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EPSRC
Engineering and Physical Sciences
Research Council

EPSRC Programme Grant:

Enabling Next Generation Additive Manufacturing Annual Report 2018

ToF-SIMS map of a cross section of
a hybrid layered organic/inorganic
3D inkjet printed sample

UNIVERSITY OF
BIRMINGHAM

WARWICK

Vision

Twenty-first century products demand a new toolset of manufacturing techniques and materials; next generation multifunctional Additive Manufacturing (AM) is one such key tool.

As an enabler for new smart, cost-effective, functional 3D heterogeneous devices, products and advanced materials, it will be an essential instrument for future industrial applications and advanced research across a wide spectrum of disciplines and sectors. To accelerate next-generation AM, we have established a multi-institution, multidisciplinary team which spans both basic/applied sciences and engineering and involves collaborations with three leading research groups and eight multinational industry partners.

Our vision is to establish controlled next generation multifunctional AM and translate this to industry and researchers. Initially focussing on novel electronic and pharmaceutical/healthcare applications, we aim to move beyond single material AM by exploiting the potential to deposit multiple materials contemporaneously for the delivery of spatially resolved function and structure in three dimensions (3D). Owing to potentially radical differences in physical state, chemistry and compatibility, our primary challenge is at the interface of the deposited materials.

This programme will focus on overcoming the challenges of spatially controlled co-deposition of dissimilar materials in 3D and we will establish new understanding and methods of both modelling and controlling co-deposition. Exploitation of our findings will be undertaken through higher TRL schemes with our network of research and industrial partners and the wider innovation ecosystem through existing and future projects.

> “Our vision is to establish controlled next generation multifunctional AM and translate this to industry and researchers.”

