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UKRI Engineering and Physical Sciences Research Council

EPSRC Programme Grant:

Enabling Next Generation Additive Manufacturing

Annual Report 2019

UNIVERSITY OF BIRMINGHAM

WARWICK

> “Entering our third year of operation, the scene is set for the Programme to achieve a step change in multi-material Additive Manufacturing”

Cover image:
Secondary ion mass spectrometry imaging of gold nanoparticles selectively coated onto micro-structures fabricated by two-photon lithography. There is an entire mass spectrum for each pixel and the image looks pixelated because its resolution is defined by the spot size of the rastered primary ion beam

This page:
A planar spiral inductor inkjet printed onto a flexible substrate using a new gold ink formulation

Overview

Additive Manufacturing (AM) is fast becoming accepted as a viable 21st Century manufacturing solution that has revolutionised the way products can be designed and manufactured. This EPSRC Programme Grant has the ambitious goal of developing next generation AM for the *in situ* production of multi-functional devices.

We aim to control the co-deposition of functional and structural materials to generate whole systems, as opposed to single material component parts. Delivering this goal challenges us to establish compatibility at the interfaces where differences in the physical and chemical properties of various materials meet. The Programme’s multi-institution and multidisciplinary team is using state-of-the-art equipment and approaches to analyse such interfaces, thereby accurately modelling and simulating multi-material AM – from constituent materials to multi-functional components – and developing novel materials to manufacture working electronic and bio/pharmaceutical devices.

The Programme is organised into a series of interlocking research challenges. Progress over the first two years of the Programme has identified a spectrum of distinct yet related areas for research advancement, including: Novel Processes, Interface Analysis, Modelling, Functional Material, and Application & Demonstrators. Encouragingly, there has been intensive cross-Programme, cross-University working alongside the formation of fruitful external collaborations with high-profile academic and industrial partners eg NPL (UK), Canon Production Printing (formerly Océ, Netherlands), AWE, and the Lawrence Livermore National Laboratory (USA).

Having now completed its second year and having built up excellent momentum, we are currently engaged in optimising our AM processes of interest, developing relevant analytical and modelling methodologies and developing new materials and interfacing techniques, with a focus on matching these with applications. For example, our high temperature metal jetting work now utilises the second iteration of a bespoke MetalJet platform on loan from our partner Canon Production Printing, which is used extensively for new material development, and we have recently installed a new “Projection Micro Stereolithography” (PuSLA) system to further the scope of potential processes to be investigated. Our ambitious Programme is fortunate to be fully staffed by an excellent cohort of specialised researchers. These researchers are augmented by outstanding PhD students and technical/administrative support personnel, as well as being guided by the Investigator team from the University of Nottingham, University of Birmingham and University of Warwick.

Now that the Programme is working at full steam, in the coming year we will continue to focus on delivering impact from our research to develop a ground-breaking suite of publications, inventions and industrially-relatable exemplars to disseminate our research outcomes. To help the Programme’s staff and students optimise the opportunity that a research Programme of scale gives, we have arranged a series of interactive training sessions in presentation skills and engaging with non-specialist audiences, as well as arranged a successful researcher retreat, which encouraged the research staff and students across the Programme to discuss and develop new ideas. We are also happy to report that our researcher, Dr Qin Hu, has been awarded first prize in the Innovation category of the 2019 EPSRC Photography Competition, as well as a grant from the UNICAS Sandpit, and that one of our Research Fellows, Dr Laura Ruiz Cantu, has been awarded two grants from the MSK MEC and UKMRP. These, along with our recently successful application to showcase our work at the prestigious Royal Society Summer Exhibition in July 2020, are pleasing exemplars of the Programme’s established position.

We fully appreciate that our success depends on the contributions of all team members, as well as our ability to work together as a close-knit unit across the Programme’s diverse research areas. As such, we are delighted to welcome Dr Lyudmila Turyanska as a new academic member of the Centre for Additive Manufacturing (CfAM) at Nottingham, postdoctoral researchers Dr Peng Zhao, Dr Jisun Im, Dr Geoffrey Rivers, Dr Carlos Galeano Rios and Leonidas Gargalis, and PhD students Maria Inês Evangelista Barreiros, Kevin Bandeira, Kristian Plender and Joseph Sefton. We are grateful for the support received from the EPSRC and the significant commitment of our industrial and academic partners. We would also like to thank the members of the Programme’s Advisory Board for their ongoing contributions. Entering our third year of research, we now have a full team in place and have begun establishing essential links to wider audiences. The scene is now set for the Programme to deliver its key contribution towards realising the Next Generation of Additive Manufacturing.

Professor Richard Hague,
Principal Investigator

Technical highlights of year two

- Sample preparation and analytical methodologies have been developed to use the University of Nottingham's new 3D orbiSIMS instrument for complex, multi-material samples produced by all three overarching processes. This, amongst other results, has enabled new insights on the morphology and chemical composition of inkjet printed silver nanoparticles
- Computational models for various stages of the metal jetting process, such as in-flight cooling of droplets, are ready to be verified using experimental results
- Established a general model of the cure process in polymer inkjet printing. This work has been submitted for publication
- Various routes for multi-material two-photon polymerisation (2PP) have been demonstrated
- Established a dual-material inkjet based jetting system for photoreactive ink formulations
- Developed new conductive/piezoelectric ink formulations in which surface ligands and an adhesion promoter play a critical role to enhance the interfacial compatibility and enable the co-deposition of multi-functional materials
- Used a hyperbranched (HB) polymer as a stabiliser to successfully develop a methodology for obtaining organic-solvent dispersed graphene flakes for inkjet printing. Additionally, the inclusion of HB polymers has been shown to affect the curing behaviour of both inkjet and 2PP formulations
- The inkjet printing of graphene has been fully characterised and understood with the help of chemical charcterisation, electrical and optical measurements, and theoretical modelling. This has enabled the fabrication of devices such as the top gated transistor, and paves the way for in-house graphene ink formulation and customisation for different applications
- Optimised the MetalJet system to successfully fabricate 3D copper parts
- Biocompatible and biodegradable materials for manufacturing bioactive bone implants with complex morphologies have been optimised for jetting. The feasibility of printing micro vascular, perfusable channels with a similar diameter to arterioles, using jetting technologies, has also been demonstrated

Joseph Sefton using the Fujifilm Dimatix inkjet system for ink formulation exploration

Key individuals

Academics

Professor Richard Hague

Professor of Innovative Manufacturing
Director of the Centre for Additive Manufacturing, Faculty of Engineering
University of Nottingham
Principal Investigator and Joint RC1 Lead

Professor Derek Irvine

Professor of Materials Chemistry Faculty of Engineering,
University of Nottingham
Co-Investigator and Joint RC3 Lead

Professor Clive Roberts

Professor of Pharmaceutical Nanotechnology, Head of the School of Pharmacy, University of Nottingham
Co-Investigator and Joint RC1 Lead

Professor Chris Tuck

Professor of Materials Engineering
Associate Pro-Vice Chancellor for Research and Knowledge Exchange
Faculty of Engineering
University of Nottingham
Co-Investigator and Joint RC4 Lead

Professor Ian Ashcroft

Professor of Mechanics of Solids, Head of the Department of Mechanical, Materials and Manufacturing Engineering
Faculty of Engineering
University of Nottingham
Co-Investigator and Joint RC2 Lead

Professor Mark Fromhold

Professor of Physics
School of Physics and Astronomy
University of Nottingham
Co-Investigator and Joint RC4 Lead

Dr James Sprittles

Associate Professor
Mathematics Institute
University of Warwick
Co-Investigator and Joint RC2 Lead

Professor Yulii Shikhmurzaev

Professor of Applied Mathematics
School of Mathematics
University of Birmingham
Co-Investigator

Professor Ricky Wildman

Professor of Multiphase Flow and Mechanics, Faculty of Engineering
University of Nottingham
Co-Investigator and Joint RC3 Lead

Dr Lyudmila Turyanska

Assistant Professor
Faculty of Engineering
University of Nottingham

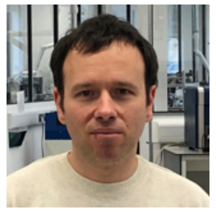
Research fellows

Dr Gustavo Ferraz Trindade

Research Fellow
School of Pharmacy
University of Nottingham

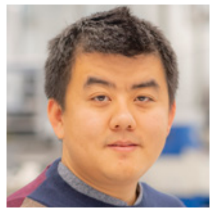
Leonidas Gargalis

Research Associate
Faculty of Engineering
University of Nottingham



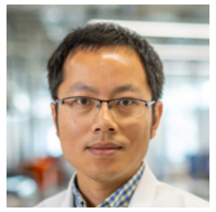
Dr Mykyta Chubynsky

Research Fellow
Mathematics Institute
University of Warwick



Dr Feiran Wang

Research Fellow
Faculty of Engineering and School of Physics and Astronomy
University of Nottingham



