

Materials chemistry

Molecular engineering enables bright blue LEDs

Hendrik Utzat & Maria Ibáñez

Future LEDs could be based on lead halide perovskites. A breakthrough in preparing device-compatible solids composed of nanoscale perovskite crystals overcomes a long-standing hurdle in making blue perovskite LEDs. **See p.679**

Light-emitting diodes (LEDs) now serve as energy-efficient replacements for incandescent light bulbs, and provide high colour saturation and brightness in display technologies. Nevertheless, the search for even more efficient devices continues, and LEDs based on a class of semiconductor called lead halide perovskites show particular promise¹. The development of stable blue-emitting perovskite LEDs has long been hampered by challenges in the materials chemistry of these semiconductors. On page 679, Jiang *et al.*² report a remarkably simple process that provides stable light-emitting layers of nanosize perovskite crystals. The authors used these films to make blue-emitting LEDs that convert charge carriers into photons with record-breaking efficiency, a key advance in the development of perovskite-based lighting and displays.

LEDs work by converting electrical energy into photons in a layer made of a semiconductor. Research into new semiconductor materials is key not only to further improving the energy efficiency of these devices, but also to enabling new functionalities – flexible LEDs, for example, or devices that control the polarization of the emitted light, as is needed for holography and 3D displays.

Various classes of semiconductor are used in LEDs, including those composed of chemical elements from groups III and V of the periodic table (III–V semiconductors) and organic semiconductors. In general, the development of LEDs that emit blue light has proved especially challenging, because blue-emitting materials are typically particularly sensitive to imperfections in their crystal structures and surfaces and are prone to degradation – the 2014 Nobel Prize in Physics was awarded to scientists who made great progress in addressing this problem (see go.nature.com/3hcsch8).

In an LED, an electric current injects charge carriers (negatively charged electrons and positively charged ‘holes’) into the semiconductor. When the two types of carrier meet, they annihilate, emitting photons of a colour that

corresponds to the energy difference between the carriers. To shift the wavelength of the light emitted by crystalline inorganic semiconductors towards the blue end of the visible spectrum, a common strategy has been to reduce the crystal size to a few nanometres (see ref. 3, for example). In such tiny crystals, an effect known as quantum confinement increases the energy difference between electrons and holes, thereby blue-shifting the emission. The quantum confinement of charge carriers in semiconductor nanocrystals – aptly referred to as quantum dots – ideally also enhances the luminosity of the semiconductor, and thereby the carrier-to-photon conversion efficiency.

However, reducing the size of semiconductor crystals down to a few nanometres

can produce surface defects that lower this efficiency by dissipating the charge carriers’ energy as heat. Diverse types of defect are known, but for quantum dots, broken chemical bonds at the surface are the main culprit. Intricate synthetic strategies are therefore required to remove defects by fixing (passivating) surface bonds. These strategies include covering the quantum dot with organic ligand molecules, which bind to its inorganic surface, or with a layer of a different inorganic semiconductor. Decades of research into III–V semiconductor quantum dots were required to formulate the robust materials syntheses needed to produce efficient quantum-dot LEDs (see ref. 4, for example).

Although surface ligands can passivate defects and provide a handle with which to control the size of the quantum dot, they add an extra challenge to the fabrication of devices. The ligands typically constitute a ‘head’ group, which binds chemically to the inorganic semiconductor, and a long organic ‘tail’. These tails are needed during the chemical synthesis, but act as electrical insulators that impede the injection of charge carriers when the resulting quantum dot is used in devices. Chemical procedures to exchange the long insulating ligands with shorter, conducting ones are therefore required, adding complexity to the fabrication of LEDs. Charge injection can also be hampered when passivation is achieved by a secondary layer of a different semiconductor, and crystal strain produced at the interface between the two semiconductors

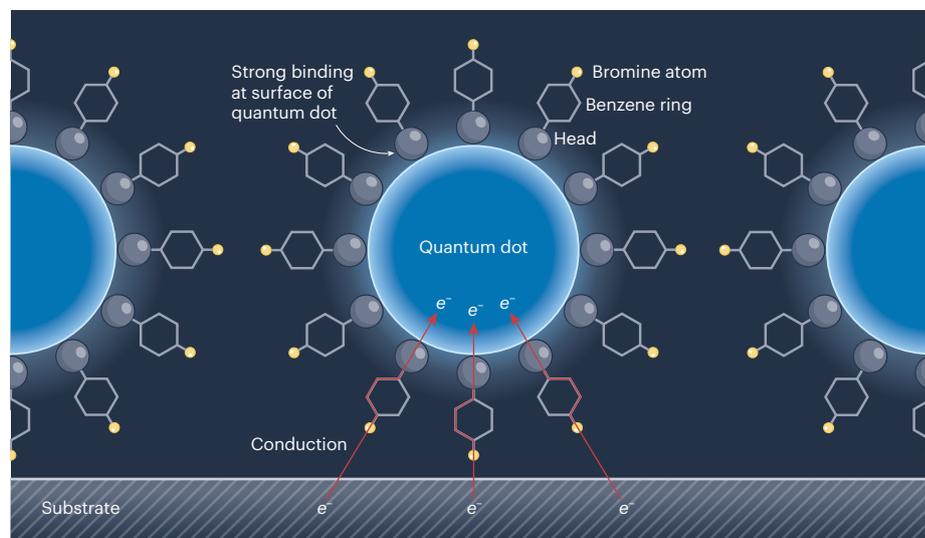


Figure 1 | *In situ* formation of solids for blue-emitting perovskite quantum dots. Jiang *et al.*² report a simple method for preparing nanoscale crystals (quantum dots) of semiconducting materials known as lead halide perovskites. The quantum dots form in a 2D array on the surface of a substrate, surrounded by a protective layer of organic ligand molecules. The ligands have a bulky ‘head’ and an electrically conductive ‘tail’, which consists of a benzene ring with a bromine atom attached. The tail allows charge carriers such as electrons to be injected into the quantum dots from the substrate, and the bulky head prevents ligands from becoming part of the perovskite crystal structure. The bromine atom alters the electronic properties of the ligands, increasing the strength with which the head binds to the perovskite core. Overall, the ligands promote the formation of small, stable quantum dots that emit blue light when injected with electrons. The authors use the assembled quantum dots to make LED devices.

can reduce the emission quality.

