Institution: Ulster University

Unit of Assessment: Engineering (12)

Title of case study: Micro and Nanomaterials from Lab to Industrial Production

Period when the underpinning research was undertaken:
1 January 2000 to 31 December 2020

Details of staff conducting the underpinning research from the submitting unit:

Name(s):	Role(s) (e.g. job title):	Period(s) employed by submitting HEI:
Professor J Anthony Byrne	Professor of Photocatalysis	2005-present
Professor Jim McLaughlin	Professor of Functional Materials	1990-present
Professor Pagona Papakonstantinou	Professor of Advanced Materials	1998-present
Professor Brian J Meenan	Professor of Biomedical Materials	1989-present
Dr Patrick Lemoine	Lecturer Engineering	2002-present

Period when the claimed impact occurred:
1 August 2013 to 31 July 2020

Is this case study continued from a case study submitted in 2014? N

1. Summary of the impact

Micro and nanoscale materials research at Ulster has had a quantifiable socio-economic impact in regard to company profitability and the creation or retention of jobs in Northern Ireland. Researchers in the Nanotechnology and Integrated Bioengineering Centre (NIBEC) have had sustained collaboration with **AVX Ltd. Coleraine,** which is part of the AVX Corporation, with plants and distribution centres in Europe, the Americas and Asia. In our most recent collaboration, eight of ten target parts were successfully developed and launched. [redacted] Knowledge gained through our collaborative activities has allowed AVX Coleraine to gain substantial credibility with customers such as NASA, BMW, Ford, and the European Space Agency. In addition, expertise in micro- and nano-materials research at Ulster contributed to the development of a **spin-in company SiSaf Ltd**. [redacted] Research into 2D materials has provided a sustained and fruitfulcollaboration with **spin-in company 2DTech** with a patent licensed from Ulster to the company. Our nanotechnology research has underpinned significant funding from GCRF UKRI & H2020 addressing the global water challenge**.**

2. Underpinning research

Micro- and nano-scale materials research at NIBEC has focused on developing a fundamental understanding of how materials processing impacts resultant properties for targeted applications. Research includes micro-, nano- and 2D carbon materials (nanotubes, graphene, C_3N_4), metal oxides (ferroelectrics, TiO_2) and Si and Group IV alloys. Much of this research has been supported by EPSRC, the Royal Society, EU Framework Programmes (H2020), US-Ireland Collaborative Partnerships (NSF,SFI & DEL/DfE) and Invest Northern

Ireland R&D funding in collaboration with industry (AVX, SiSaf, Intel, Glaxo-Smith-Kline, Schrader Electronics, Analog Devices, TFX Medical, Medtronic, Labcoat, Kelvatech, Randox). Targeted equipment grants have led to the creation of one of the most advanced academic micro and nanomaterials characterisation facilities in Europe (GBP20,000,000 of capital investment since 2011 e.g., NI Government funding for TEM (2011, **G1**), FE-SEM with EDX (2018) and EPSRC Awards for UPS/XPS Facility (2018), XRD (2020) and AFM (2021)).

Our fundamental strengths have centred on: (i) advancing metrology for the measurement of nano-scale hardness, film thickness, internal stress and adhesive strength on ultra-thin (1–50nm) carbon layers; (ii) nanoparticle fabrication (via laser, microplasma, milling and wet chemical/electrochemical synthesis) and characterisation of both the materials and the synthesis processes; and (iii) nano-scale surface-engineering and functionalisation with associated high-resolution analysis (TEM, ToF-SIMS, XPS, AFM). In material synthesis, a primary strength is in plasma-based deposition, surface engineering and bespoke functionalization. For example, a custom-built microwave plasma system (Seiki, Japan) developed at NIBEC was the world's first system for the deposition of highly oriented nanotubes (McLaughlin & Papakonstantinou 2004-11) **[R1-R2]**.

The ability to deliver impact with AVX **[I1]** was due to our underpinning research on micro- and nanomaterials. There have been three research awards in collaboration with **AVX Coleraine** totalling GBP3,000,000 to Ulster since 2008 (total cost GBP6,000,000 match funded by AVX), addressing key areas of advanced production and characterisation (Byrne, McLaughlin, Lemoine) [**G2-G4].** From 2008 to 2014 AVX co-funded a GBP1,700,000 project (GBP874,000 to Ulster) **[G2]** with support from Invest NI, to improve the quality of the dielectric layers in the Multi-Layer Ceramic Capacitors (MLCCs) that the company produces in millions of units per day. Research into ceramic slip processing led to significantly improved production efficiencies for the company (Byrne, McLaughlin, 2015) **[R3]** which the company has now fully integrated into its high-volume production lines in Coleraine and internationally (Penang, Malaysia). AVX co-funded a second project (GBP300,000, GBP151,000 to Ulster) focusing on improvements to the base metal electrode (BME) system in MLCCs by utilising nano-particle nickel **[G3].** This project identified improvements in nanoparticle nickel BME ink formulation and its subsequent processing. From 2014 to 2019, NIBEC and AVX undertook a third larger R&D project (GBP4,500,000 in total, GBP2,000,000 to Ulster **[G4]**) to develop novel dielectric formulations for new MLCC parts operating at higher voltage. This project delivered 10 new part numbers, **8 of which were qualified and moved into production,** [redacted]

