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MATERIALS RESEARCH DEPARTMENT

FOCUS ON: Design of Functional Inorganic Materials



Materials Research Department



FOCUS ON:

DESIGN OF FUNCTIONAL INORGANIC MATERIALS

Due to their intrinsic properties, functional inorganic materials are pivotal in advancements across various industries, from electronics and energy to healthcare and environmental sustainability. Our 19th Newsletter explores MRD's research in this field.

Like all previous newsletters, this issue is also accessible through the MRD website at www.mrd.rub.de.

Enjoy reading,

Ralf Drautz and Tong Li MRD Speakers Anastasiia Petrova and Denisa Voicu MRD Science Managers

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Co-Mn SPINEL ELECTRO-CATALYSTS FOR **OER**

An atomic-scale insights into surface changes during the reaction

With the global population predicted to double by 2070, and with the energy requirements of developing nations increasing significantly, access to affordable and renewable energy is one of the cornerstones of continuing global prosperity and economic growth. Most renewable energy devices and systems use catalyst materials to increase energy conversion rates. The morphology, composition and electronic structure of active sites and chemical species within the topmost atomic layers of electrocatalysts are crucial in the activity and selectivity of electrochemical reactions. In order to make technological promises reality and to achieve meaningful environmental impact, we must fully understand the state of individual atoms within the surface layers of the electrocatalysts in order to link the fabrication, structure and properties. To date, it has not been possible to undertake a full three-dimensional (3D) structural and chemical characterisation of the topmost atomic layers of the electrocatalysts. This has hindered a complete evaluation of the contribution made by individual atoms in this extended zone to the interplay of catalytic activity, selectivity and stability in several important chemical reactions such as the oxygen reduction/evolution reaction (OER) for water electrolysis.

Thus, there is an urgent need for a new approach to characterize catalyst materials. My group employs atom probe tomography (APT) to resolve individual atoms of electrocatalyst surfaces and elemental distribution at battery interfaces and interphases. APT is a non-routine characterisation technique for catalyst materials. APT, which combines field ion microscopy with mass spectrometry, provides a uniquely powerful insight into the 3D atomic-scale chemistry and structure of materials. APT analysis requires needle-shaped samples with a tip diameter of 30-



Figure 1: a) working principle of atom probe tomography, and b) atom probe located in ZGH.

100 nm. Surface atoms are field-evaporated by a combination of constant voltage and either a high voltage pulse or a laser pulse, as illustrated in Figure 1. Then the field-evaporated ion is projected on a single-ion-sensitive detector which records its x-y-z coordinates, and the time between the applied pulse and arrival of the ion, allowing a built-in mass-to-charge spectrometer to measure the mass-to-charge ratio. A 3D APT reconstruction can be achieved with individual atoms spatially and chemically resolved.

In a recent study (https://doi.org/10.1002/ aenm.202403096), we develop a multimodal method by combining X-ray fine structure absorption and photoemission spectroscopy, transmission electron microscopy, APT with electrochemical measurements to interrogate the temporal evolution of oxidation states, atom coordination, structure and composition on Co_2MnO_4 and Co- Mn_2O_4 cubic spinel nanoparticle surfaces upon OER cycling in alkaline media.

We reveal that Co₂MnO₄ is activated at the onset of OER due to the formation of ~2 nm Co-Mn oxyhydroxides with an optimal Co/Mn ratio of ~3. As OER proceeds, Mn dissolution and redeposition occur for the CoMn oxyhydroxides, extending the OER stability of Co₂MnO₄. Such dynamic dissolution and redeposition is also observed for Co- Mn_2O_4 , leading to the formation of less OER active Mn-rich oxides on the nanoparticle surfaces. Our study provides mechanistic insights into how dynamic surface reconstruction and transformation affect activity and stability of mixed CoMn cubic spinels towards OER. This work is within the Collaborative Research Center 247 "Heterogeneous Oxidation Catalysis in the Liquid Phase" led by Prof. Kristina Tschulik. We join the forces to provide a fundamental understanding of cobalt-based spinels and perovskites for heterogeneous oxidation catalysis.



