How atomic level control of functional materials design is driving science innovation

Chris Allen, Principal Scientist at the UK's electron Physical Sciences Imaging Centre at Diamond Light Source

The discipline of materials science aims to understand the properties of materials as emergent phenomena from knowledge of their micro and atomic structure. The ultimate goal being atomic level control for the design of functional materials. Key to achieving this goal is obtaining accurate and precise knowledge of the atomic structure of materials.

Around the turn of the millennium, Harald Rose, Maximilan Haider, Knut Urban and Ondrej Krivanek published seminal papers demonstrating the power of aberration corrected transmission electron microscopy to enable atomic resolution imaging of materials. In recognition of this work, these four scientists were awarded the Kavli Prize in nanoscience in 2020. Aberration corrected transmission electron microscopes are now a key component in the understanding and development of novel materials for almost every imaginable application from catalysts for hydrogen production to ultra-strong alloys, novel photovoltaics and nano-electronics.

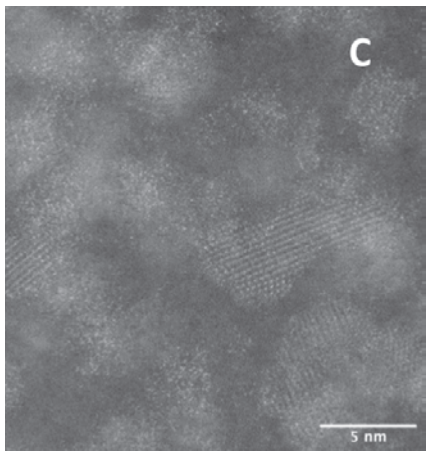
The electron Physical Sciences Imaging Centre (ePSIC) is a UK national facility for aberration corrected electron microscopy based at Diamond Light Source, the UK national synchrotron. ePSIC provides access to advanced aberration corrected electron microscopes with support from expert staff scientists. Since opening in 2016, ePSIC has welcomed users from over 50 different institutions from around the world working on over 500 different experiments.

Case study: Getting a Good Look at Quantum Dots

At the nanoscale, the properties of matter are determined by quantum phenomena, and governed by size. Quantum Dots (QDs) are nanoparticles of light-emitting semiconductors, so tiny that the wavelength of light they emit is determined by their size, not their chemistry. By carefully controlling the synthesis process, manufacturers can create QDs that emit light across the breadth of the visible spectrum and into the infrared.

QDs are already used for QLED televisions, computer monitors and for medical applications such as identifying and mapping tumours. However, most are based on cadmium selenide, a toxic metal system that creates challenges for manufacturing, disposal and medical use. Indium phosphide (InP), already in commercial use, is a promising replacement. However, the standard synthesis of InP requires the use of tris(trimethylsilyl) phosphine, a highly reactive and dangerous phosphorous precursor.

In work recently published in Nanoscale Horizons, researchers from King's College London, the University of Oxford, the University of Cambridge, London South Bank University and Indiana University developed a significantly simpler synthetic methodology using a solid, air- and moisture-tolerant primary phosphine. This new methodology greatly improves the ease of QD synthesis in the lab, and potentially in industry.



High angle annular dark field (HAADF) STEM images of InZnP/ZnS (InZnP/ZnS, core grown at 45 minutes/120ºC degassing followed by 10 minutes 220ºC growth, followed by shell addition).

However, when you get down to the quantum scale the surface of the material becomes all-important, so any defects or oxidation can affect the optical properties. The performance of the QDs is improved by adding zinc (which enhances their optical brightness) and coating them with zinc sulphide, to give them a core/shell architecture.

Professor Green from Kings College London led the experiment and explained:

"We were aiming for a InZnP/ZnS core/shell structure, but how do we know we've achieved that, rather than simply a big mix of indium, zinc, phosphorus and sulphur? We brought our QDs to the electron Physical Science Imaging Centre (ePSIC), because it's one of the few facilities where we can look at these particles under a microscope. We can see the particles, and we can do an elemental analysis to see which elements are there, and where they are. We can check we've got the crystalline structure. Without looking at the particles, we can't know we've made what we hope we've made, so ePSIC is vital to this research."