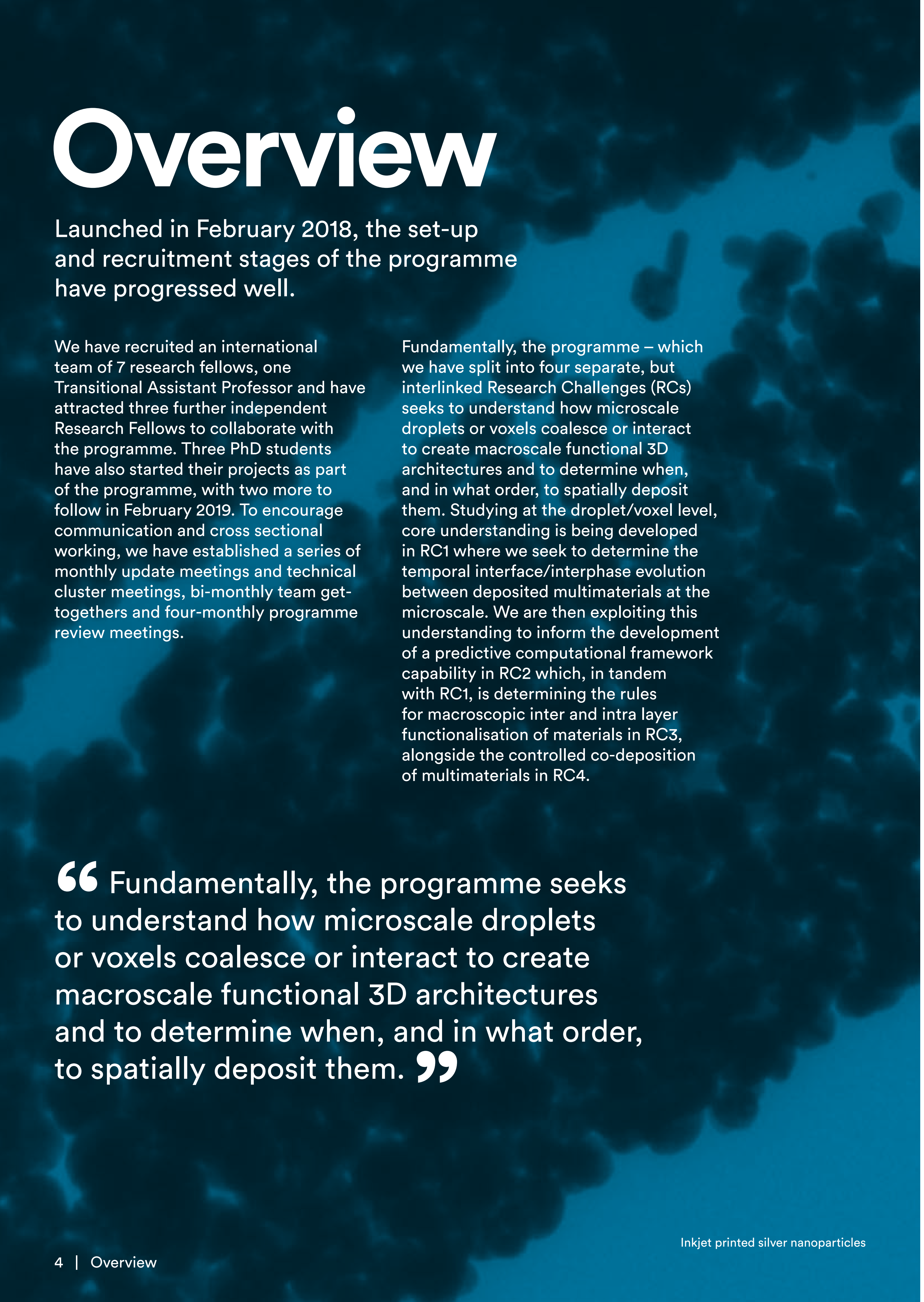
Overview

Launched in February 2018, the set-up and recruitment stages of the programme have progressed well.

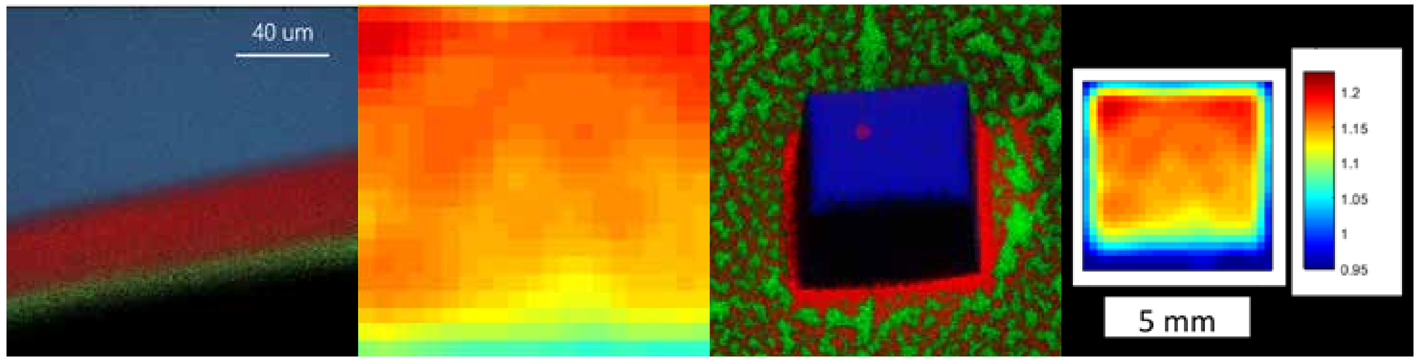
We have recruited an international team of 7 research fellows, one Transitional Assistant Professor and have attracted three further independent Research Fellows to collaborate with the programme. Three PhD students have also started their projects as part of the programme, with two more to follow in February 2019. To encourage communication and cross sectional working, we have established a series of monthly update meetings and technical cluster meetings, bi-monthly team get-togethers and four-monthly programme review meetings.

Fundamentally, the programme – which we have split into four separate, but interlinked Research Challenges (RCs) seeks to understand how microscale droplets or voxels coalesce or interact to create macroscale functional 3D architectures and to determine when, and in what order, to spatially deposit them. Studying at the droplet/voxel level, core understanding is being developed in RC1 where we seek to determine the temporal interface/interphase evolution between deposited multimaterials at the microscale. We are then exploiting this understanding to inform the development of a predictive computational framework capability in RC2 which, in tandem with RC1, is determining the rules for macroscopic inter and intra layer functionalisation of materials in RC3, alongside the controlled co-deposition of multimaterials in RC4.

> “Fundamentally, the programme seeks to understand how microscale droplets or voxels coalesce or interact to create macroscale functional 3D architectures and to determine when, and in what order, to spatially deposit them.”