Figure 2: Schematic representation showing that Co_2MnO_4 is activated due to the formation of -2 nm thick Co-Mn oxyhydroxides. In contrast, Mn-rich oxides are formed on the surfaces of $CoMn_2O_4$ upon OER cycling. Mn dissolution and redeposition occur for CoMn oxyhydroxides and Mn-rich oxides grown on the surfaces of Co_2MnO_4 and $CoMn_2O_4$, respectively, extending their stability towards OER.



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Figure 1: Schematic representation of the developed interdisciplinary coherent workflow.

INTERDISCIPLINARY ELECTROCATALYST DEVELOPMENT FOR THE ALKALINE OER

Bridging the gap between academic and industrial research

Considering the shortage of fossil fuels and the associated global warming, the necessary electrification of energy systems has become of fundamental importance. Here, the anion exchange membrane (AEM) water electrolysis, which is characterized by high current densities and abundant low-cost transition metal oxide catalysts, is the go-to technology but is not yet available on a large scale. One of the main reasons is the lack of efficient and long-term stable catalytic layers for the sluggish oxygen evolution reaction (OER) that meet the requirements of industrial applications, which highlights the gap between academic and industrial research [1].

Since the performance of a catalytic layer is linked to a highly complex multiparameter space, we, in a joint effort with the groups of Doris Segets, Christof Schulz, Corina Andronescu, Viktor Čolić, Harry Hoster and Hartmut Wiggers from UDE, developed an interdisciplinary coherent workflow that includes large-scale synthesis, electrode fabrication and advanced electrochemical testing, the key steps to rapidly move a promising electrocatalyst from the laboratory – exemplified here with $La_{0.8}Sr_{0.2}CoO_3$ (LSCO)– to an application-ready stage (Figure 1) [2]. The presence of several feedback loops within the workflow allows problems to be recognized early and, at best, eliminated in the next iteration process without having to go through the whole cascade, resulting in well-understood and comparable catalytic materials.

For the large-scale production of catalytically active transition metal oxides the sprayflame synthesis (SFS) is particularly suitable, as the materials can be obtained as powders in a phase- and size-specific manner, whereby the properties of the materials produced can be specifically controlled via the metal precursor, solvent, additives and combustion parameters used [3]. However, it must be ensured that the original material properties from the lab-scale synthesis are retained in order to guarantee the same catalytic activity. Consequently, after optimization of the reaction conditions, phase-pure, highly crystalline, quasi-spherical primary LSCO nanoparticles ($d_n^{BET} = 7$ nm) were synthesized).

For the subsequent electrode fabrication step, which consists of ink formulation and substrate coating, we developed procedures with analytical anchor points to evaluate the ink and electrode properties and ensure high-quality and reproducible electrodes. Analysis of the ink via Hansen solubility parameters and analytical centrifuge revealed good dispersion stability for the LSCO nanomaterial in water/ethanol, and even further enhanced stabilities in the presence of Nafion or Sustainion as binder. To ensure maximum uniformity of the electrodes, the nickel substrates were coated with an automated spraying device, followed by a comprehensive surface topographical and electrochemical examination using scanning electron microscopy (SEM), atomic force microscopy (AFM) and scanning droplet cell (SDC) tests to evaluate the homogeneity of the electrode (physical and electrocatalytic) as well as the interaction of substrate and catalytically active layer). Here, the LSCO-based materials showed a homogeneous coating with a high root-mean-square roughness of 1100 nm and an averaged potential of ~1.56 V vs. RHE at 10 mA cm⁻² with a standard deviation of $\sim \pm 9.5\%$ in activity for the OER.

Once these stages have been successfully completed, the potential electrocatalyst system is subjected to full-cell-related stability tests as part of the advanced electrochemical testing. While the chemical stress of a full cell is tested in a compression cell, which is characterized by a homogeneous potential distribution across the electrode and a locally high O_2 concentration, the mechanical stress of a full cell is tested in a flow cell, which exhibits constant electrolyte convection and increased O_2 bubble development due to higher current densities. From the stress tests it can be concluded that the mechanical stress does not affect the performance of the different LSCO materials, but the chemical stress leads to a performance loss of 50 mV at 10 mA cm⁻² in case of the Sustainion-based electrode compared to the Nafion-based electrode.