The team need to do more analysis, but their initial results suggest that they have done exactly what they set out to do – make luminescent QDs using a safe phosphorus source. That means – for QDs at least – the future could be very bright indeed.

Related publication: Wang Y et al. Phosphinecarboxamide based InZnP QDs–an air tolerant route to luminescent III–V semiconductors. *Nanoscale Horizons (2023). DOI:10.1039/D3NH00162H.*

Case study: Nanoscale impurities seed degradation in novel solar materials

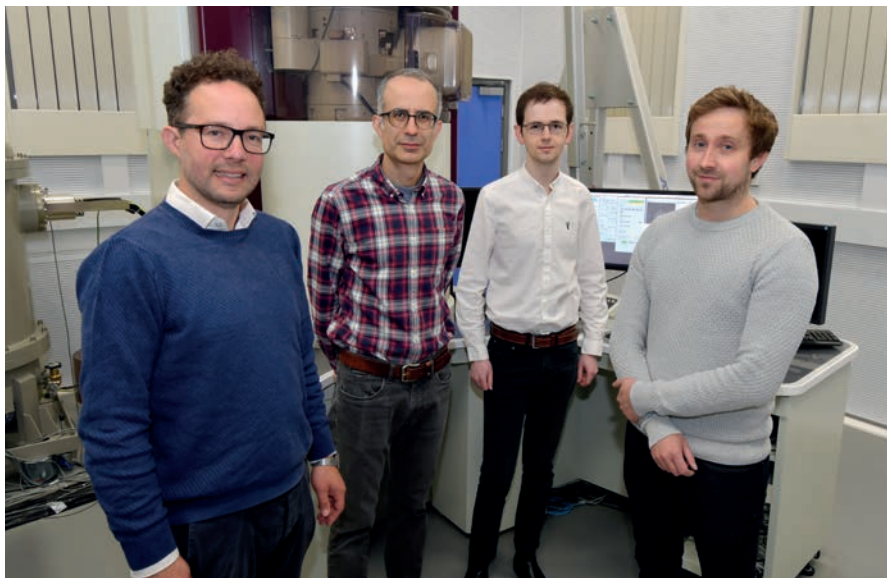
Perovskite materials offer a cheaper alternative to silicon for producing solar cells and also show great potential for other optoelectronic applications, including energy-efficient LEDs and X-ray detectors.

Metal halide salts – abundant and much cheaper to process than crystalline silicon – can be prepared in a liquid ink used to print a thin film of the material. In the past decade, improvements in the design and fabrication of metal halide perovskite (MHP) based solar cells have seen their efficiencies rise to compete with incumbent technologies and have laid the pathway to commercialisation. However, MHP stability, and thus the longevity of these light-harvesting devices, remains deficient.

A multidisciplinary team of researchers used Diamond's Hard X-ray Nanoprobe beamline (I14) and the electron Physical Science Imaging Centre (ePSIC) to gain new insight into the perovskite materials that hold so much potential in the field of optoelectronics. Low-dose Scanning Electron Diffraction (SED) measurements performed at ePSIC allowed the team to map the crystallography of their MHP samples with 5 nm resolution at various stages of ageing under light exposure, without triggering additional electron beam-induced degradation. They also used complementary experiments at I14 to survey the various crystallographic structures present.

Their results showed that photochemical degradation of the MHP samples (manifesting as a change in crystal structure and eventual morphisation) initially occurs in very localised sample regions. Crucially, these sample regions are crystalline grains or boundaries associated with unwanted material phases such as hexagonal polytypes and lead iodide – the same nanoscale structures that compromise light harvesting efficiency. The team concludes that degradation seeds at phase impurities due to their high density of defects, which act as both non-radiative recombination sites for charge carriers and fuel for fatal redox photochemistry. They uncovered one method of mitigating the formation of sinister hexagonal polytypes: controlled octahedral tilting of the perovskite lattice.