Dr Peng Zhao

Research Fellow
Faculty of Engineering
University of Nottingham

Dr Jisun Im

Research Fellow
Faculty of Engineering
University of Nottingham

Dr Carlos Galeano Rios

Research Fellow
School of Mathematics
University of Birmingham

Dr Geoffrey Rivers

Research Fellow
Faculty of Engineering
University of Nottingham

Amy Stimpson

Research Associate
Faculty of Engineering
University of Nottingham

Dr Yinfeng He

Transitional Assistant Professor
Faculty of Engineering
University of Nottingham

Dr Qin Hu

Research Fellow
Faculty of Engineering
University of Nottingham

Dr Laura Ruiz Cantu

Transitional Assistant Professor
Faculty of Engineering
University of Nottingham

Dr Nesma Aboulkhair

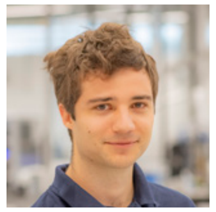
Anne McLaren Fellow
Faculty of Engineering
University of Nottingham

Dr Marco Simonelli

Nottingham Research Fellow
Faculty of Engineering
University of Nottingham

PhD students

Negar Gilani
PhD Student
Faculty of Engineering
University of Nottingham



Eric Lehder
PhD Student
Faculty of Engineering
University of Nottingham

Jonathan Gosling
PhD Student
School of Physics & Astronomy
University of Nottingham

Maria Inês Evangelista Barreiros
PhD Student
Faculty of Engineering
University of Nottingham

Kevin Bandeira
PhD Student
Faculty of Engineering
University of Nottingham

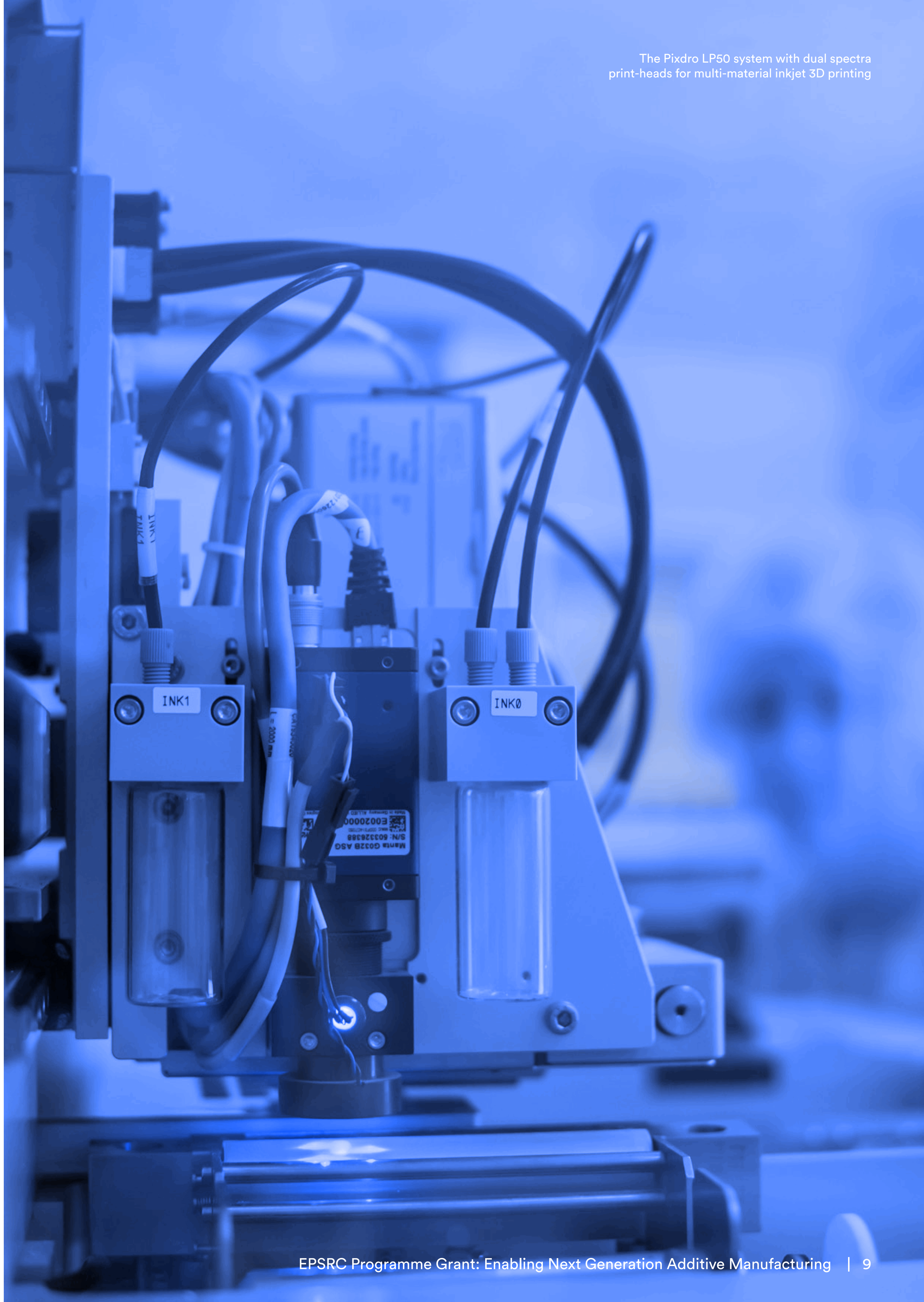
Joseph Sefton
PhD Student
Faculty of Engineering
University of Nottingham

Kristian Plender
PhD Student
School of Pharmacy
University of Nottingham

Support staff

Dr Harinee Selvadurai
Programme Manager
Faculty of Engineering
University of Nottingham

Mark East
Senior Research Technician
Faculty of Engineering
University of Nottingham



The Pixdro LP50 system with dual spectra print-heads for multi-material inkjet 3D printing

Research

Processes

Jetting

Aim: To establish an inkjetting based, highly efficient multi-material AM platform and investigate the interaction within and between materials to enable a high performance multi-functional product for applications.