Finally, the most promising candidates are tested in a scalable full cell under industrial-like conditions. Based on polarization curves, longterm electrolysis at room temperature and at elevated temperatures (here 60 °C) as well as post-mortem analyses of the electrodes, the performance and stability of the catalyst system can be determined and a statement can be made about the status of industrial applicability, taking into account techno-economic aspects. Similar to the compression cell measurements, the LSCO-Nafion electrodes show a better performance by about 210 mV cell potential at 500 mA cm⁻² compared to the Sustainion-based electrodes (Figure 2). Although the cell potential drop for electrolysis carried out at 60 °C is higher for LSCO-Sustainion than for LSCO-Nafion, indicating a lowering of the chemical stress, the LSCO-Nafion performance is still >100 mV better. In addition, the long-term stability of LS-CO-Nafion with a cell potential increase of 1.5 mV/h is better than the corresponding increase of 2.0 mV/h for LSCO-Sustainion. However, although the cell potential of LSCO-Nafion is sufficiently good, the potential increase of 1.5 mV/h is too high to classify the catalyst system as "application-ready".



Figure 2: Averaged chronopotentiometries held at 500 mA cm⁻² for 12 h at room temperature and additional 12 h at 60 °C in a zero-gap full cell.



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NEW HIGH-TEMPERATURE PIEZOELECTRIC CRYSTALS

Exploring structure-property relationships with resonant ultrasound spectroscopy

After the discovery of the piezoelectric effect on tourmaline in 1880 by the brothers Jacques and Pierre Curie, it was initially little more than a curiosity. Today, along with semiconductor crystals, piezoelectric crystals are among the most important materials in electronics. The inverse piezoelectric effect, i.e., the excitation of elastic oscillations by alternating electrical fields, is primarily used. For example, oscillators based on quartz are the heart of almost all microchips due to their excellent frequency stability combined with high mechanical and chemical resistance. As the elastic properties of a crystal depend on external conditions such as temperature, pressure, and the composition of the atmosphere, changes in the natural vibrations of a crystalline device can be used to monitor the corresponding process parameters [1]. If the crystal is piezoelectric, random mechanical vibrations of a suitable orientation, shape, and size can excite natural oscillations that generate a radio signal via the piezoelectric effect, which can be read without contact in a similar way to RFID technology. Unfortunately, classical piezoelectric materials such as quartz and lithium niobate are of limited use for obvious applications in engines and turbines to optimize the combustion process. They fail at high temperatures due to decomposition, structural phase transitions, or increasing electrical conductivity. The search for or targeted development of new high-temperature piezoelectrics that can withstand harsh environments represents a significant challenge, as predictions of electromechanical behavior based on atomistic model calculations have yet to achieve the necessary reliability. Instead, empirical structure-property correlations are explored experimentally on larger collectives of structurally or chemically related crystal species.

One of the first large families to be intensively explored since the mid-1990s consists of the so-called langasites, which belong to the calcium gallium germanate structure type. In contrast to quartz, which crystallizes in the same trigonal point group, langasites have four different cation positions, which allow numerous substitutions that can be used to optimize their electrome-



Figure 1: Boules of rare earth calcium oxoborates ($RCa_4O(BO_3)_3$ with R = Er, Dy, Tb, Gd, Sm, Nd, La from left to right) grown by Christoph Reuther (TU Bergakademie, Freiberg) [5].



Figure 2: Part of the resonance spectrum of a freely vibrating *RCOB* sample. The inset depicts mounting of a sample with about 5 mm edge lengths for high-temperature resonant ultrasound spectroscopy experiments.

Figure 3: Representation surfaces of longitudinal elastic stiffness (upper row) and longitudinal piezoelectric stress effect (lower row) of (a) α -quartz (SiO₂, point group 32), (b) langasite (La-₃Ga₅SiO₁₄, 32), and (c) gadolinium calcium oxoborate (GdCa₄O(BO₃)₃, m). The piezoelectric effect of *GdCOB* is most promising. However, a challenge with *RCOBs* is the change in the directions of extreme values of electromechanical effects with temperature, whereas in quartz and langasites these are fixed by symmetry.

