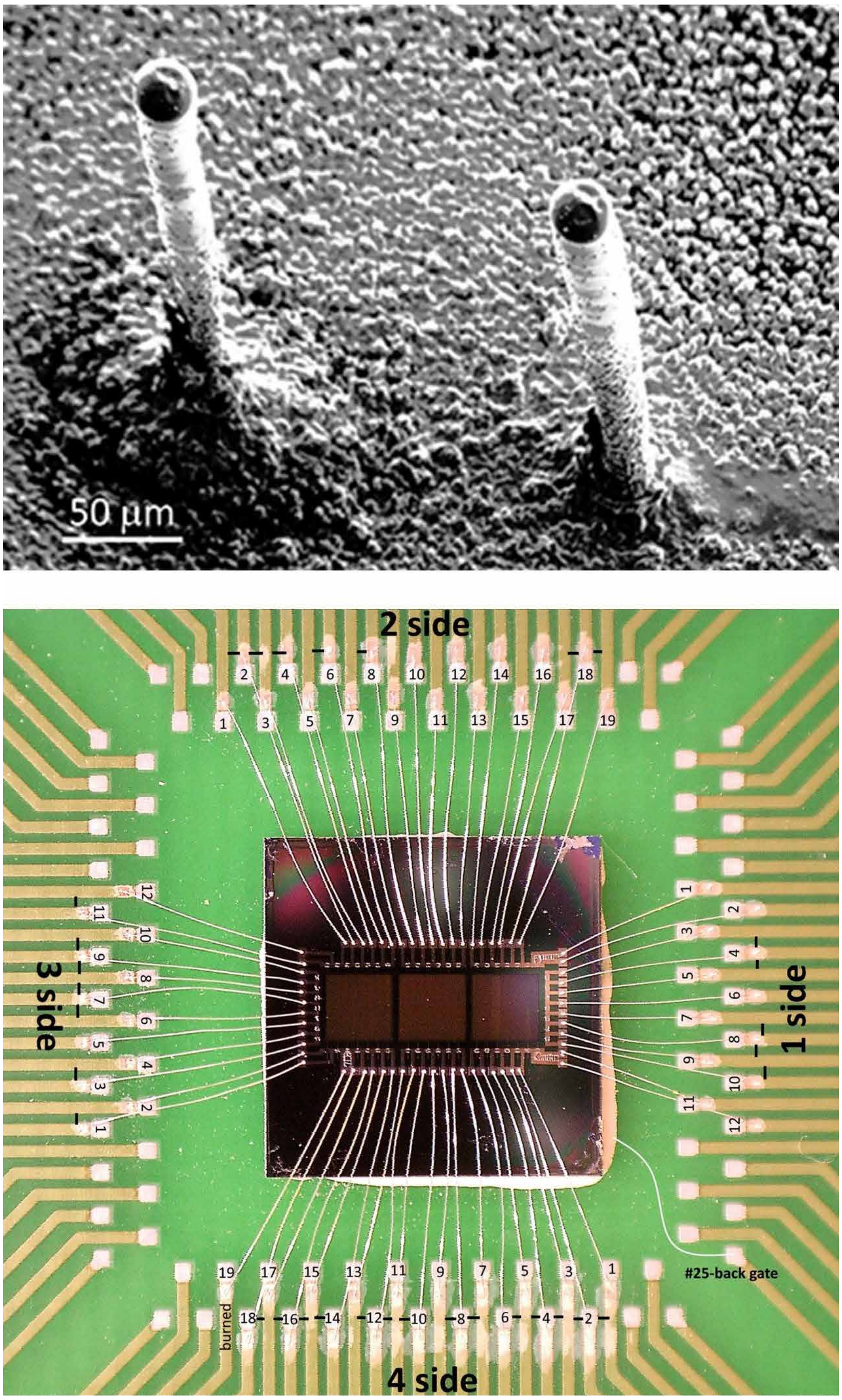


Figure 4: Pillars of perovskite deposited by aerosol jet printing for detecting x-rays (top). Chip for the image plate of the x-ray detector (bottom).

clear success of the team's approach could now open up new routes towards safer x-ray diagnostics, without incurring significant costs for healthcare organisations. This achievement was another victory for the team, but their work was still not done yet.