Inkjet printed silver nanoparticles



Raman and Tof-SIMS analysis of 3D printed heterogeneous specimens

As it is not feasible to process all materials and all length scales via one system, we are exploiting four promising deposition techniques:

1. 3D piezo-driven inkjet
2. High-viscosity jetting
3. High temperature metal-jetting using magneto hydrodynamic actuation
4. Functional multi-photon fabrication, specifically two photon polymerisation (2PP).

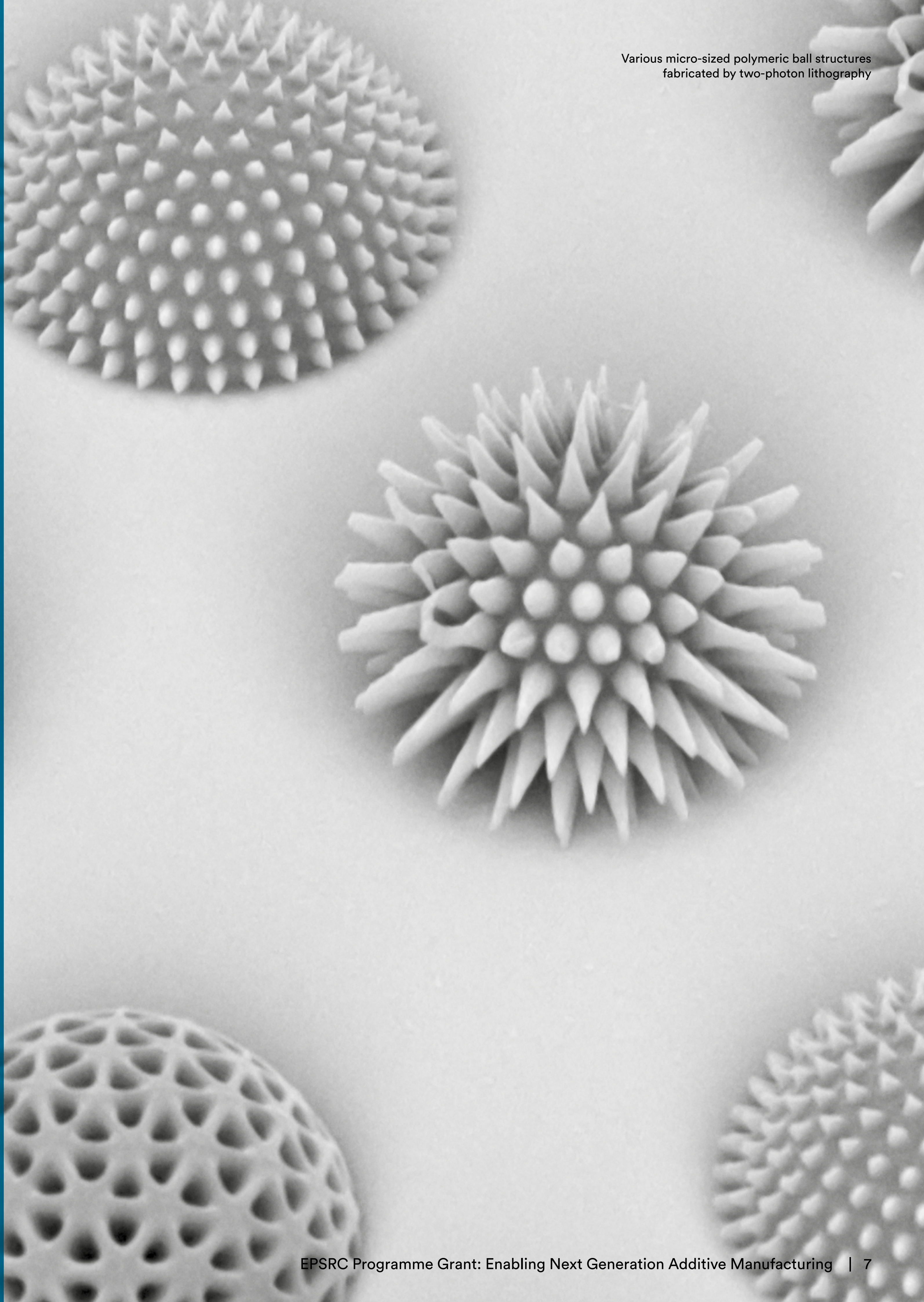
These processes have differing levels of maturity, which require alternate approaches. For example, with ink-jetting, we are exploiting a library of new structural materials from complementary EPSRC initiatives, alongside co-deposition of novel (e.g. low dimensional) functional materials. Whereas metal-jetting’s low TRL status dictates a focus on elemental metallic/semi-conducting materials, prior to the investigation of more exotic alloys later in the programme.