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chanical properties. The advantages for use as piezoelectric materials in applications include piezoelectric coefficients that are two to three times larger than those of α -quartz and the lack of phase transitions up to their melting temperature, which in some crystal species is above 1400 °C. Unfortunately, all known langasites develop strong ultrasound dissipation at higher temperatures. Although anelastic relaxation processes of point defects could be identified as the cause of this phenomenon [2, 3], the nature of the point defects is still unclear and must first be clarified to control these by crystal chemical design.

In recent years, rare earth calcium oxoborates (*RCOBs*) have become one focus of interest as potential high-temperature piezoelectrics (Figure 1). Structurally, these materials are related to the non-piezoelectric hexagonal fluorapatite $Ca_5(PO_4)_3F$, which occurs widely in nature as an accessory mineral. Replacement of the tetrahedral PO₄ groups by planar BO₃ groups and additionally coupled substitution of fluorine and divalent calcium by oxygen and trivalent rare earth cations increases the crystal-chemical variability. This 'crystal engineering' allows for a piezoelectric effect but comes at the cost of a considerable reduction in symmetry, which increases the number

27 (13 elastic, 10 piezoelectric, and 4 dielectric coefficients). Although there is a procedure based on the resonance-antiresonance technique to determine these parameters, it is highly error-prone since at least 15 samples with different geometry and orientation are required for each crystal species. We have, therefore, developed an alternative approach that utilizes the particular advantages of resonant ultrasound spectroscopy [4]. Here, the natural vibrations of a sample with a well-defined shape and orientation are excited, similar to a tuning fork (Figure 2). As its eigenmodes depend on all electromechanical parameters, one sample is sufficient in principle. Employing this approach, we succeeded in determining complete electromechanical data sets of 7 RCOB crystal species with high internal consistency [5, 6] (Figure 3). The RCOBs are stable up to their melting temperatures and, in contrast to the langasites, do not develop ultrasound attenuation below about 1300 K, making them, in principle, suitable for the application as high-temperature piezoelectric materials. However, order/disorder processes on specific cation sites above approx. 800 K and their impact on the RCOB's electromechanical behavior are currently the subject of our investigations.

of independent electromechanical parameters to

TOWARDS TRANSPARENT ELECTRONICS

Optimizing Copper Iodide-based transparent semiconductors

Zinc blende copper iodide (CuI) is a promising p-type semiconductor for transparent electronics, yet practical challenges persist that hinder its application. In a recent study, we employed high-throughput density functional theory calculations to optimize CuI by adding chalcogens. By investigating the ternary phase diagrams of Cu-I-S and Cu-I-Se, we identified new compounds with promising electronic properties. Our findings suggest that chalcogen alloying can significantly enhance CuI's performance by control of the hole density, paving the way for advanced transparent electronic devices.

Transparent electronic components, which combine high electrical conductivity with transparency in the visible spectrum, are crucial for future technologies like transparent electrodes, thin-film transistors, solar windows, and electrochromic displays. The market for these technologies is expected to grow significantly in the next decade. As shown in Figure 1, while n-type transparent conducting materials (TCMs) like ZnO and indium-tin oxide are well-established, high-performing p-type TCMs are still lacking [1]. This issue prevents the creation of transparent p-n junctions.

The best available p-type TCM is Cul, a widegap, naturally p-conductive semiconductor with a zinc blende crystal structure at ambient conditions. It combines high transparency in the visible spectral range with unsurpassed hole conductivity. Despite recent progress, several fundamental material science issues and practical problems remain before Cul can be used as a multifunctional material. In this context, the Research Unit FOR2857 "Copper Iodide as a Multifunctional Semiconductor" aims to bridge the gap between current promising results and the explotation of copper iodide's unique properties in real-world applications employing thin films. As a member of this collaboration, Botti's group uses high-throughput calculations within the framework of density functional theory to propose new routes for doping and alloying engineering of this material.

The most critical problem is that Cul's hole conductivity remains significantly lower than that of n-type TCMs. Enhancing conductivity requires increasing hole concentration or mobility. Experimental evidence suggests that film quality improvements are marginal, making doping a more viable route. Chalcogen doping, particularly with



Figure 1: Conductivity of various reported p-type compounds (circles) vs. their optical transparency. Two n-type TCMs are shown for comparison (squares). Adapted from Ref. [1].