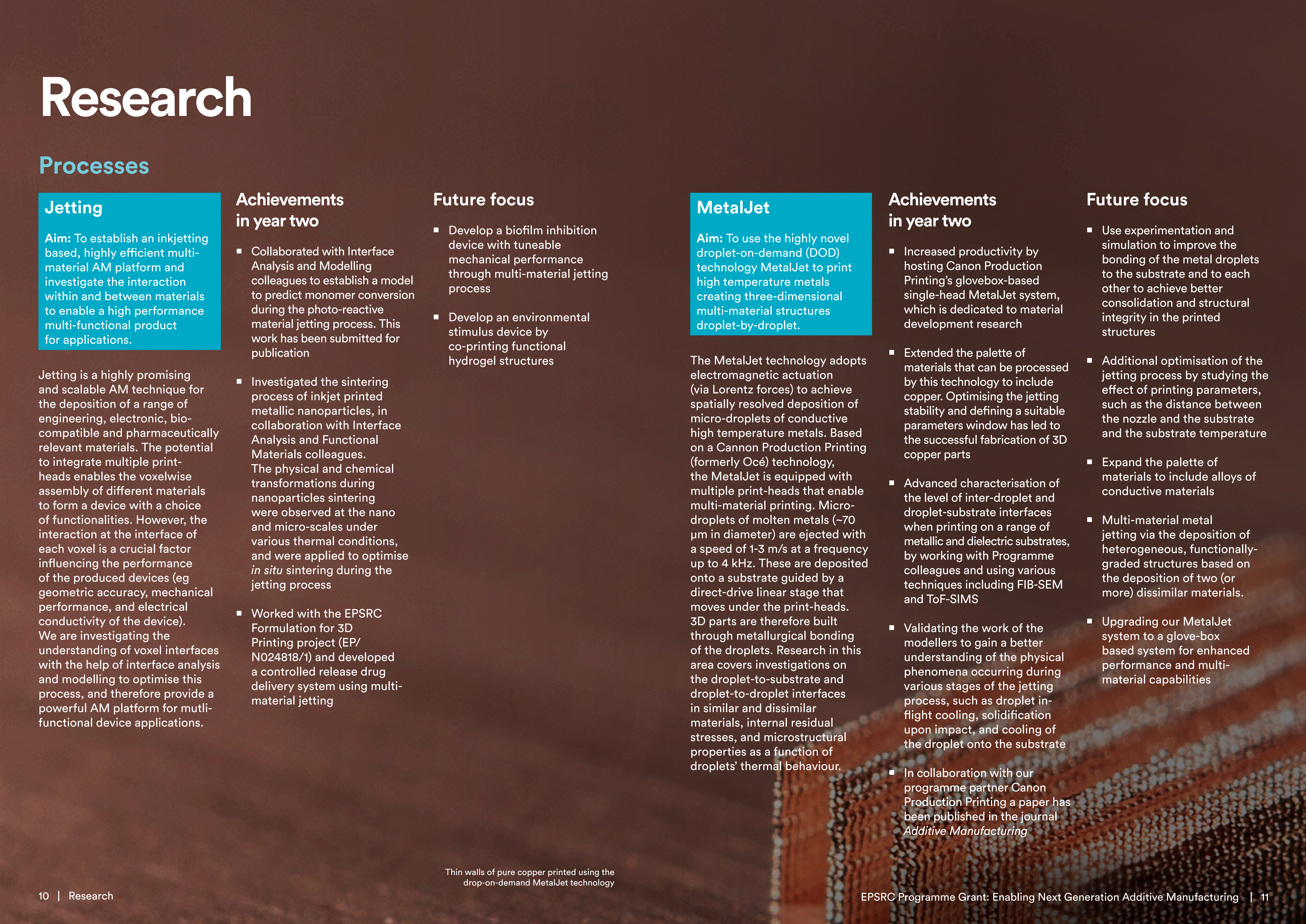
Jetting is a highly promising and scalable AM technique for the deposition of a range of engineering, electronic, bio-compatible and pharmaceutically relevant materials. The potential to integrate multiple print-heads enables the voxelwise assembly of different materials to form a device with a choice of functionalities. However, the interaction at the interface of each voxel is a crucial factor influencing the performance of the produced devices (eg geometric accuracy, mechanical performance, and electrical conductivity of the device). We are investigating the understanding of voxel interfaces with the help of interface analysis and modelling to optimise this process, and therefore provide a powerful AM platform for mutli-functional device applications.

Achievements in year two

- Collaborated with Interface Analysis and Modelling colleagues to establish a model to predict monomer conversion during the photo-reactive material jetting process. This work has been submitted for publication
- Investigated the sintering process of inkjet printed metallic nanoparticles, in collaboration with Interface Analysis and Functional Materials colleagues. The physical and chemical transformations during nanoparticles sintering were observed at the nano and micro-scales under various thermal conditions, and were applied to optimise *in situ* sintering during the jetting process
- Worked with the EPSRC Formulation for 3D Printing project (EP/N024818/1) and developed a controlled release drug delivery system using multi-material jetting

Future focus

- Develop a biofilm inhibition device with tuneable mechanical performance through multi-material jetting process
- Develop an environmental stimulus device by co-printing functional hydrogel structures



Thin walls of pure copper printed using the drop-on-demand MetalJet technology

MetalJet

Aim: To use the highly novel droplet-on-demand (DOD) technology MetalJet to print high temperature metals creating three-dimensional multi-material structures droplet-by-droplet.

The MetalJet technology adopts electromagnetic actuation (via Lorentz forces) to achieve spatially resolved deposition of micro-droplets of conductive high temperature metals. Based on a Cannon Production Printing (formerly Océ) technology, the MetalJet is equipped with multiple print-heads that enable multi-material printing. Micro-droplets of molten metals (~70 µm in diameter) are ejected with a speed of 1-3 m/s at a frequency up to 4 kHz. These are deposited onto a substrate guided by a direct-drive linear stage that moves under the print-heads. 3D parts are therefore built through metallurgical bonding of the droplets. Research in this area covers investigations on the droplet-to-substrate and droplet-to-droplet interfaces in similar and dissimilar materials, internal residual stresses, and microstructural properties as a function of droplets' thermal behaviour.

Achievements in year two

- Increased productivity by hosting Canon Production Printing's glovebox-based single-head MetalJet system, which is dedicated to material development research
- Extended the palette of materials that can be processed by this technology to include copper. Optimising the jetting stability and defining a suitable parameters window has led to the successful fabrication of 3D copper parts
- Advanced characterisation of the level of inter-droplet and droplet-substrate interfaces when printing on a range of metallic and dielectric substrates, by working with Programme colleagues and using various techniques including FIB-SEM and ToF-SIMS
- Validating the work of the modellers to gain a better understanding of the physical phenomena occurring during various stages of the jetting process, such as droplet in-flight cooling, solidification upon impact, and cooling of the droplet onto the substrate
- In collaboration with our programme partner Canon Production Printing a paper has been published in the journal *Additive Manufacturing*

Future focus

- Use experimentation and simulation to improve the bonding of the metal droplets to the substrate and to each other to achieve better consolidation and structural integrity in the printed structures
- Additional optimisation of the jetting process by studying the effect of printing parameters, such as the distance between the nozzle and the substrate and the substrate temperature
- Expand the palette of materials to include alloys of conductive materials
- Multi-material metal jetting via the deposition of heterogeneous, functionally-graded structures based on the deposition of two (or more) dissimilar materials.
- Upgrading our MetalJet system to a glove-box based system for enhanced performance and multi-material capabilities

Two-photon polymerisation

Aim: To achieve multi-material multi-functional 3D micro printing via two-photon polymerisation (2PP) with highly controlled co-deposition of dissimilar materials.

2PP based micro AM can overcome the limitations of traditional photo-lithography based manufacturing techniques to fabricate complex 3D micro/nano structures without a mask, in a fast and cost effective way, with high levels of design freedom achieving a resolution close to 100 nm. The current challenge is how to achieve multi-material 3D micro fabrication with highly controlled co-deposition of dissimilar materials to manufacture multi-functional 3D micro devices.

Achievements in year two

- Established multi-material 2PP via different routes, including direct loading of nanomaterials into the polymer resin, *in situ* generation of nanomaterials, and sequential loading of different materials
- Micro-printed acrylate-thiol 3D structures and selectively decorated them with gold nanoparticles at the design surface
- Achieved further control over 2PP connectivity by establishing the influence of solvent and monomer molecular weight

Future focus

- Demonstrate the pharmaceutical/healthcare and device applications of selectively gold decorated acrylate-thiol and acrylate-graphene printed structures

Multi-material micro structures printed on a flexible substrate by two-photon polymerisation

Interface analysis

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

To enable next generation AM, our primary challenge is the difficulty of inter- and intra-layer coalescence/bonding for functional-structural or functional-functional materials. This is due to differences in the physical state, chemical properties, and temperature at deposition or conversion, of the materials. To overcome these problems, one of the requirements is the development of a suite of ex-situ interface analysis techniques capable of delivering complete 3D characterisation of samples at the micro/nano scale, with chemical specificity and high spatial resolution. These involve specific methodologies for analytical techniques, such as focused ion beam for scanning/transmission electron microscopy (FIB-SEM-TEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), Raman microscopy and X-ray photoelectron spectroscopy (XPS). Moreover, the University of Nottingham has recently acquired a state-of-the-art 3D orbiSIMS instrument that further broadens the analysis of complex materials.

Achievements in year two

- A protocol for measuring the relative degree of UV conversion monomer/polymer of inkjet printed objects has been developed and data has been systematically recorded to validate the work done by Modelling colleagues
- Sample preparation and analytical methodologies have been developed to use the new 3D orbiSIMS instrument for complex samples, both in terms of geometry and chemical composition
- New insights into the morphology and chemical composition of inkjet printed silver nanoparticles were presented at the Materials Research Society Meeting in Boston, USA in December 2019
- An overview of the interface analysis methodologies has been presented at the Vacuum Expo in Coventry, UK in October 2019

Future focus

- In-depth investigation of hybrid organic/inorganic demonstrators produced by inkjet printing and 2PP, with a focus on the gold-polymer interface and low-dimensional materials
- Study complex organic/organic interfaces with a focus on pharmaceutical and healthcare demonstrators
- Continue interface characterisation of new materials/samples

Modelling

Aim: To accurately model and simulate multi-material AM; from constituent materials to multi-functional components.