To either maintain or activate the integrity and functionality of the separate, but combined, structural and functional materials over many thousands of deposited layers, the team are successfully addressing the following objectives:

1. Develop understanding at the droplet, voxel and layer levels of how multimaterials interact as they progress through the various states and stages of deposition for 3D ink-jetting, high-viscosity jetting, metal-jetting and multi-photon fabrication
2. Generate new predictive modelling capability for multi-material coalescence where we may want materials to remain discrete, or may require mixing, inter-diffusion or chemical reactions for the in-process formation of new materials
3. Find strategies to overcome inter and intra layer functional anisotropy for electronic/healthcare functional materials
4. Identify key strategies to control the material deposition and dynamically changing inter/intra layer interfaces and interphases between multiple structural and functional materials in 3D

Technical highlights of year 1

- In collaboration with our programme partner, the National Physical Laboratory (NPL), a paper has been published in the journal *ACS Applied Materials & Interfaces*
- Cross-cutting work has been published in the journal *Additive Manufacturing*
- Established a series of analytical strategies for *ex situ* materials interface analysis which has enabled a deeper and better understanding of not only the samples produced, but also their printing processes. Examples include a systematic study of in-process UV curing of bespoke inkjet printing inks
- Started developing a Volume-of-Fluid simulation framework for AM based on the Basilisk software and carried out test simulations of drop coalescence and deposition on a solid surface, in a non-isothermal environment
- Determined the potential chemical modifications needed to improve/change the behaviour of existing ink formulations
- Achieved control over 2PP connectivity by establishing the influence of hatching distance and slicing distance on connectivity
- Acrylic based polymers were printed alongside silver nanoparticle conductive inks, as well as graphene based inks, in order to study the interfacial phenomena between a combination of these materials
- Fabrication of microscale low dimensional hexagonal graphene-based devices featuring a quantum transport behaviour, and electronic characterisation to demonstrate the devices' functionality, as confirmed by theoretical modelling and simulation



Various micro-sized polymeric ball structures fabricated by two-photon lithography

Key individuals

Investigators

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Principal Investigator and Joint RC1 Lead

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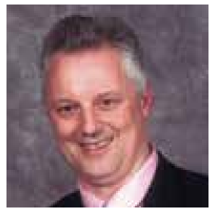
Co-Investigator and Joint RC3 Lead



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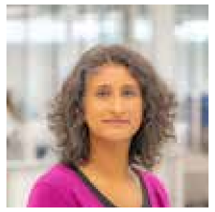