Their findings suggest that the localised presence of phase impurities are direct indicators of failure points in the absorber layer. The detection of such species through nanoscopic screening (such as high resolution electron microscopy) offers a means of predicting sites of instability during film optimisation and manufacturing for application in solar cells.



The ePSIC team at Diamond Light Source

There are several strategies for inducing beneficial octahedral tilt, including tuning the perovskite A-site cation or adding passivating organic molecules. New approaches should be developed to realise scalable, uniformly tilted and, thus, photo-stable MHP films on the manufacturing line. This research could significantly accelerate the development of long lasting, commercially available perovskite photovoltaics.

Related publication: Macpherson, S. et al. Local nanoscale phase impurities are degradation sites in halide perovskites. *Nature 607, 294–300 (2022). DOI: 10.1038/s41586-022-04872-1*

Case Study: Developing new catalysts for green hydrogen peroxide production

Hydrogen peroxide (H_2O_2) is one of the top 100 most important chemicals globally, in high demand in both daily life and industrial processes, including disinfection, sanitisation, wastewater treatment, paper pulp bleaching, chemical synthesis and textile production. It is considered an excellent 'green' oxidant due to the absence of byproducts (except water) upon use, relatively high redox potential, relative safety and low toxicity. However, the current industrial production method, the anthraquinone process, is energy- and waste intensive, requiring complex infrastructures. Therefore, a more ecofriendly and sustainable alternative technology for hydrogen peroxide production is needed.

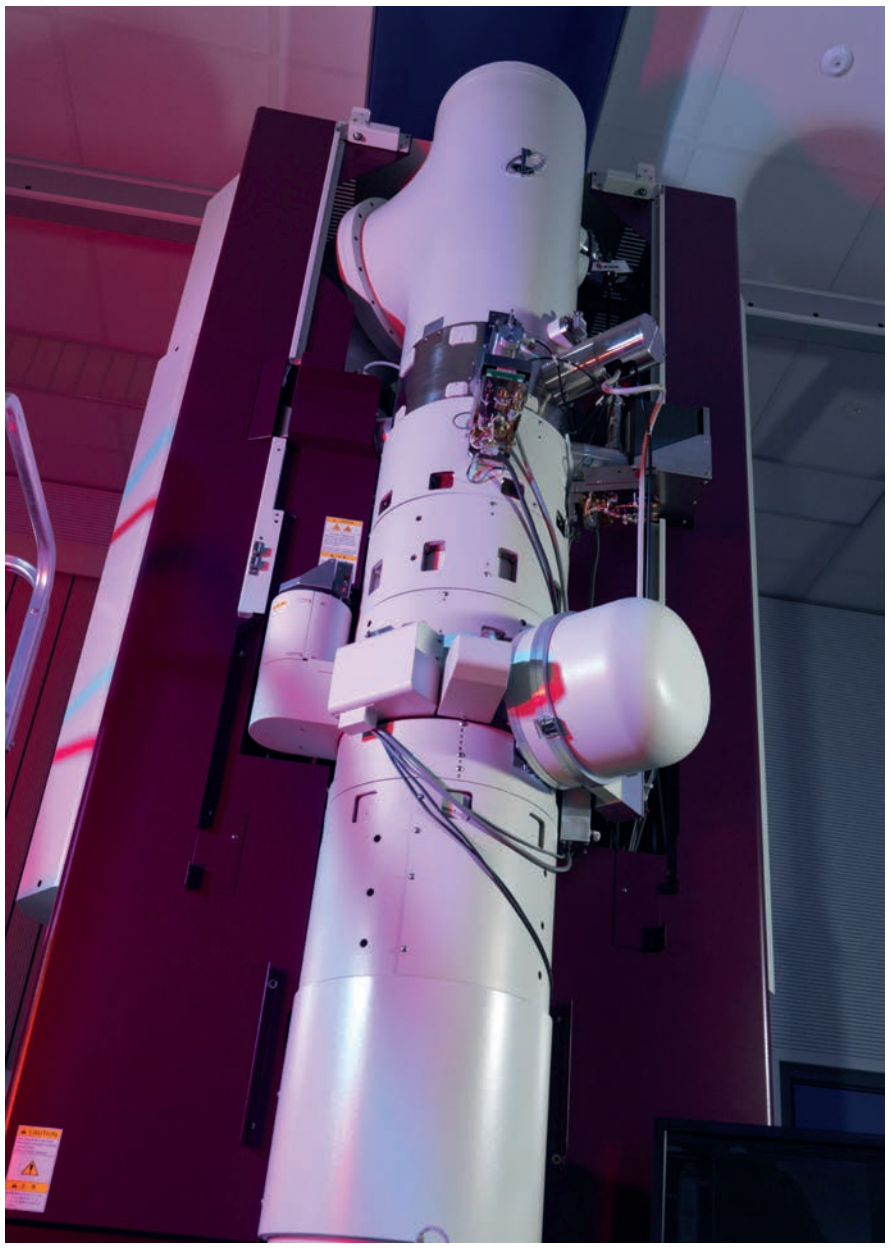
Selective electrocatalytic oxygen reduction reaction (ORR) via the 2-electron pathway appears to be an attractive and feasible route that enables portable, on-demand, and distributed hydrogen peroxide synthesis. However, hydrogen peroxide production through ORR requires highly active and selective electrocatalysts.