The basis of all AM processes in this Programme is the solidification of small, carefully controlled amounts of fluid (micro-drops or voxels) to build complex structures. The complexity of the process and extremely short time and length scales involved, make a trial-and-error approach to the design of AM processes inefficient and often unfeasible, hence, the process must be understood using accurate quantitative models. This is particularly the case when the complexity of the process is compounded by the presence of multiple materials.

The models and computational tools that we are developing are based on the theoretical understanding of the physical and chemical processes involved in AM (fluid dynamics, heat transport, photochemistry, light absorption, polymer rheology, solidification and microstructure formation, dynamic wetting, etc). However, close collaboration with experimentalists is essential for defining the model parameters, validation and fine-tuning. While this initial input from experiments is necessary, we aim to give more in return, contributing to better understanding by exploring sets of parameters and scenarios not available to experimentation, and observing details that are hard to measure experimentally because of limited spatio-temporal resolution. Ultimately, the goal is optimising the functional component designs and manufacturing processes; for this, both the AM processes and the performance of the manufactured parts in-service need to be modelled.

Achievements in year two

- Computational approaches for modelling the cooling in-flight and solidification upon deposition of MetalJet droplets have been completed and are being experimentally validated
- A thermomechanical model of cooling and deformation of MetalJet droplets after solidification has been developed
- A general model of the optical cure process in polymer inkjet printing has been validated by parameters obtained from experiments
- Started developing a CFD Volume-of-Fluid computational framework, based on the Basilisk software for inkjet printing of photocurable polymers

Future focus

- Complete the development and validation of the CFD frameworks to represent the processes of deposition and solidification of inkjet and MetalJet droplets
- Coupling of the thermomechanical model of MetalJet droplets to the CFD model of their deposition and solidification, to describe solidification and deformation as concurrent processes; extend to model the microstructure
- Initiate the development of a model of the 2PP process, describing in particular, the dependence of the processing window on the process parameters
- Apply the developed computational models to optimise process parameters and deposition strategies for various AM processes

Optical image of the surface of a multi-layer silver structure printed by material jetting

Functional materials

Co-deposition of functional materials for energy harvesting

Aim: To develop multi-functional materials for inkjet printing, and control the interfacial compatibilities between dissimilar materials, in order to fabricate an energy harvesting system.

Construction of a 3D multi-functional device, such as an energy harvester, requires printable multi-functional materials including conductive elements, piezoelectric materials, and dielectric materials. In addition, it is essential to control the interfacial compatibility of inter- and intra-layers in order to successfully co-deposit these materials in three dimensions. Interfacial compatibility can be achieved by the surface modification of metal/piezoelectric nanoparticles with organic ligands, which can react with the substrate or matrix materials. Another strategy is to employ an adhesion promoter or a coupling agent, which will allow us to achieve both cohesion and adhesion in the printed structure, for optimal functionality of the device.

Achievements in year two

- Developed a new gold nanoparticle-based ink formulation for printed electronics applications. The nanoparticles were functionalised with organic ligands for improved dispersion and stability in the ink formulation. An adhesion promoter was used to enhance the cohesion and adhesion in the printed electrodes
- Formulated a UV-curable piezoelectric ink for energy harvesting applications. Barium titanate nanoparticles were surface-functionalised with UV-curable ligands, which are then reacted with matrix materials to achieve better interfacial compatibility and printability

Future focus

- Using the new formulations of conductive ink and piezoelectric ink, we will co-deposit these materials using an inkjet printer to demonstrate the piezoelectric properties and manufacture an energy harvesting and generation unit
- Develop new materials to print a functional diode
- Develop new dielectric materials, which can be used to print an energy harvesting system

Hyperbranched pDVB stabilised graphene composite powder and ink

Functional composites

Aim: To develop and characterise inkjet printable composites with electrical conductivity in the range of $1 \times 10^{-2}\ S\ m^{-1}$ to $5 \times 10^{3}\ S\ m^{-1}$ or higher, while exhibiting either optical transparency, the ability to be stretched, or both.

When printing functional structures, properties such as optical transparency, mechanical flexibility or stretch-ability, and electrical conductivity are highly valued. However, electrically conductive materials are rarely transparent or stretchable. Three widely applicable avenues of investigation are being utilised to overcome this problem: spatial structuring of multiple inks through printing techniques to intertwine small quantities of conductive ink inside transparent or stretchable structural inks; control of nano-fillers in composite inks, by developing surface-tailored nanoparticles, to orchestrate self-assembly and conduction at low concentrations; and development of new print-compatible conductive materials, which are intrinsically transparent and/or stretchable. These are complex and exciting materials, wherein small alterations to the particle interactions and polymer chemistry can have large influences on the resulting printability and final properties.

Achievements in year two

- Composites utilising conductive nano-fillers (an in-house developed graphene variant, nano-silver, and modified PEDOT:PSS) in various polymer inks are in development. Formulation of a printable and stretchable composite containing conductive channels of oligomers derived from ionic liquids is underway
- Started developing new formulations for inkjet printable and UV-curable elastomers
- New chemical concepts to promote removal of stabilisation ligands from nanoparticle surfaces during post-processing are under investigation, which are intended to allow the onset of conductivity at lower temperatures

Future focus

- Carry out parametric studies of the relationship between filler contents and modifications on the conductivity, opacity, stretch-ability, and printability of composites comprised of in-house synthesised graphene, and in-house developed photopolymer elastomers
- Develop a liquid-liquid phase-separated and curable conductive composite mixture, containing chemically confined short chain ionic gels, as an inkjet printable formulation

3D macromolecules

Aim: To investigate the potential applications and effects of 3D macromolecules in AM processes.

Hyperbranched (HB) polymers are large, globular structures with a high density of functional end groups, which can take part in further polymerisation or cross-linking reactions. In comparison to their linear analogues, HB polymers can be incorporated into formulations without causing a large increase in viscosity. They also allow us to process multiple materials, where the HB polymer can be pre-formed from monomers, which exhibit lower curing kinetics than those commonly used to-date, which greatly increases the range of materials and co-polymers that can be AM processed. We are also developing a series of bio-compatible/biodegradable inks.

So far, we have developed a novel methodology to drive a number of different HB polymer syntheses from 40% to 90% yield, via the use of thiol chain transfer agents (CTAs). Thiol CTAs introduce additional functionality to the polymer chains, which can allow for post-functionalisation.

Achievements in year two

- Developed a promising polymeric stabiliser for graphene-based ink formulations. The HB material seems to promote good dispersion of graphene flakes in organic solvents and the formulation has been inkjet-printed to produce conductive printed parts, hence showing potential for applications in electronic and sensor manufacture
- Improved inkjet formulations - HB polymers have been added to UV-curable monomer inkjet formulations and are seen to increase the rate of curing/ reduction in free monomer. This has been achieved whilst keeping the ink viscosity within processing limits
- HB materials have been incorporated into 2PP formulations and preliminary results suggest that the processing window for polymerisation is widened by the addition of HB polymers

Future focus

- Continue to develop suitable HB materials for AM processes from multi-functional meth/acrylates, using the methodology developed so far. This will contribute to both inkjet and 2PP material libraries and could have interesting effects on structural properties, which will be determined. Block copolymers that can act as surfactants will also be synthesised to aid in multi-material processing
- Apply the method of formulating stabilised graphene ink to other low dimensional materials

Applications and demonstrators

Electronic devices

Aim: To inkjet print 3D multi-material electronic devices using inherently two-dimensional materials (graphene and its analogues) to offer the possibility of enhanced functionality, particularly in the vertical directions.

Controlled deposition of alternating low-dimensional materials will provide emergent functionality. The functionality of the printed stack is along the vertical direction, but materials are constructed by laying down droplets in the x and y planes. We exploit multiple tentative low-dimensional materials, using quantum modelling, to 'design-in' and manufacture topology that will enable control over the precise function of the herterostructures. As multiple materials with largely different physical and chemical characteristics will be deposited, further post deposition processing will be required to convert them into their final functional form.