The electronic structure of lead halide perovskites makes photon emission in these materials much more resilient to the presence of crystal and surface defects than in III–V semiconductors, and might allow quantum-dot devices to be made without the need for rigorous surface-passivation methods. Highly efficient emission from perovskite quantum dots in solution has been demonstrated, including in the notoriously challenging blue spectral region⁵, but the fabrication of blue-emitting LEDs has been challenging. This is because ultra-small, quantum-confined perovskite quantum dots are not stable enough to withstand the elaborate procedures used to deposit them from solution to form solids and to exchange ligands at their surfaces, as is needed to enable effective injection of charge carriers into the quantum dots in devices⁶.

Jiang and colleagues now report a conceptually novel method for forming quantum-confined, blue-emitting quantum dots directly on the substrate of a device, circumventing the need for deposition and ligand exchange. Their method is remarkably easy to carry out: chemical precursors of perovskites are simply mixed with ligands on the surface of a substrate, directly yielding a layer of the desired quantum dots.

The key to success lies in the rational design of the ligands (Fig. 1). First, the authors' choice of a small, electrically conductive tail allows injection of electrons and holes into the inorganic quantum dots in the emissive layer of the devices. Second, the use of a bulky head group stops the ligand molecules from binding in the voids in the perovskite crystal structure, thus preventing the formation of a phase known as a layered perovskite, which has undesirable properties⁷. Finally, the incorporation of an electron-attracting halogen atom (such as a bromine atom) into the tail increases the strength of binding of the head group to the perovskites. Overall, these ligand effects thermodynamically favour the formation of stable perovskite quantum dots that are small enough to have the quantum confinement needed for blue emission.

The authors' method provides highly emissive, colour-pure solids of quantum dots, meeting the stringent requirements of energy-efficient blue-emitting perovskite LEDs. Indeed, the authors used their method to make LEDs that surpass the best carrier-to-photon conversion efficiencies of previously reported perovskite devices by a factor of up to two⁸.

The reported method for making solids of perovskite quantum dots might lead to further advances in the development of perovskite LEDs. It should be noted that the stability of perovskite quantum-dot LEDs is not yet competitive with that of equivalent devices that use III–V semiconductor quantum dots, but there is likely to be room for improvement

as the chemistry of lead halide perovskites becomes better understood and controlled. Advances such as those of Jiang *et al.* might also present opportunities for making solids composed of strongly coupled quantum dots, for example as non-classical light sources that exhibit exotic quantum behaviour⁹.

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The authors declare no competing interests.

Medical research

A refined use of mutations to guide immunotherapy

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Assessment of a tumour's mutational profile offers a way of predicting a person's response to anticancer therapies called immune-checkpoint inhibitors. It seems that such approaches might fall short for people who are not of European ancestry.

Immunotherapy harnesses the immune system to target tumour cells, and is used to treat several types of cancer. The therapy targets 'immune checkpoint' proteins, such as the protein PD-1, that can dampen immune responses. However, only a subset of people respond to treatment with what are called immune-checkpoint inhibitors (ICIs)¹. Writing in *Cancer Cell*, Nassar *et al.*² provide insight into how decisions to use such treatments might be improved.

A measurement called the tumour mutation burden (TMB) is defined as the number of somatic mutations in the protein-coding

“Reference genomes tend to have a European-descent bias in terms of the genetic variation represented.”

region of the genome (the exome) per million bases of DNA. (Somatic mutations are those that are not inherited (germline) and that instead arise after birth.) The TMB correlates with the overall response to ICIs: in general, a better response is observed in certain types of cancer, such as melanoma and lung cancer, that have a high TMB. For a specific type of cancer, tumours with a high TMB are thus more likely to respond to ICIs than are those with a low TMB. A high TMB could mean that many abnormal proteins have been generated that might be recognized by the immune

system and trigger an anticancer response.

A clinical study of the anti-PD-1 inhibitor pembrolizumab reported an objective response rate (corresponding to a reduction in tumour size) of 31.4% in people with a TMB of at least 175 mutations across the exome, compared with 9.5% for individuals with a TMB of fewer than 175 mutations across the same region³. The predictive value of TMB for a person's response was independent of other potentially relevant factors, such as expression of the protein PD-L1 (PD-1's binding partner); the tumour type; or the status of a genomic feature called microsatellite instability, which is associated with a high rate of a specific type of mutation.

Nassar and colleagues investigated how an individual's genetic ancestry affected TMB estimates obtained from sequencing specific genomic regions (Fig. 1). For this, the authors used sequencing panels, which focus on a selected set of genes that have variants known to be associated with cancer. Tissues from two groups of patients were assessed: one from the Dana–Farber Cancer Institute (DFCI) and the other from the Memorial Sloan Kettering Cancer Center (MSKCC), both in the United States.

People in the DFCI group had one of seven types of solid tumour, and their cancer had spread to other parts of their bodies. They had been treated with antibodies targeting PD-1, PD-L1 or another checkpoint protein called CTLA-4. The TMB of samples from these patients was determined using OncoPanel, a