Although platinum-group metals (PGMs) are known to be state-of-the-art ORR catalysts, their scarceness and low mass activity significantly hinder their practical use, calling for alternative electrocatalysts. Single-atom catalysts (SACs) have the potential for catalysing the ORR. However, they suffer from limited activity and selectivity, and we currently lack methods to improve their performance. Therefore, it is important to develop synthetic strategies to obtain SACs with tuned coordination environments and electronic structures that can enhance catalytic performance for realising highly efficient hydrogen peroxide electrosynthesis.

A team of researchers from China performed Annular Dark-Field Scanning TEM (ADF-STEM) at ePSIC as part of a project to develop a highly selective and active Co-N-C electrocatalyst for hydrogen peroxide electrosynthesis. The setup at ePSIC enabled them to minimise the sample damage caused by the electron beam and identify the metal atoms dispersed on the graphene support as bright dots. The team successfully developed a facile and transient microwave irradiation treatment to simultaneously achieve the regulation of the coordination number and the surrounding oxygenated functional groups in cobalt-nitrogen-carbon SACs.

The as-prepared catalyst possesses a low coordinated Co-N_2 configuration and high content of C-O-C epoxide groups (Co-N_2 -C/HO). Compared to the conventional Co-based SAC, Co-N_2 -C/HO shows a significantly enhanced performance for hydrogen peroxide production with a high selectivity, prominent mass activity and large kinetic current density, making it one of the most active SACs for hydrogen peroxide electrosynthesis. Considering the generality of the present synthetic methodology, this work offers a pathway toward the exploration of catalysts with unconventional structure and composition for catalysing reactions beyond ORR, such as CO_2 reduction and N_2 reduction reactions.

Related publication: Gong, H. et al. Low-co ordinated Co-N-C on oxygenated graphene for efficient electrocatalytic H_2 O_2production. *Advanced Functional Materials 32, 2106886 (2022). DOI: 10.1002/adfm.202106886*



View of a microscope at the electron Physical Sciences Imaging Centre (ePSIC)

Further suggested reading

Case study: Mapping nanoscale electrostatic field fluctuations around graphene dislocation cores using four-dimensional scanning transmission electron microscopy (4D-STEM)

In 2004, researchers at the University of Manchester were awarded the Nobel Prize in Physics for their discovery of graphene, a single atom thick material made of carbon atoms arranged in a hexagonal lattice. This discovery heralded the beginning of a new field of research into 'low dimensional' materials with the subsequent discovery of numerous other single atom thick materials.

In any crystalline material the presence of defects has profound implications on its physical properties. This is especially true in low dimensional materials due to the lack of three-dimensional structure.

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www.diamond.ac.uk/Instruments/Imaging-and-Microscopy/ePSIC.html

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