Figure 2: Schematic representation of the filtering procedure to extract from the high-throughput calculations the candidate systems for further characterization.

sulfur and selenium, was previously predicted by Botti's group [2] and experimentally confirmed [3] as a method to increase hole concentration without significantly affecting transparency.

Recently, Botti's group has also predicted [4] that creating ternary compounds, adding S and Se to Cu and I, can lead to improved control of electronic properties. To further tune Cul's electronic properties, they investigated from first-principles the ternary phase diagrams of Cu-I-S and Cu-I-Se using the minima hopping method (MHM) for structure prediction, relying of energy and forces extracted from density functional theory calculations [4]. The whole range of compositions was considered before applying a series of filters (thermodynamic stability, band gap size for transparency, valence effective mass for hole mobility) to select the most interesting compounds for further characterization of their electronic properties. The adopted procedure is schematically represented in Figure 2.

This method identified 11 stable crystalline ternary structures, 9 of which are unreported. Some of these compounds can exist in the form of binary alloys. Among this selection, 4 materials were identified as promising p-type transparent materials. Additionally, unreported metallic phases with intriguing topological properties were discovered.

The most interesting ternary compounds were characterized for their electronic, transport, and optical properties using density functional theory (DFT) with state-of-the-art hybrid functionals for accurate band structures (Figure 3). The analysis revealed a large variety of electronic properties, with compounds ranging from semiconductors to metals and topological semimetals. The promising p-type TCMs exhibited strong p–d hybridization, essential for high hole mobilities. They also showed potential for tuning hole concentration through alloy composition.

These findings indicate that chalcogen doping and alloying can significantly enhance the control of Cul's properties for transparent electronics. Experimental work in the research unit is now focusing on synthesizing and characterizing the newly predicted compounds and alloys to validate their potential and integrate them into new transparent devices.







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CRAFTING QUANTUM DOTS WITH MOLECULAR BEAM EPITAXY

Building blocks for future quantum technology

Molecular Beam Epitaxy (MBE) is a sophisticated thin-film deposition technique enabling the precise growth of crystalline structures. In MBE, beams of atoms or molecules are directed onto a heated substrate in an ultra-high vacuum, creating high-purity semiconductor materials with sub-atomic layer control. This precision makes MBE ideal for fabricating advanced nanostructures, including quantum dots (QDs).

Quantum dots are nanoscale semiconductor structures that confine electrons and holes in three dimensions, resulting in size-dependent quantum confinement effects. These "artificial atoms" exhibit discrete energy levels and can emit high-quality single photons, making them promising candidates for various quantum technologies, including computing, communication, and sensing.

Epitaxial QDs grown by MBE have gained significant attention across engineering, materials science, physics, and quantum information technologies. Two self-assembly processes stand out in particular: Stranski-Krastanov (SK) growth and local droplet etching (LDE) (Figure 1). SK growth relies on strain-induced self-assembly, resulting in the formation of tiny islands approximately 10 nm in size. A prominent example of this technique is the growth of InAs QDs on GaAs substrates, where the lattice mismatch induces the necessary strain. In contrast, the LDE method involves the creation of nanoholes through metal droplet etching, followed by potentially strain-free QD growth. A notable example of this approach is the formation of GaAs QDs within an AlGaAs matrix, where the similar lattice constants minimize strain. Both techniques produce high-quality QDs suitable for a wide range of quantum experiments and applications, making them indispensable in the advancement of quantum technologies.

Dr. Arne Ludwig and his team have been at the forefront of developing MBE-grown InAs and GaAs QDs for such quantum experiments and applications. Their work focuses on creating ultra-lownoise InAs and GaAs quantum dots [2, 3], while improving ensemble homogeneity and density [4]. Self-assembly processes are inherently subject to random statistical fluctuations, which influence the properties of the resulting assembled particles. A key concept in understanding and controlling this phenomenon is the Voronoi cell, as described by Löbl et al. [5]. The size of these Voronoi cells plays a crucial role in determining the dimensions of the quantum emitters. By gaining control over the Voronoi cell size, one can effectively manipulate the size of the quantum emitters, offering a pathway to more precise and tailored quantum dot fabrication.



Figure 1: Transmission electron microscopy images of single quantum dots: (Left) Strain-driven InAs quantum dot (coloured green) grown in a GaAs matrix via Stranski-Krastanov mode. (Right) Strain-free GaAs quantum dot (coloured blue) formed by filling a local droplet etched nanohole in an AlGaAs matrix [1].