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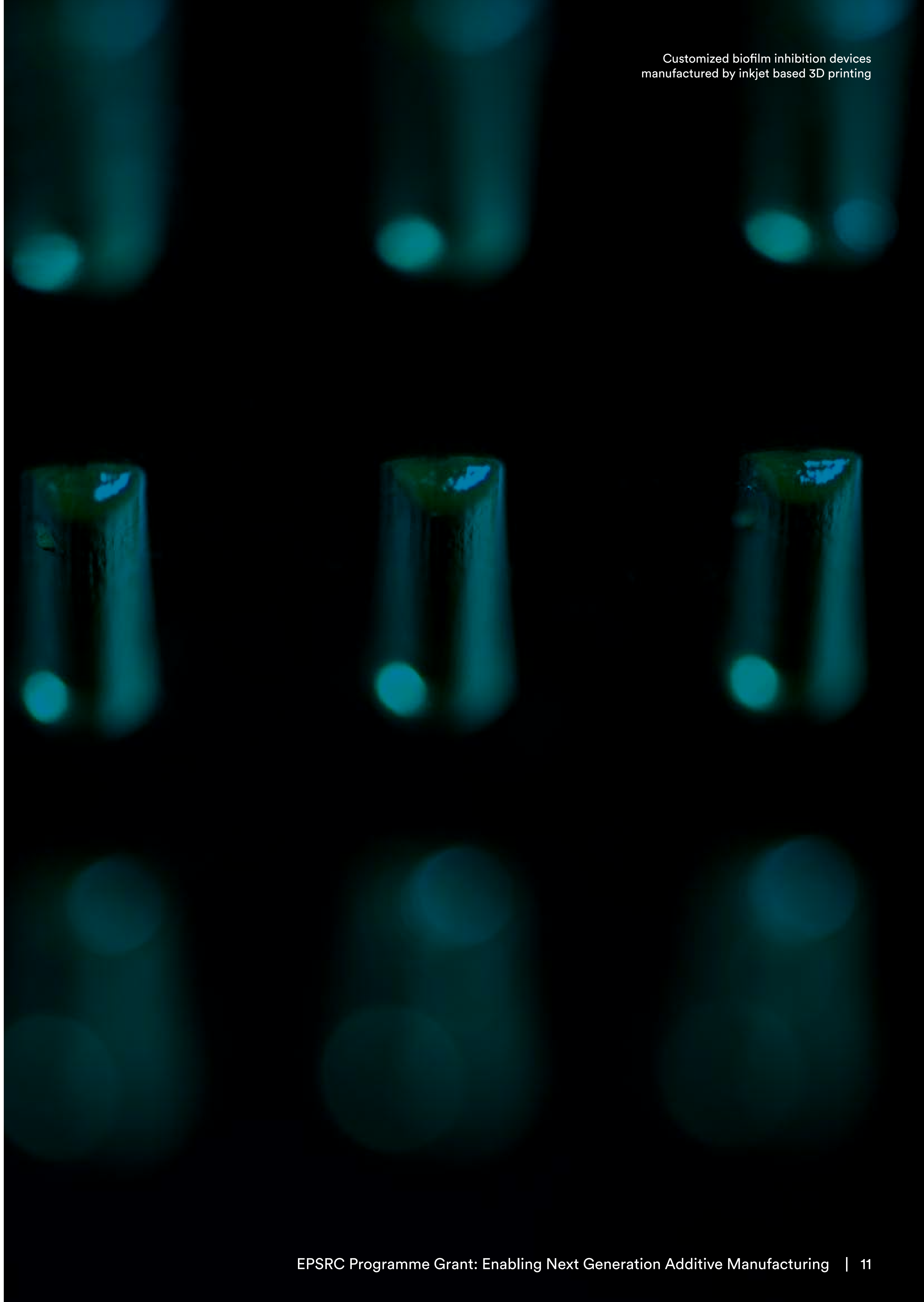
Senior Research Technician, Faculty of Engineering, University of Nottingham



Customized biofilm inhibition devices manufactured by inkjet based 3D printing

Research

The programme is organised into four inter-related research challenges.

Research challenge 1 (RC1):

Determination of the interface/interphase evolution at the microscale

Jointly led by Clive Roberts and Richard Hague

AIM: To understand, through precision experiments, the spatio-temporal interface/interphase evolution between successively deposited droplets or voxels of multimaterials at the microscale.

To enable controlled next-generation multifunctional Additive Manufacturing at the macroscale, where we overcome the two primary challenges of functional anisotropy and agglomerating highly dissimilar materials, it is first necessary to deduce experimentally, at the micro and nanoscale, how individual droplets/voxels of multiple materials temporally coalesce or interact with neighbouring material(s) to form continuous structures. This determination is required for the four process families of interest that deposit functional and structural materials rather than the idealised materials investigated in prior work. RC1 is therefore key to this programme; understanding gained at the microscale will enable us to deduce more general rules of behaviour to predict macro-level performance (RCs 3&4) and, if used inversely, predict and optimise the precise deposition strategies (RC2) for the manufacture of future multifunctional devices.

Single layer of silver droplets deposited by MetalJet

Achievements in year 1

- Established a series of analytical strategies for *ex situ* materials interface analysis. These comprise sample preparation procedures suitable for samples produced by each printing method and also baseline material characterisation for a suite of core analytical techniques, such as time-of-flight secondary ion mass spectrometry (ToF-SIMS), focused ion beam secondary electron microscopy (FIB-SEM), Raman microscopy, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).
- Worked alongside RCs 2, 3 & 4 to establish a deeper and better understanding of not only the samples produced, but also their printing processes. Examples include a systematic study of in-process UV curing of bespoke inkjet printing inks, evaluation of metallurgical bonding between subsequently jetted molten metal droplets; and the study of interphase chemistry in a buried interface between a polymer and sintered metal nanoparticles in a hybrid organic-inorganic 3D inkjet printed device.
- In collaboration with our programme partner NPL, a paper has been published in the journal *ACS Applied Materials & Interfaces*.