Kilogram-scale Crystals

Occupying the highest range of energies of all frequencies in the electromagnetic spectrum, gamma rays are released during the decay of highly radioactive atomic nuclei. They can be highly damaging if they come into contact with many materials, particularly biological tissues – creating a crucial need to tightly monitor gamma ray photons wherever they are produced. However, with such high energies, gamma rays are very rarely absorbed even within higher-density materials, passing straight through most crystals, making them incredibly difficult to detect.

In their latest research, Professor Forró's team overcame this issue through a new technique for fabricating perovskites on scales of kilograms. To overcome limitations in the sizes of the crystals – which are typically just millimetres across, the researchers aligned many smaller, cube-shaped crystals side by side. Then, they immersed them in a solution, fusing them seamlessly together.

The result was a single block of perovskite some 3.8 kilograms in mass (Figure 5) – which was by no means an upper limit, with even heavier crystals possible through the fusing of further smaller crystals. Within this highly sensitive block, enough heavy atomic nuclei were present to absorb a fair proportion of incoming gamma ray photons, producing a reliable electrical signal.

Safer Nuclear Reactors

Unlike many previous studies into the capture of gamma rays, Professor Forró and his colleagues are not solely focused on detecting them. Rather, they propose that just like visible light and x-rays, the large amounts of energy they contain could be harvested for practical use. This idea is particularly relevant in nuclear power generation.

With its high energy yield, and complete lack of carbon emissions, many researchers believe that an increased rollout of nuclear power alongside renewable sources will be key to tackling climate change. All the same, due to several catastrophes being triggered by nuclear power plant malfunctions in previous decades, there is still a strong reluctance among governments and the public alike to take these steps.

Although the chances of such malfunctions are now minuscule with present-day technologies, Professor Forró's team proposes that their safety could be improved even further with the ability to harvest the energy of gamma