Figure 2: (Top) Schematic illustration of roughness-modulated surfaces resulting from gradient growth of material 1 (blue). (Bottom left) Atomic force microscopy (AFM) image of a near-integer atomic layer thickness (approximately 0 monolayers, ML). (Right) AFM image of a half-integer, sub-monolayer grown surface. (Bottom centre) Surface profile along the wafer, demonstrating clear modulation in step density. Each dot corresponds to a 2 x 2 μ m² AFM measurement. Points 'a' and 'b' correspond to the respective AFM images shown in the figure. (Top right) Early quantum dot nucleation (material 2, green) occurs preferentially at specific growth phases; the underlying surface morphology impacts the nucleation. Adapted from Ref. [4].



Figure 3: (Left) Quantum dot (QD) density variation across a wafer: The photoluminescence (PL) intensity, directly correlated with QD density, follows the surface roughness modulation. The profile mirrors the material source emission pattern (adapted from ref. [4]). (Right) Wavelength modulation of LDE-QDs: The emission wavelength of local droplet etched quantum dots (LDE-QDs) varies due to gradient growth and is further modulated by surface roughness variations (adapted from ref. [7]). The absence of QD photoluminescence in the upper part of the wafer indicates a critical material nucleation transition: this area is QD-free [8].

A critical hurdle in quantum dot fabrication, particularly for achieving high device yield, is the precise control of QD density and properties across an entire wafer. This challenge arises because even minute fluctuations in growth flux can result in significant and nonlinear variations in the resulting QD density [6].

Our recent research has shed light on a crucial aspect of this process: the growth phase in epitaxial QD formation [4]. This phase represents a universal characteristic of layer-by-layer epitaxial growth and can be leveraged to alter nucleation, density, and emitter properties.

We demonstrated the significance of the growth phase in modulating the QD density [4]. Through the growth of material gradients, we generate variations in material thickness across the substrate (Figure 2). Given the discrete nature of atoms, this process naturally results in alternating regions of integer (smooth) and non-integer



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Growth (2022), 591,

9 Tiranov A., et al., Science (2023), 379, 389–393. (rough) atomic layer thicknesses. These surface roughness modulations effectively modify surface diffusion and thus directly influence the characteristics of Voronoi cells, which are crucial in determining the spatial distribution and properties of quantum dots. Using this approach, we achieved unprecedented control over QD nucleation, creating ensembles with tailored densities ranging from one to tens of QDs per μ m².

Notably, this is accomplished by substrate growth phase control without altering the nominal QD material layer thickness or composition. It is however robust to material variations occurring during full wafer growth. Our approach allows for density modulations in one and two dimensions (Figure 4), produces QDs with improved size uniformity and reduced inhomogeneous broadening, and is applicable to full wafers.

The growth phase concept extends beyond density control. Babin et al. showed it could alter the emission wavelength of LDE QDs across entire wafers [7] (Figure 3), valuable for creating QDbased devices with specific optical properties.

The implications of growth phase manipulation are far-reaching. While theoretical modelling is still in the early stage, it already opens new possibilities for designing QD-based quantum devices with precise control over emitter density and properties. This control is crucial for developing advanced multi-emitter single-photon sources for quantum communication and may find applications in photonic quantum computing, where many identical emitters are needed for complex error-proof gubit states [9].

The ability to craft QDs precisely using MBE, combined with the newfound understanding of growth phase implications, represents a significant advancement in designing functional inorganic materials for quantum technologies. Allowing the researchers to refine these techniques promises even more sophisticated quantum devices. These developments promise to accelerate the journey towards realizing practical, transformative quantum technologies that could revolutionize fields from computing to communication and sensing. The future of quantum materials science appears brighter than ever, fuelled by innovative fabrication methods and a commitment to excellence in quantum dot engineering.

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Figure 4: (Left) Photoluminescence image displaying a Moiré pattern of quantum dot density. (Centre) At higher resolution, the Moiré pattern disappears, revealing a density modulation period of 300 µm. (Right) By combining multiple gradient layers, two-dimensional patterns can be achieved. Adapted from Ref. [4].

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