Future focus

With analytical strategies established, the RC1 team can now work towards a more fundamental understanding of the interfaces of materials produced by the four process families.

- Focus on new developments in 3D nanoscale mass spectrometry by exploring a state-of-art hybrid ToF- SIMS (OrbiSIMS) instrument recently acquired by the University of Nottingham. This is the first instrument of its kind in an academic setting, and has great potential for the characterisation of multi-material and multi-functional additive manufactured objects.

Clive Roberts

Richard Hague

Gustavo Ferraz Trindade

Research challenge 2 (RC2):

Multifunctional AM computational modelling framework

Jointly led by Ian Ashcroft and James Sprittles

AIM: To accurately model and simulate multimaterial AM; from constituent materials to multifunctional components.

The essence of all AM processes in this programme is the targeted deposition of small, carefully controlled amounts of fluid (microdrops or voxels) and their controlled agglomeration and solidification, to build complex structures. The complexity of the process and extremely small time and length scales involved make a trial-and-error approach to the design of AM processes unfeasible, hence, the process must be understood on the basis of accurate quantitative models. This is particularly the case when the complexity of the process is compounded by the presence of multiple materials.

Modelling plays a number of inter-related essential roles in the programme:

1. Descriptive modelling, in which the model is used to aid understanding of the fundamental physical mechanisms and supplement experimental work with targeted virtual experiments, that enable scenarios not available to experimentation to be explored, e.g. due to the limited spatio-temporal resolution of measurements. This type of modelling is integral to the development of understanding in RC1 and is the essential foundation for the other modelling roles.
2. Predictive modelling, in which validated models are used to accurately forecast the outcome of real processes, and the properties of structures made by these processes, enabling cost–efficient, rapid exploration of process or design variables. This class of modelling is closely linked to the processes and applications developed in RC3.
3. Optimisation, in which predictive modelling is combined with optimisation algorithms to identify the best possible functional component designs and manufacturing processes for specific applications. This type of modelling is essential to the development of optimised manufacturing methods and strategies (RC3&4) and multifunctional devices (RC4).

In this programme, modelling includes simulation of the manufacturing process and the functional performance of the manufactured parts in-service. When combined with the novel processes and explicit consideration of complex dynamic interfaces/interphases and multicomponent/multiphase interactions that are at the core of the programme, a unique challenge emerges. We aim to create a mathematical modelling framework that simulates the transformation of constituent materials through the various physical and chemical processes involved in the manufacture of a functional part, in order to seamlessly link the constituent materials and processes to the form of the manufactured part and its functional performance in-service.


Contact between copper droplets deposited by MetalJet

Achievements in year 1

- Started developing a Volume-of-Fluid simulation framework for AM based on the Basilisk software and carried out test simulations of drop coalescence and deposition on a solid surface in a non-isothermal environment.
- Initiated a sub-project into the convective cooling of Metaljet droplets prior to deposition, identification of key physics, development of a simplified model and model verification via simulations.
- Carried out preliminary investigations of a model for the 'self-peeling' of metaljet droplets discovered in a recent Nature Physics article [J. de Ruiter, D. Soto and K. K. Varanasi, Nature Physics 14 (2018) 35] coupling elasticity and heat transfer via thermal expansion.
- Preliminary investigation of a model to predict transient cure development in the ink jet printing of photocurable polymers.

Future focus

- Incorporate the specific physics of dynamic wetting and phase change into the computational framework to capture the spreading, solidification and/or evaporation of inkjet printed droplets.
- Fine tune the computational models in close collaboration with experimentalists.
- Exploit the computational model to discover the physical mechanisms governing the Metaljet process and hence optimise its performance.
- Complete the development and validation of a general model for the prediction of cure in the inkjet printing of photocurables with in-process UV irradiation.
- Apply the UV-inkjet model to optimise process parameters and deposition strategies for 3D inkjet printing.


Ian Ashcroft


James Sprittles


Yulii Shikhmurzaev


Mykyta Chubynsky

Research challenge 3 (RC3):

Controlling connectivity and anisotropy for enhanced functionality

Jointly led by Ricky Wildman and Derek Irvine

AIM: To be able to control the connectivity of additively manufactured objects to enable full functionalization.