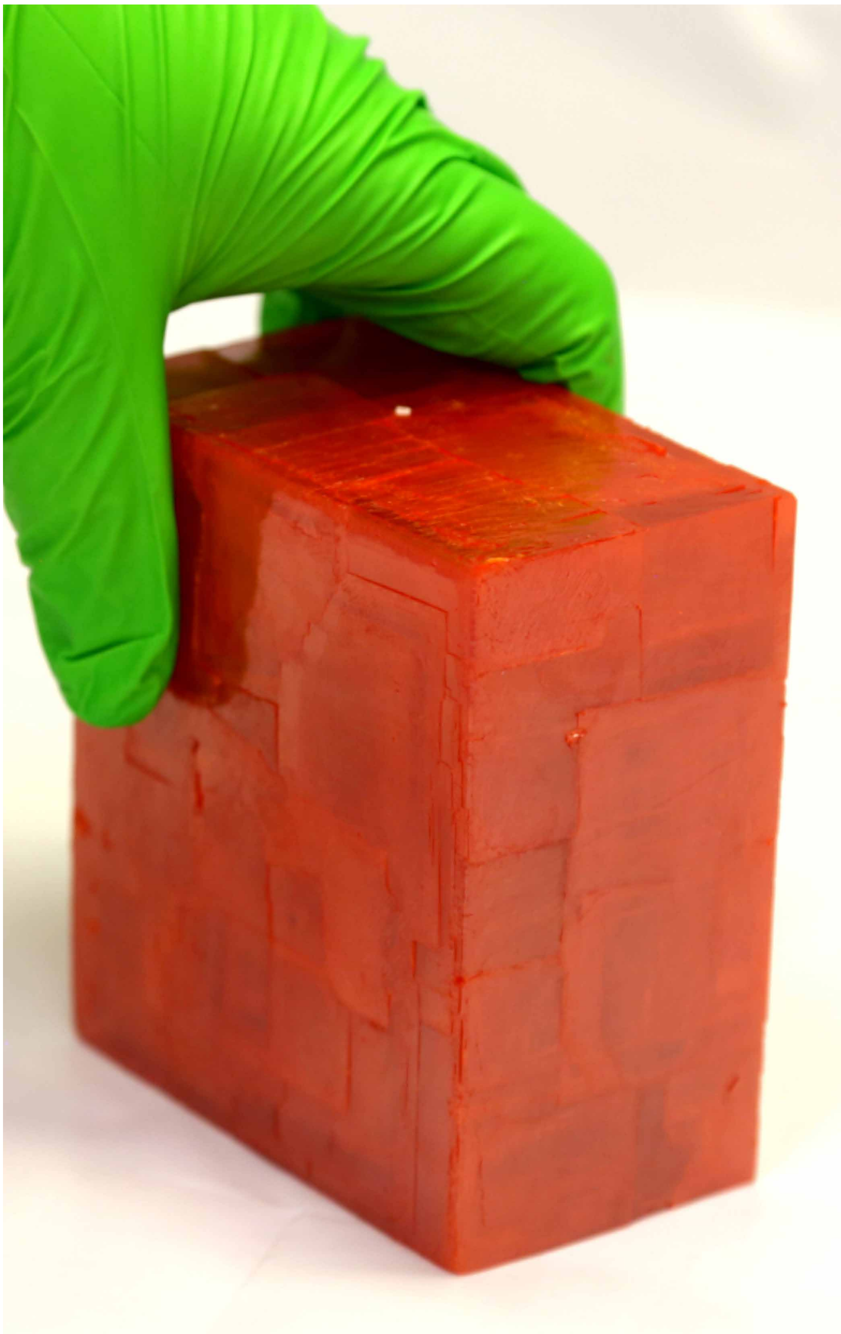


Figure 5: 3.8-kilogram perovskite crystal for gamma ray detection.

rays directly. For example, they propose that the 2011 Fukushima disaster could have been largely prevented, had just 1% of the reactor's remnant gamma radiation been converted into electricity, helping to power the reactor's cooling system. Such conversions could be easily achieved using the team's massive perovskite crystal. By utilising the electrical signals produced as gamma ray photons interact with such a material, their radiation could finally become useful, instead of solely damaging.

Powering Interplanetary Spacecraft

One final promising application of the team's techniques relates to spacecraft undergoing interplanetary voyages. While on Earth's surface, the atmosphere largely protects us from intense x-rays and gamma rays produced by the Sun, any vehicle travelling through outer space will be completely unshielded from this radiation. This is a particular problem for solar cells, which can be crucial power sources for spacecraft undergoing missions spanning many years. Without adequate protection, these devices can steadily diminish in performance over time.

To address the issue, Professor Forró and his colleagues propose that lead halide perovskites can be used to convert high-energy x-ray and gamma ray photons into electrical power in outer space – where sunlight is faint, but cosmic radiation is abundant. Since they absorb these photons very efficiently, they can also protect the delicate parts of the spacecraft. 'It is kind of a miracle, that these perovskite materials withstand high energy radiation, without being damaged,' says Professor Forró.

Through further improvements, their high-durability over long periods of time could make them suitable for use in spacecraft electronics. If integrated onto solar cells, these materials could enable unmanned probes to travel to distant regions of the Solar System in far better condition.

A New Region for Energy Harvesting and Detection

With such a wide array of important applications, Professor Forró's team hopes that through the growth of perovskites on carbon nanotubes, their deposition on graphene substrates through aerosol-jet printing, and the production of massive perovskite blocks, we could soon see widespread use both in research, and in our everyday lives.

For now, the researchers will continue to improve the capabilities of their materials and techniques even further, with the ultimate aim of making them widely available. They also hope to expand their applications into other areas, such as neutron detection. If their goals are achieved, these technologies could lead to the widespread ability to detect and harness photons in the highest-energy regions of the electromagnetic spectrum.

Meet the researcher

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László Forró obtained his BS in physics at Eötvös Loránd University, Budapest, and his MS at Université Paris XI. He then received his PhD from the University of Zagreb in 1985. He was full professor at the Ecole Polytechnique Fédérale de Lausanne, holding the chair of Nanostructures and Novel Electronic Materials. This autumn, he will move to University of Notre Dame (USA), where he will create and direct the Stavropoulos Center for Complex Quantum Matter. Through his work, Professor Forró develops experiment-driven partnerships, with a focus on correlated matter, the design of new nanostructured materials and biological physics. This vision has led him to founding and organising a bi-annual conference in Dubrovnik (http://dubrovnik.epfl.ch/) with the theme: From Solid State to Biophysics. Throughout his career, he has achieved many honours and awards, including the Spiridon Brusina Award of the Croatian Society of Natural Sciences and the Serbian Material Science Society Award. He is also a Doctor Honoris Causa of the University of Szeged and the Technical University of Budapest, and a Member of the Hungarian Academy of Sciences, the Croatian Academy of Sciences, and the Serbian Academy of Sciences.

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