Achievements in year two

- A transistor based on multi-material stacks of low dimensional materials was fabricated by inkjet printing a multi-layer graphene channel with a boron nitride gate and a silver electrode on top. The electrical measurements show a characteristic gate effect on the electrical conduction of printed graphene layers. The chemical characterisation confirmed the interface effects between multiple materials, which had been observed electronically, and predicted by the theoretical modelling
- In-house graphene hyperbranched polymer ink and the printed film have been characterised, including rheology measurements, Raman spectroscopy, transmission measurements, and electronic characterisation. The post processing strategy for annealing has been investigated and this has provided feedback for the optimisation of ink formulations
- Showed that UV absorption enhanced the conductivity of the graphene polymer composites, making them promising for printing solar-blind UV detectors

Future focus

- A fully inkjet printed solar-blind UV detector will be fabricated using the graphene-polymer ink, including material synthesis improvements and optoelectronic characterisation
- Inkjet printed graphene will be investigated as a material for electrical contacts for other 2D, 1D or 0D materials, such as contacting indium selenide, to construct a wideband photodetector with high quantum efficiency
- Explore the use of graphene as an active material to create other orthogonal functional devices, eg a sub-THz emitter based on electron resonant tunnelling between coupled graphene layers through a boron nitride barrier

Fully Inkjet printed multi-material transistor with graphene and Boron Nitride

Bioactive bone implant

Aim: To develop a clinically relevant sized bioactive implant for bone repair with integrated vasculature by using additive multi-material jetting and smart bioactive materials.

Hard tissue repair costs hundreds of billions of dollars annually worldwide, and the demand is substantially increasing as the population ages. Fragility fractures are estimated to cost the UK around £4.4 billion/year. Finding ways to improve bone healing after a fracture is a priority, as part of the governmental goal of developing a healthy ageing strategy for the population. The work developed in this project using additive manufacturing and smart materials represents an attractive approach for effective, accurate, and clinically relevant tissue manufacturing. By using multi-material jetting, we will create large sized bioactive implants without compromising the resolution, as happens with other multi-material systems, such as extrusion. Additionally, the 30 μm resolution of our bespoke multi-material jetting (Toucan) system will allow the incorporation of an integrated vasculature that mimics the arterioles of bone. The bioactive and biodegradable materials will enhance cell migration into the implant and bone formation.

Achievements in year two

- Biocompatible and biodegradable materials for implants have been optimised for jetting
- The feasibility of printing micro vascular channels in the size range of arterioles (50-100 μm) has been demonstrated; something that is not possible using other multi-material AM technologies
- Demonstrated the viability of manufacturing the vascular micro channels in the x, y, and z directions
- Perfusion through the vascular micro channels was achieved

Future focus

- Print large scale implants (in the range of 10 cm) to demonstrate scalability
- Develop a perfusion micro fluidics system for the *in vitro* culture of the implants
- Print different bone lattice structures to control the mechanical properties of the implant
- *In vitro* culture of the implants with cells to demonstrate bone and vascular formation

Aligned doctoral research

The Programme is proud to also be developing the next generation of leaders in AM. Our team of high calibre doctoral research students are working on projects ranging from controlling metal jetting to the long term release of biomacromolecules.

Jonathan Gosling
(started October 2018)

Electronic properties of graphene-based electronics

This project aims to develop analytical and computational methods for the characterisation of 3D printed stacks of 2D hetero-structures, incorporating inkjet printed graphene. In particular, the work considers the electrostatic capabilities of graphene under the influence of multiple sources of external electronic scattering, such as graphene phonons, charged impurities, lattice defects and interfacial phonons between layers. Additionally, this PhD aims to understand the difference between single layer graphene devices and multiple layer devices, to enable inkjet printing of graphene flakes.

A Discontinuous Galerkin (DG) simulation was used to model the effects of scattering. The results accurately described the experiments on mono-layer graphene devices reported in the literature, under variation of physical parameters. A semi-classical Monte Carlo simulation can be used to reproduce the results of the DG simulation.

The future focus will include a classical take on the Monte Carlo simulation to model printed multi-material devices, such as quantum-dot coated graphene.

Eric Lehder
(started October 2018)

Optimising the geometry of cell seeded TPMS scaffolds for bone fracture healing

Currently the standard procedure to treat large bone defects or fractures is to use bone allografts, autografts, and metallic implants. However, these involve complex and time-consuming surgeries, there is high donor site morbidity when using autografts, and metallic implants tend to fail due to the excessive stress caused by the higher mechanical strength. Additively manufactured scaffolds with biocompatible, biodegradable, and bone matched mechanical properties could improve the outcomes of bone healing and regeneration in these cases.

This work aims to develop a computational method to compare and optimise triply periodic minimal surface (TPMS) scaffold geometries in order to maximise their regenerative capacity, while ensuring matched mechanical performance. A curvature dependent model that predicts scaffold tissue growth was used, together with a mechanical performance finite element-based model to optimise the geometry of different TPMS scaffolds, thus maximising tissue formation.

In the upcoming year, cell culture experiments will be undertaken to validate the results obtained. Moreover, the expansion of the model to consider other parameters, such as fluid shear stress, microtopologies, and inclusion of growth factors will be investigated.

Eric Lehder and Jonathan Gosling operating the sputter coater to prepare samples for further characterisation and analysis

Negar Gilani

(started October 2018)

Control of high-temperature drop-on-demand metal jetting through numerical modelling and experiments

Metal jetting works by dispensing and depositing individually controlled micro-droplets (~70 µm) of molten metal at precise locations, and opens up new opportunities for the additive manufacturing of metallic components. MetalJet is exclusively available to the Centre for Additive Manufacturing (CfAM), including colleagues in this Programme, and has the capability of producing micro-droplets of conductive metals with melting points up to 2000 °C.

The aim of this project is to understand the 3D deposition of high-temperature metallic droplets through computational modelling and validate it through experimentation. This provides insights into the fundamental physical phenomena of the MetalJet process, such as the level and nature of inter-droplets bonding and adhesion to the substrate, residual stress build-up and deformations, and the microstructural evolution.

A 3D sequentially coupled thermo-mechanical FE model has been developed using Abaqus Software. The model predicts the physical state, temperature, and stress evolution of single and multiple droplets during MetalJet printing. In parallel, metallographic observations have been performed to investigate the morphology of the droplets, bonding between the droplet and substrate, and the microstructure of droplets using SEM, FEG-SEM and FIB-SEM. In general, a good agreement between the experimental results and numerical simulation was observed.

In the year ahead, the focus will be on modelling the microstructural evolution of single and multiple droplets and perform experiments to validate the established models.

Maria Inês Evangelista Barreiros

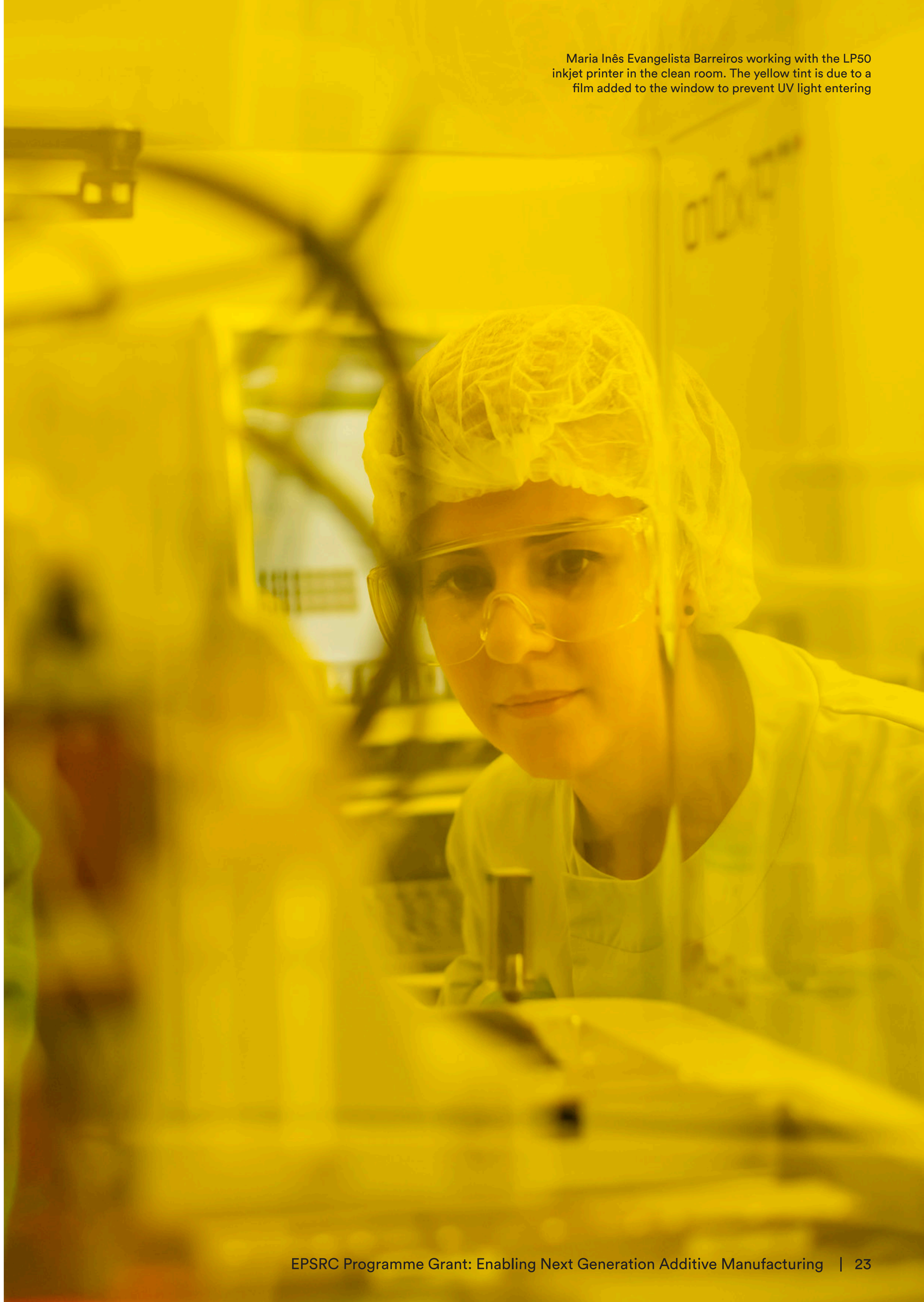
(EPSRC Centre for Doctoral Training in Additive Manufacturing, started February 2019)