The voxelwise approach inherent in AM enables the cost-effective manufacture of highly complex geometries, but can impart anisotropy into the resultant part as material must be deposited and then connected. When processing functional materials this can lead to uncontrolled inter and intra layer connectivity and functional anisotropy can emerge. There are two examples of this phenomenon. Firstly, the production of 3D conducting tracks/circuitry with nano-particulate Ag inks can result in weak connectivity in the “z” build direction, resulting in reduced functional conductivity in the “z” direction. A second example can be seen during metaljet deposition for some materials, where very poor control over interface/interphase behaviour is observed and sub-optimal levels of functional performance can be expected in all directions.

Were we able to gain control over the connectivity, this could give rise to tailored performance in any desired direction. In the future, it is desired that new classes of material, such as low dimensional materials, can be incorporated into AM fabricated objects to offer enhanced properties, such as high conductivity, fast electron transport, thermal conductivity and structural response but without control, creating 3D dimensional functionality from inherently 2D materials is unfeasible. In this challenge then, we aim to utilise the understanding developed in RC1 and RC2, to achieve control over microscale properties to realise macroscale functionality in devices as diverse as pharmaceutical delivery systems and electronic circuits.

Single chip with hundreds of 3D architecture patterns fabricated by two-photon lithography for high throughput screening

Achievements in year 1

- Collaborated with colleagues looking at processes, specifically two photon polymerisation (2PP) and inkjet, to determine the potential chemical modifications needed to improve/change the behaviour of existing ink formulations.
- Worked with colleagues in RC4 to develop a polyimide formulation to inkjet electronics for high temperature applications, which has been published in the journal *Additive Manufacturing*.

And specifically for 2PP:

- Established a strategy for high throughput 2PP material identification.
- Created a demonstrator for testing 4 material process capability in a single step.
- Developed a material library with 46 monomer process capability (in collaboration with another EPSRC programme grant “Next Generation Biomaterials Discovery” EP/N006615/1).
- Achieved control over 2PP connectivity by establishing the influence of hatching distance and slicing distance on connectivity.
- Started looking at the influence of the degree of polymer conversion, performance of the co-polymer, scan strategy and the influence of solvent on connectivity.

Future Focus

- Identify low dimension materials (LDMs, e.g. graphene) which can be hard to process and devise a methodology for printing.
- Continue investigating the influence of scan strategy, co-polymer and solvent on connectivity.

Ricky Wildman

Derek Irvine

Qin Hu

Amy Stimpson

Research challenge 4 (RC4):

Controlled co-deposition of multimaterials

Jointly led by Chris Tuck and Mark Fromhold

AIM: To investigate and demonstrate strategies for the macroscale co-deposition of functional and structural materials via piezo driven jetting, high temperature metal-jetting and functionalised multi-photon techniques.

The goal for this programme is to execute controlled co-deposition of disparate micro-droplet materials at the **macroscale** and achieve the required coalescence or interaction necessary for both structural integrity and functional performance. By working closely with our industrial partners, where we have a foci of 3D electromagnetic and pharma/healthcare applications, we will build on the microscale understanding, observation and analytical techniques investigated in RC1, and the macroscale single material functionality gained in RC3 to investigate the production of 3D architectures that contain multiple (functional and structural) materials. Based on the four process families already identified as being suitable for multifunctional AM, build strategies for functional 3D devices will be derived using the mathematical and computational framework developed in RC2. We will also use RC4 structures and devices to further enhance our computational framework (RC2) and understanding (RC1) in order to optimise our co-deposition and process strategies.

To achieve the aim of RC4, a symbiotic relationship with RC3 is required, wherein the strategies for realisation of functionality in the vertical ("z") axis will be extended to include co-deposition. However, though conceptually simple, this is further complicated in that there are usually significant differences in the process requirements between the functional and structural deposited layers, for example in voxel size (layer thickness), requirement for in-situ processing (functionalisation), as well as surface texture and wetting characteristics. In RC1, at the microscale, the differential in layer thickness is not a primary issue as the main concern is to understand how to successfully interface dissimilar materials; though this is critical information that will inform our macro-level build strategies. In RC4, we are primarily interested in achieving macro-level co-deposition and therefore a key challenge will be how to address the differentials in layer thickness between structural and functional elements throughout the build volume in macroscale production.

