

News & views

Materials chemistry

Triple-decker layered perovskite materials

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Layered perovskites are useful materials that contain sheets of a perovskite semiconductor enclosed by organic molecules. Crystals of layered perovskites that include sheets of a second inorganic lattice can now be grown from solution. **See p.355**

Materials consisting of atomically thin layers of semiconductors or metals are at the heart of a revolution in energy and information technologies, and constitute an inspiring platform for basic research into physical phenomena¹. The co-assembly of different types of these 2D materials can produce systems that have new functionalities. To ensure predictable and reproducible physical properties of such systems, the atomic order at the interfaces between the co-assembled materials must be well defined². However, current assembly approaches are time-consuming and technically demanding. On page 355, Aubrey *et al.*³ propose a different strategy based on solution chemistry, in which organic molecules promote the crystallization of further atomically

thin inorganic sublattices between the organic and inorganic layers of materials known as layered perovskites. The authors' method provides a highly versatile approach to engineering single crystals containing multiple heterostructures – in this context, referring to the interfaces between different 2D materials – with unusual and potentially useful properties.

The discovery of 2D materials such as graphene and metal dichalcogenides inspired the design of heterostructures in which atomically thin layers of materials that have different electronic behaviours are stacked in a controlled way. The resulting properties of such stacked materials have transformed the field of thin-film optoelectronics⁴. However,

these fascinating structures are produced by a costly, tedious and difficult process of layer-by-layer assembly, which in some cases involves mechanically stacking individual flakes that have been peeled (or exfoliated) from a van der Waals material (one in which 2D layers of atoms are weakly held together in the third dimension by van der Waals forces). This approach is challenging to scale up, and is severely limited in terms of its reproducibility and the number of layers that can be stacked, hindering the development of practical applications.

By contrast, materials known as layered perovskites are crystalline solids grown in solution through the spontaneous self-assembly of organic and inorganic components, thus stacking dielectric (electrically insulating) organic layers with semiconducting perovskite layers. Layered perovskites are analogues of materials called metal-halide perovskites (Fig. 1a,b) – which have a 3D lattice rather than a multilayered architecture, and are key components of a promising class of solar cell. Research into layered perovskites was boosted by the discovery that encapsulation of the semiconducting layers by organic molecules helps to stabilize lead-containing perovskites used in solar cells⁵.

Layered perovskites can be fabricated by using bulky, positively charged organic molecules that do not fit into the perovskite's 3D lattice, and that instead direct the formation of a layered architecture. A huge variety of organic cations can be used to make layered

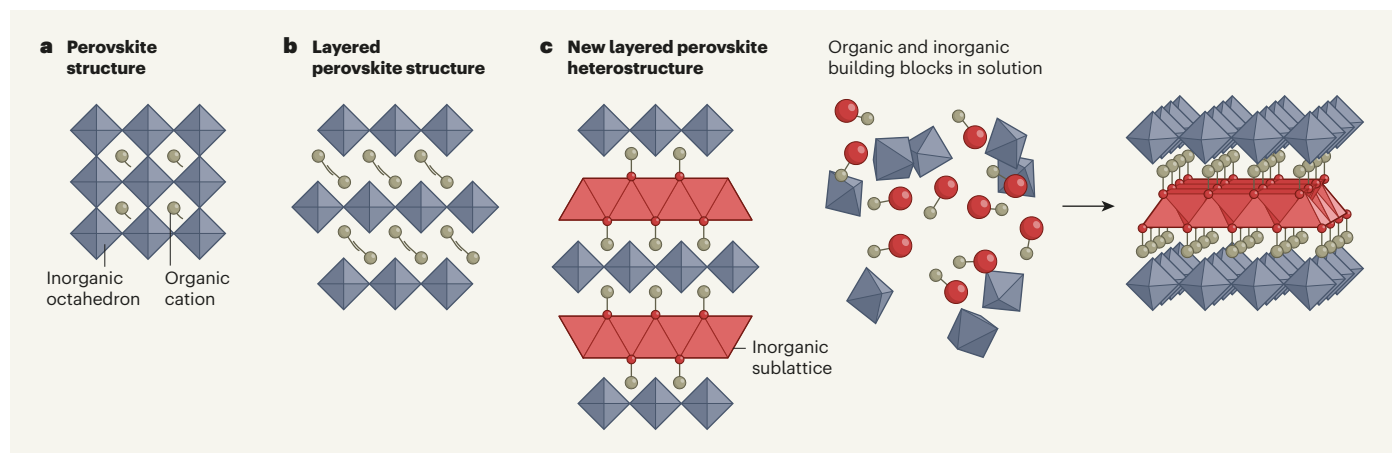


Figure 1 | Multilayer perovskite architectures. **a**, Perovskite materials consist of a 3D array of negatively charged inorganic octahedra that share corners and are held together by positively charged ions, such as organic cations. These cations can be organoammonium molecules that consist of a 'head' attached to a hydrocarbon 'tail', as shown in the cross-section of the 3D structure. **b**, If the organoammonium ions are too bulky to fit into the 3D lattice, a layered perovskite structure forms: the heads associate with layers of perovskite

octahedra, and the tails interact through van der Waals forces. The 2D inorganic perovskite layers are therefore encapsulated by organic phases. **c**, Aubrey *et al.*³ show that layered systems with greater complexity can form in solution if the organoammonium tails contain a chemical group that triggers the growth of another inorganic sublattice (red). This directed assembly process produces single crystals in which 2D layers with different electronic properties are stacked.

perovskites, thereby opening up a versatile strategy for designing new 2D nanomaterials⁶. This approach has already led, for example, to the preparation of materials that emit white light⁷, exhibit electrical conduction between layers⁸ or take advantage of the chirality (lack of mirror symmetry) of the organic groups⁹.