Exploring the use of responsive materials for the controlled release of pharmaceutical drugs

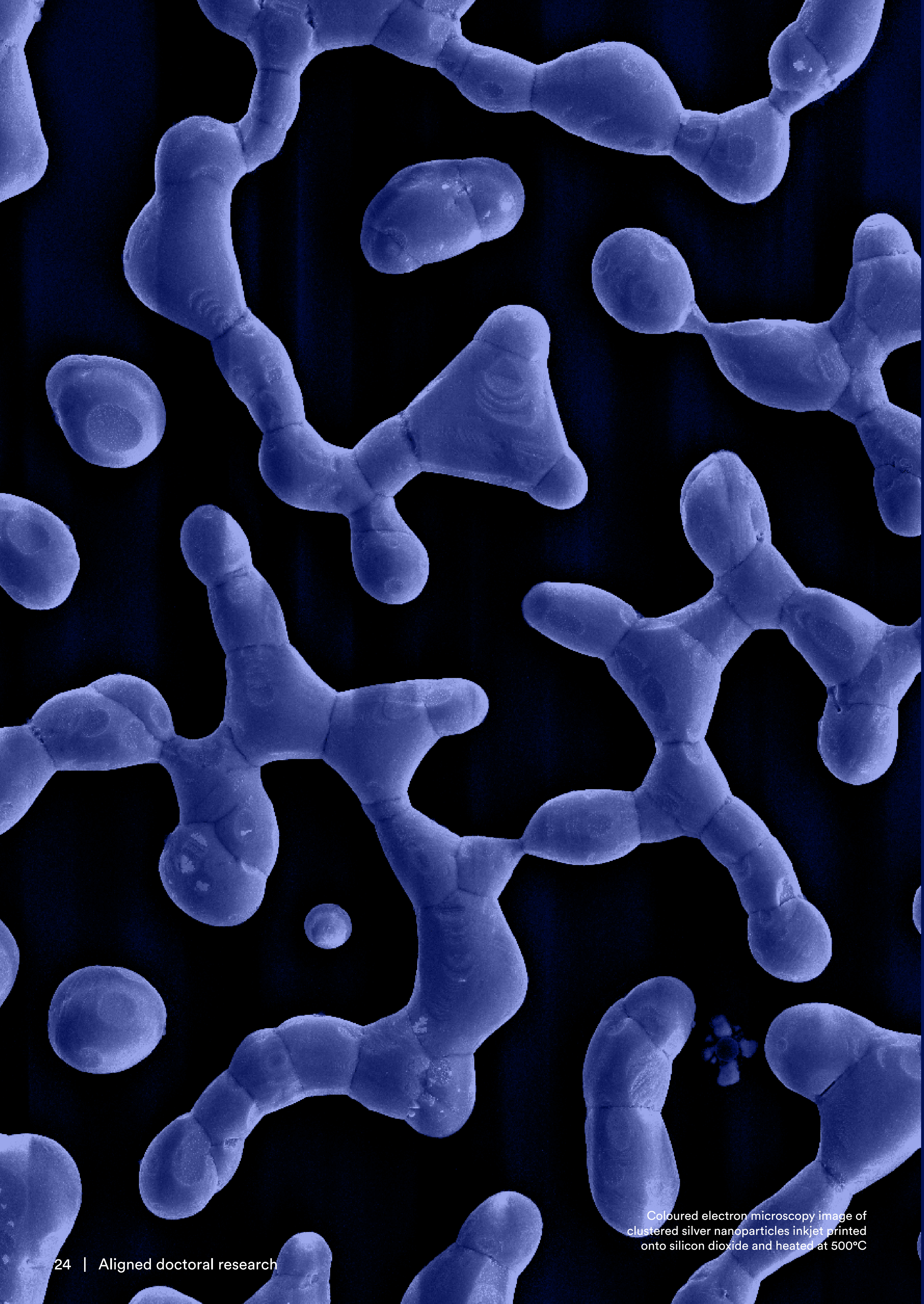
The use of stimulus-responsive materials in pharmaceutical formulations enables the release of pharmaceutical drugs in highly specific sites. Combining these responsive materials with gastro-retentive systems can also lead to prolonged drug retention times and sustained release profiles that can be further studied and understood by using computational models. Using 3D printing to produce these dosage forms allows the exploration of different and more complex structures, as well as different dosage forms that have not been possible with conventional manufacturing methods.

In the year ahead, the plan is to explore possible materials for use in such systems, characterise them and identify the properties required for ink formulations.

This is also dependant on the target release site and the properties of the drug. The project will also be working on extrusion printed implants using self-healing polyurethane, in collaboration with the EPSRC Formulation for 3D Printing project (EP/N024818/1).



Maria Inês Evangelista Barreiros working with the LP50 inkjet printer in the clean room. The yellow tint is due to a film added to the window to prevent UV light entering



Coloured electron microscopy image of clustered silver nanoparticles inkjet printed onto silicon dioxide and heated at 500°C

Kevin Bandeira
(EPSRC Centre for Doctoral Training in Additive Manufacturing, started February 2019)

Long-term controlled release of 3D printable implants

The primary aim of this project is to further develop a drug-loaded formulation with a monomer that has previously been shown to exhibit resistance to microbial attachment. Using 3D inkjet printing with UV photo initiation, we will print an implant for medical applications.

Currently, results have shown that it is possible to successfully load high levels of Ibuprofen, an anti-inflammatory drug, and that the monomer is printable. In the year ahead, we will print the drug-loaded formulation. Following full characterisation of the ink, future applications will be explored, eg in ear implant coatings.

Kristian Plender
(started October 2019)

Novel approaches to the long term release of biomacromolecules

The delivery of biomacromolecules is particularly challenging due to their large and typically unstable nature. This demands methodologies that are capable of ensuring their protection during the manufacturing process and prior to their required release. It is also beneficial and of great interest to be able to personalise and tailor delivery on an individual patient basis, with additive manufacturing presenting a pathway for this.

As such, the plan is to develop methods of protecting biomacromolecules to allow for long-term release, and consider the use of depots/implants created using multi-material additive manufacturing processes. Additionally, methods of delivering and incorporating proteins will be considered, to aid the development of *in vitro* models.

Joe Sefton
(started October 2019)

Production and use of oligomers in additive manufacturing

One of the key issues in AM is the limited palette of materials. The overarching goal of this project is to deliver new polymeric materials with novel mechanical properties that are compatible with existing AM processes. This entails tuning the physico-chemical and mechanical properties of the polymers. The target AM method, such as inkjet printing or selective laser sintering, will depend on the physical properties of the synthesised materials.

Over the coming year I will synthesise and characterise various novel monomers and corresponding polymers to identify ideal candidate materials to bring forward for use in AM. Synthesised polymers will ideally be functional oligomers (low molecular weight polymers). This will be achieved by using catalytic chain transfer polymerisation, as this has been shown to provide excellent control over polymerisations and produce end-functionalised polymers, which are compatible with current photo-initiated curing techniques in AM.