An inkjet printed graphene hall bar with silver contacts

Achievements in year 1

Inkjet printing of multi-materials was the prime focus in year 1 of the project.

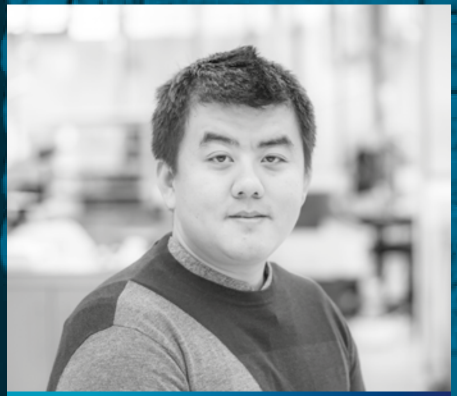
- Acrylic based polymers were printed alongside silver nanoparticle conductive inks, as well as graphene-based inks, in order to study the interfacial phenomena between combinations of these materials.
- Microscale low dimensional hexagonal graphene based devices featuring a quantum transport behaviour have been fabricated by piezo driven jetting, including a transistor and a quantum hall bar.
- Electronic characterisation has demonstrated the devices' functionality, which has also been analysed and confirmed by developing a theoretical model and simulation.
- In collaboration with RC3, work on the use of inkjet printing electronics for high temperature applications was published in the journal *Additive Manufacturing*.

Future focus

- The RC4 team will carry out a further characterisation and optimisation of current devices, especially the study of voxel size (layer thickness) in a symbiotic relationship with RC3 to reveal the subtle chemical mechanism of layer deposition. This would help to improve the piezo jetting process and device functionality, thus pushing the technique into a mature deposition strategy.
- Fabrication and analysis of structures stacked by multiple materials to realise functionality in the vertical ("z") axis, and to demonstrate controlled co-deposition of multi-materials.

Chris Tuck

Mark Fromhold



Feiran Wang

Ehab Saleh

The year ahead

The programme has got off to a strong start with two journal papers already published during year one. Further papers are being drafted, which we aim to submit to high quality, high impact journals.

The programme has established relationships with our academic and industrial partners and will strengthen these through research visits, three monthly team meetings to which partners are invited, and at the Additive International 2019 conference.

We will complete recruitment of research fellows for RC2. We have agreed the loan of an additional metaljet system from our programme partners Océ, which will arrive in early 2019. We will therefore recruit a research fellow to expand on our work in this area.

Student recruitment is going well, with three PhD students on board already, two starting in February 2019, followed by a further two by October 2019.

In the year ahead the programme will:

Focus on new developments in 3D nanoscale mass spectrometry by exploring a state-of-art hybrid ToF-SIMS Orbitrap instrument recently acquired by the University of Nottingham.

Exploit the computational model to discover the physical mechanisms governing the Metaljet process and hence optimise its performance.

Identify low dimensional materials and devise a methodology for printing.

Continue to investigate the influence of scan strategy, co-polymer and solvent on 2PP connectivity.

Further characterise and optimise current devices, especially the study of voxel size (layer thickness) to reveal the subtle chemical mechanism of layer deposition. This will help to improve the piezo jetting process and device functionality, thus pushing the technique into a mature deposition strategy.

> “The programme has established relationships with our academic and industrial partners which has already resulted in new work being published.”

Management structure

Executive team

Professor Richard Hague
Principal Investigator and joint RC1 lead

Professor Clive Roberts
Co-Investigator and joint RC1 lead

Professor Ian Ashcroft
Co-Investigator and joint RC2 lead

Professor James Sprittles
University of Warwick,
Co-Investigator and joint RC2 lead

Professor Ricky Wildman
Co-Investigator and joint RC3 lead

Professor Derek Irvine
Co-Investigator and joint RC3 lead

Professor Chris Tuck
Co-Investigator and joint RC4 lead

Professor Mark Fromhold
Co-Investigator and joint RC4 Lead

Professor Yulii Shikhmurzaev
University of Birmingham, Co-Investigator

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Gerard Davies (EPSRC)

Professor David Rosen (SUTD)

Laura Jones (Dstl)

Mark Swan (AWE)

Dr Paul Gellert (AstraZeneca)

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