A family of organic cations called organoammonium ions has been widely used to make layered perovskites. These ions contain a positively charged ‘head’ group that binds to certain octahedrally arranged atoms in the inorganic perovskite layers, together with a hydrocarbon ‘tail’, which assemble into organic bilayers in the layered-perovskite architecture because of van der Waals interactions. Aubrey and colleagues now report that further chemical groups can be incorporated into the tails to direct the formation of the crystal lattice of a second inorganic compound (Fig. 1c).

The authors find that different chemical groups can act as templates for the formation of various sublattices that have distinct compositions and structures. A key achievement is that the resulting layered perovskites can be synthesized in acidic aqueous solutions – the metal salts that act as precursors of the sublattices are soluble in such environments, thus enabling their use in these reactions. In the resulting crystals, the two types of inorganic sublattice can, for example, either be well separated by large organic cations, and therefore be non-interacting, or can be linked by single atoms, which leads to interactions and mixing of the sublattices’ electronic properties.

Aubrey and colleagues’ method allowed them to make macroscopic single crystals of layered perovskites containing several hundreds to thousands of stacked layers, with perfect control of the atomic order at the interfaces between layers. The authors highlight the design freedom of their approach by integrating six different sublattices into layered-perovskite structures. For example, the authors report the formation of a material that contains lead chloride layers, in which the two different inorganic sublattices are separated by just one bridging chloride ion. The authors’ optical experiments and computational modelling show that the electronic wavefunctions of this material extend over both inorganic layers and exhibit a phenomenon called state mixing – which alters the optical properties of the material, such as its wavelength of emission and bandgap.

One advantage of heterostructures made from graphene and related 2D materials is that they have clean (uncontaminated), well-defined surfaces that enable investigation of their optoelectronic properties, and that aid their integration with other device platforms, such as silicon-based technologies. By contrast, solution-based fabrication

methods usually produce surfaces that are contaminated by organic residues. Innovative approaches for cleaning the surfaces of Aubrey and co-workers’ triple-decker perovskite crystals are therefore needed – perhaps involving cleavage or exfoliation of the crystals.

Nevertheless, the versatility of Aubrey and colleagues’ fabrication strategy raises expectations that a wide variety of single-crystal materials could be produced in the future. The impact of these findings will depend on whether the materials exhibit exciting phenomena, such as quantum effects, ‘topological’ electronic states that lead to spatially dependent conductivity, or unusual optical behaviour. An even greater range of compositions and optoelectronic properties might become possible using post-fabrication processes such as ion exchange¹⁰ (in which a specific type of inorganic ion in the perovskite layers is replaced by a different type). Future device applications will depend on whether the sublattices can improve key functionalities

of layered perovskites – for example, their electrical conductivity, which would make them useful as integrated electrodes in light-emitting diodes and solar cells.

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Genetics

Mutation fingerprints encode cellular histories

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Cells continually acquire mutations and pass them on to their progeny. The mutation profiles of human cells shine a light on the cells’ developmental history and their dynamics in adult tissue. **See p.381, p.387, p.393 & p.398**

The human body consists of trillions of cells that perform innumerable tasks as members of different organ systems. They are all descendants of the fertilized egg, which divides again and again to generate large numbers of progeny during embryonic development. Later in life, cells continue dividing to compensate for cell death and to ensure consistent tissue function. The ancestral relationships between the body’s cells can inform us about their division and migration histories. Park *et al.*¹ (page 393), Coorens *et al.*² (page 387), Li *et al.*³ (page 398) and Moore *et al.*⁴ (page 381) now provide insights into human embryonic development and tissue maintenance by uncovering the lineage relationships between cells that reside in different parts of the body.

The common principle uniting the four studies is that they use mutations in the genome as markers for tracing lineage. Throughout their lives, cells continually acquire random mutations that are passed on to all their descendants as permanent tags. A

cell’s mutation profile therefore represents a fingerprint that encodes its ancestry back to the fertilized egg. By sequencing the genomes of cells from different parts of the body, ancestral relationships can be determined and a cellular ‘family tree’ can be constructed, enabling a retrospective view of the cells’ provenance and past behaviour.

The four studies showcase several fascinating applications of this principle. Park *et al.*¹ and Coorens *et al.*² shed light on the earliest stages of human embryonic development. They inferred the mutation profiles of individual cells from tissues collected from recently deceased adults at autopsy and constructed cell-lineage trees that visualize how the cells relate to each other. The branching points of such trees represent cells that existed in the past and can resolve the first embryonic cell generations in great detail (Fig. 1a).

Consistent with previous work^{5–7}, Park *et al.* and Coorens *et al.* observed that the first two discernible lineages (which could well be the two cells that arise from the first division of