Outputs

Conference presentations

Title	Speaker	Event	Date	Venue
Low-temperature sintering of inkjet printed metal nano particles for additive manufacturing: chemical and morphological assessment	Gustavo F Trindade	Materials Research Society (MRS) Fall 2019 Conference	December 2019	Boston, USA
Three-dimensional plasmonic nano-composites fabrication by two-photon lithography based 3D printing (poster)	Qin Hu	Materials Research Society (MRS) Fall 2019	December 2019	Boston, USA
3D printing acrylate-thiol nanocomposites by two-photon lithography and functionalisation by au nanoparticles (poster)	Qin Hu	Polymer Research Symposium 2019	November 2019	Nottingham, UK
Production of multi-functional devices by reactive material jetting	Yinfeng He	Polymer Research Symposium 2019	November 2019	Nottingham, UK
Applications of 3D printing graphene and other low dimensional materials	Feiran Wang	Technology Innovation, Entrepreneurship and Creativity Forum	November 2019	Chongqing, China
Jetting of high temperature metals using the novel droplet-on-demand technology 'Metaljet'	Nesma Aboulkhair	Materials Science and Technology (MS&T) 2019	Sept-Oct 2019	Portland, OR, US
Jetting of high temperature metals using the droplet-on-demand technology 'Metaljet'	Nesma Aboulkhair	Additive International Summit (2019)	July 2019	Nottingham, UK

Title	Speaker	Event	Date	Venue
Characterisation of metallic material produced using the novel droplet-on-demand technology 'Metaljet'	Nesma Aboulkhair	International Conference on Advanced Computational Engineering and Experimenting (ACEX) 2019	July 2019	Athens, Greece
Novel biomaterials for inkjet 3D printing drug delivery implants	Laura Ruiz Cantu	Tissue and Cell Engineering Society (TCES) 2019	June 2019	Nottingham, UK
Novel biomaterials for inkjet 3D printing drug delivery implants	Laura Ruiz Cantu	Biofabrication 2019	October 2019	Ohio, USA
Advanced surface and interface analysis to enable next generation additive manufacturing	Gustavo F Trindade	The Enlighten Conference	October 2019	Coventry, UK
Developing materials for inkjet 3D printed drug delivery and biomedical devices	Yinfeng He	APV: Making Science Work: 3D Printing in Pharma – 4 years after the first FDA approval: where are we now?	September 2019	Antwerp, Belgium
A multi-scale computational model to predict the performance of cell seeded scaffolds with triply periodic minimal surface geometries	Eric Lehder	30th Annual International Solid Freeform Fabrication Symposium - An Additive Manufacturing Conference	January 2019	Austin, Texas, USA
Advanced materials characterisation to enable next generation additive manufacturing (poster)	Gustavo F Trindade	Institute of Physics (IOP) - Science of Printing 2018	November 2018	London, UK
Advanced sims analysis to enable next generation additive manufacturing (poster)	Gustavo F Trindade	SIMS Europe 2018	September 2018	Muenster, Germany

Microscope lenses in operation on the Buehler Wilson VH3100 Automated Hardness Tester

Publications

At the end of the Programme's second year, we are pleased that three papers have been published, one is in press, and two further papers have been submitted for publication. As we have a grant strategy of publishing high quality papers in leading journals, we have applied very strict standards to our experimental results and our manuscripts, which significantly increases development time. Now that the team is established, we have a number of impressive manuscripts in preparation and are looking ahead to a period of high productivity.

Papers aligned with the theme of the Programme

Simonelli M, Aboulkhair N, Rasa R, East M, Tuck C, Wildman R, Salomons O, Hague R. Towards digital metal additive manufacturing via high-temperature drop-on-demand jetting. Additive Manufacturing, 2019, 30, 100930

Tiddia M, Mihara I, Seah MP, Ferraz Trindade G, Kollmer F, Roberts CJ, Hague RJM, Mula G, Gilmore IS, Havelund R. Chemical imaging of buried interfaces in organic–inorganic devices using focused ion beam-time-of-flight-secondary-ion mass spectrometry. ACS Applied Materials & Interfaces, 2019, 11, 4, 4500-4500

Zhang F, Saleh E, Vaithilingam J, Li Y., Tuck CJ, Hague RJM, Wildman RD, He Y. Reactive material jetting of polyimide insulators for complex circuit board design. Additive Manufacturing, 2019, 25, 477-484

He Y, Foralosso R, Ferraz Trindade G, Ilchev A, Ruiz Cantu L, Clark E, Khaled S, Hague RJM, Tuck CJ, Rose FRAJ, Mantovani G, Irvine DJ, Roberts CJ, Wildman RD. A reactive prodrug ink formulation strategy for inkjet 3D printing of controlled release dosage forms and implants. Advanced Therapeutics, 2020. In press

Chubynsky M, Belousov K, Lockerby D, Sprittles J. Bouncing off the walls: the influence of gas-kinetic and van der Waals effects in drop impact. Physical Review Letters. Submitted

Zhao P, He Y, Ferraz Trindade G, Chen X, Wildman R, Hague R, Tuck C, Irvine D, Ashcroft I. The UV cure process in material jetting additive manufacturing. Additive Manufacturing. Submitted

Awards/prizes

EPSRC Science Photo Competition 2019 - 1st prize in the Innovation category in for 'Wonderland balls in small world' by Dr Qin Hu and Joe White

MSK MEC and UKMRP Smart Materials Sandpit Award: to develop a mechano-chemical integration at the osteochondral interface of tissue engineered implants. Dr Laura Ruiz Cantu and collaborators at Imperial College London. November 2019 – June 2020. £14,900

MSK MEC and UKMRP Smart Materials Sandpit Award: to develop a device for fatigue detection to prevent musculoskeletal injuries. Dr Laura Ruiz Cantu and collaborators at Imperial College London. November 2019 – June 2020. £14,900

UNICAS Sandpit Award. Tea for two-photon polymerisation: functional microdevice fabrication using a novel 3D printing approach for safe and controlled drug delivery. Dr Elizabeth Clark, Dr Qin Hu, Dr Lea Santu and Dr Graham Rance. April - July 2019. £12,133

Event supported by the Programme

The Polymer Research Symposium, University of Nottingham, 7 November 2019
Organised by Amy Stimpson and Rachel Atkinson

Research visits

Visitor	Venue	Purpose	Date
Laura Ruiz Cantu	Lawrence Livermore National Laboratory, USA	Printing photocurable polymers using the CAL system	October 2019
Ricky Wildman	University of Seville, Spain	Collaborative exchange	September 2019
Richard Hague	Nanjang Technological University, Singapore	Visiting professorship	May 2019
Gustavo F Trindade	NPL, Teddington, UK	Advanced materials characterisation	April 2019
Yinfeng He	University of Seville, Spain	Exchange fellowship	November 2018
Gustavo F Trindade, Yinfeng He and Ricky Wildman	Durham University, UK	Droplet characterisation	June 2018

Outreach activities

In 2018- 2019 Programme members have taken part in various outreach activities:

Pint of Science	Lacehouse, Nottingham	May 2018
Pint of Science – Creative Reactions	National Videogames Arcade, Nottingham	May 2018
New Scientist Live	ExCel Arena, London	Sept 2018
UK Quantum Technology Industry Showcase	QEII Conference Centre, London	Nov 2018
Family Discovery Day	University of Nottingham	Mar 2019
Pint of Science – Tech Me Out	Canalhouse, Nottingham	May 2019
Pint of Science – Creative Reactions	Parliament Bar, Nottingham	May 2019
Archway STEM Festival	Blucoats Beechdale Academy	Jun 2019
IntoUniversity Family Learning Graduation	University of Nottingham	Jul 2019
UK Quantum Technology Industry Showcase	QEII Conference Centre, London	Nov 2019
Royal Society Quantum Technology Showcase	Royal Society, London	Nov 2019
Faculty of Engineering Christmas Lecture	University of Nottingham	Dec 2019

Summer students

In 2019 Programme researchers supervised 6 undergraduate summer internships:

Guy Lawrence	Improving carbon fibre composite manufacturing processes by characterisation of composite preforms stabilised by inkjet printing methods
Eoin O'Connor	Formulation of graphene containing ink for 3D printing and electronic device fabrication
Adam Balogh	3D printed flexible electronic devices: optimisation of the in-line sintering process for 3D inkjet printed silver nanoparticles
Sylvia Tan	Exploring routes to overcome functional anisotropy in two-photon lithography based 3D micro/nano fabrication
Varinder Panesar	Development of a new manufacturing protocol for the production of a carbon fibre composite: integration of inkjet in carbon fibre composites manufacturing
Joni Wildman	Optimisation of the printing parameters of water-soluble polymers for the development of micro vascular channels

The year ahead

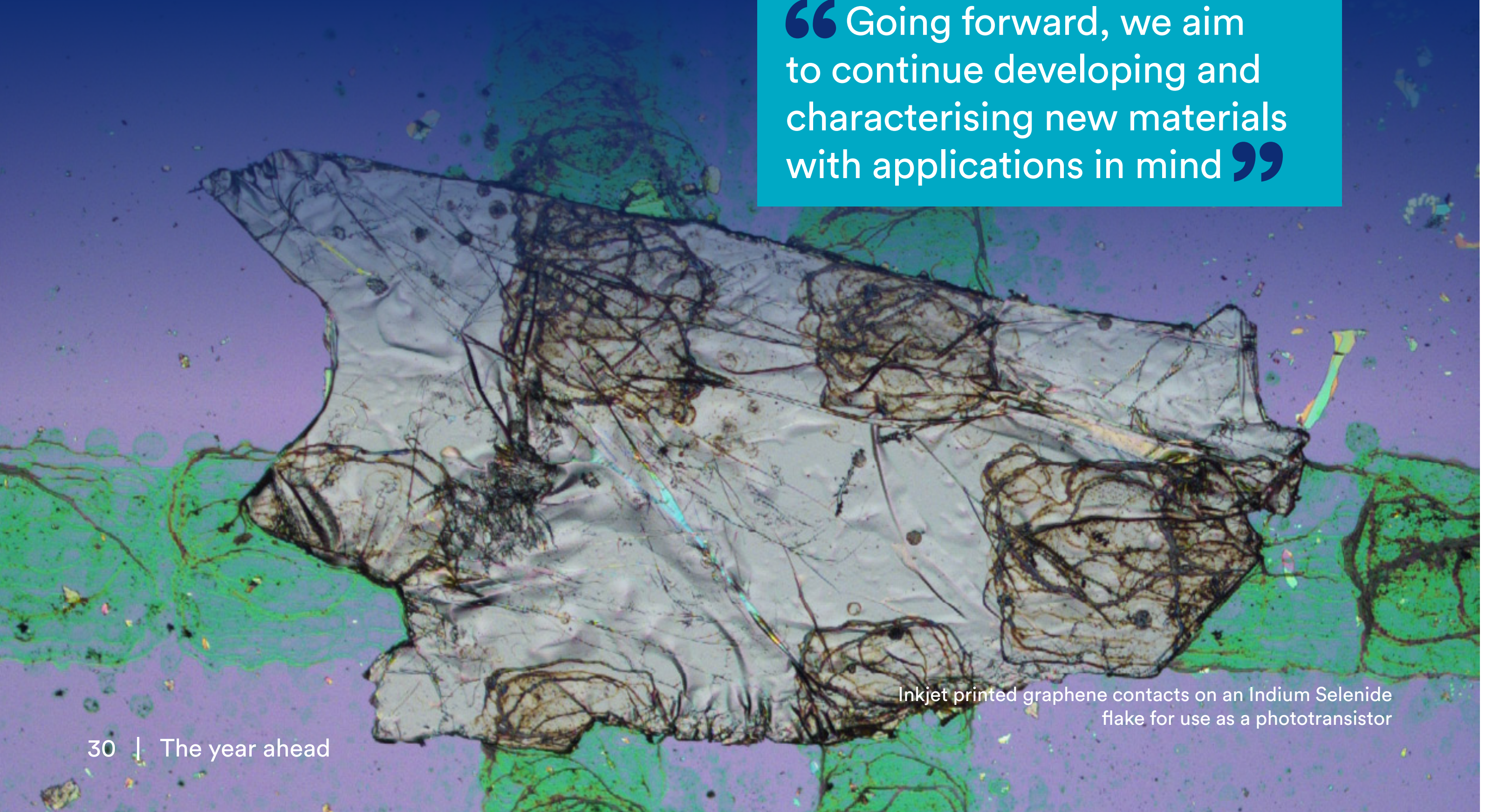
Having completed year two, we are due to submit a mid-term review to our funders, the EPSRC. We are confident that this review will confirm our strong position as leaders in the related fields of multi-material AM. We are moving forward in the co-printing of dissimilar materials by MetalJet, material jetting and 2PP, and are progressively establishing systematic analysis protocols to characterise the interfaces and the interphases, therefore advancing multi-material and multi-functional AM.

Going forward, we will build on the good relationships with our partners and collaborators, continue to explore new materials, with a focus on the applications of our research. We will also continue to publicise our work to a wider audience by publishing in high impact journals, taking part in outreach activities, and producing high specification animations of our processes and capabilities. As such, we are delighted to have been selected to present a stand at the Royal Society Summer Science Exhibition in July 2020.

In the year ahead, the Programme will:

- Enhance our multi-material process capabilities with a view to developing applications: we will install our own MetalJet system inside a glovebox, use the established computational models to develop multi-material polymer jetting for biomedical applications; and investigate the bio/pharmaceutical and electrical applications for the new materials developed for 2PP and jetting
- Investigate the hybrid organic/inorganic materials interfaces present in low-dimensional and electronic demonstrators, and also the complex organic/organic interfaces in pharmaceutical and healthcare demonstrators
- Complete computational models for the MetalJet process, and start working on modelling 2PP processes. Apply the models to optimise process parameters and deposition strategies
- Develop and fine-tune a library of materials and techniques for multi-material printing of electronic devices
- Use graphene as both an active material for orthogonal functional devices and a contacting material for other low dimensional materials. Electronic demonstrators, such as a sub-THz emitter and a wideband photodetector will be fabricated with the help of an optimised graphene ink formulation and printing strategy
- Include bioactive molecules within printed implants to enhance bone and vascular formation. In addition, we will focus on scalability, improved mechanical properties and *in vitro* testing to demonstrate multi-functionality.

> “Going forward, we aim to continue developing and characterising new materials with applications in mind”



Inkjet printed graphene contacts on an Indium Selenide flake for use as a phototransistor

Management structure

Executive team

Professor Richard Hague
University of Nottingham
Principal Investigator and joint RC1 lead

Professor Clive Roberts
University of Nottingham
Co-Investigator and joint RC1 lead

Professor Ian Ashcroft
University of Nottingham
Co-Investigator and joint RC2 lead

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

Professor Ricky Wildman
University of Nottingham
Co-Investigator and joint RC3 lead

Professor Derek Irvine
University of Nottingham
Co-Investigator and joint RC3 lead

Professor Chris Tuck
University of Nottingham
Co-Investigator and joint RC4 lead

Professor Mark Fromhold
University of Nottingham
Co-Investigator and joint RC4 Lead

Professor Yulii Shikhmurzaev
University of Birmingham
Co-Investigator

Dr Lyudmila Turyanska
University of Nottingham

Advisory board

Dr Will Barton
(WillB Consulting) - Chair

Rebecca Cheesbrough (EPSRC)

Professor David Rosen (SUTD)

Rebecca Mangham Dstl

Mark Swan (AWE)

Dr Paul Gellert (AstraZeneca)

Professor Ian Gilmore (NPL)

Robin Wilson (Innovate UK)

Dr Christopher Spadaccini
Lawrence Livermore National Laboratory (LLNL)

Partners and collaborators

Professor Christopher Barner-Kowolik
Queensland University of Technology (QUT)
Karlsruhe Institute of Technology (KIT)

Professor Martin Wegener
Karlsruhe Institute of Technology (KIT)

Dr Christopher Spadaccini
Lawrence Livermore National Laboratory (LLNL)

Professor Ian Gilmore
National Physical Laboratory (NPL)

Dr Paul Gellert
AstraZeneca

Martin Hermatschweiler
Nanoscribe GmbH

Trevor Polidore
Rogers Corporation

Mark Swan
AWE

René Waarsing
Canon Production Printing (formerly Océ)

Dr Benjamin Cook
Texas Instruments

Laura Jones
Dstl

Rebecca Mangham
Dstl

David Hallam
Dstl

Dr Brian Henry
Pfizer

Dr Martin Rowland
Pfizer

University of Nottingham
UK | CHINA | MALAYSIA

Engineering and Physical Sciences Research Council

For general enquiries please contact:

Dr Harinee Selvadurai
Programme Manager
Centre for Additive Manufacturing
Faculty of Engineering
Advanced Manufacturing Building
Jubilee Campus
University of Nottingham
NG8 1BB

Harinee.Selvadurai@nottingham.ac.uk
nottingham.ac.uk/NextGenAM
0115 846 6096

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+44 (0)115 951 5559

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