Nano-engineering of materials for environmental and energy applications is a strong research area at Ulster (Byrne 2000 to date) and this knowledge has been translated to impact on the development of novel dielectrics with AVX. Nano-engineered metal oxides have been applied for photocatalytic water treatment processes and this research track underpinned a successful bid for the GCRF UKRI SAFEWATER project (PI Byrne, GBP4,900,000 EPSRC, 2017-2021), delivering technologies for safe drinking water in the Global South. Further funding was awarded for the GCRF GRTA SAFEWATER Translate project (PI McLaughlin, GBP837,000, EPSRC, 2019) to accelerate the development and exploitation of SAFEWATER water quality devices at partner sites in the Americas, Africa and Nepal.

Nanomaterials research has also underpinned R&D for production and functionalisation of **nanoparticle silicon** for use in drug and therapeutic transdermal delivery applications by spin-in company **SiSaf** (Byrne, McLaughlin, Meenan 2009-2020) **[I2].** This work relies on the provision of high-quality and precisely controlled 50 nm particles of Si with highly defined porosity/surface properties to allow for their subsequent surface functionalisation and specific drug attachment. Key research work here initially utilised our FCVA and CVD equipment which then led to the development of a specially constructed reactor to batch

produce nanoparticles in a reproducible manner. SiSaF was initially hosted in NIBEC as a spin-in to enable characterisation, testing and rapid qualification of commercial grade Si nanoparticles supported through grant funding from Invest NI **[G5]**. Our capability in nanotoxicity testing in the NIBEC Cell Culture Facility **[R4]** allowed in-vitro testing of Si nanoparticle toxicity which formed the basis for the product's core commercialisation specifications. These data then provided the platform for a vitamin C dissolution study in an animal model which confirmed that the SiSaf drug delivery system is 30% better than a standard existing drug delivery platform. The collaboration with SiSaf is on-going and current studies are examining the use of nano-silicon for transdermal therapeutic delivery involving a human clinical trial in the USA.

Papakonstantinou at Ulster University has been working with **2-DTech [I3]** in an expanding program of R&D since 2013. The collaboration has contributed substantially to 2-DTech's position as the world leader in synthesis of 2D materials for a range of applications (e.g., polymer composites, antimicrobial materials, electrochemical sensors, anti-corrosive coatings). The process for the synthesis of graphene and other 2D layered materials was invented by Papakonstantinou's team. The intellectual property from this work was generated by a proof-of-concept project **[G6]** and is captured under the Patent US 9139439 (filed March 2012), entitled 'Process for the preparation of graphene' **[R5]** and subsequently published articles **[R6]**. The 2D materials are produced via room temperature ionic liquid (RTIL) assisted grinding exfoliation, combined with sequential centrifugation steps. As a result, the process offers several advantages including minimal defects (low oxygen content <1%) compared to conventional graphene manufacturing solutions currently on the market. The high quality of the produced 2D nanosheets has been tested by our team, 2-DTech and a number of independent testing houses. The partnership with 2-DTech has involved the synthesis, detailed characterisation and scale-up of the process.

3. References to the research Outputs can be provided by Ulster University on request.

[R1] Okpalugo T, **Papakonstantinou P**, Murphy H, **McLaughlin J.A.D**., Brown N, (2005) "High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs" Carbon, Vol.43, pp 153-161 DOI:10.1016/j.carbon.2004.08.033
[R2] Shang, N, **Papakonstantinou, P**, McMullan, M, Chu, M, Stamboulis, A,Potenza, A, Dhesi, S and Marchetto, H (2008) Catalyst-Free Efficient Growth, Orientation and Biosensing Properties of Multilayer Graphene Nanoflake Films with Sharp Edge Planes. Adv. Functional Mats, 18 (21). pp. 3506-3514. DOI:10.1002/adfm.200800951
[R3] Simpson, A.B.G.; **Byrne, J.A.; McLaughlin, J.A.D**.; Strawhorne, M., "Effect of solids concentration on particle size distribution of deagglomerated barium titanate in stirred media mills," Chemical Engineering Research and Design, 2015, 93, 287-292 DOI: 10.1016/j.cherd.2014.04.006:
[R4] Wadhwa, S.; Rea, C.; O'Hare, P.; Mathur, A.; Roy, S. S.; Dunlop, P. S. M.; **Byrne, J. A.;** Burke, G.; **Meenan, B.J.; McLaughlin, J.A.D.;** "Comparative in vitro cytotoxicity study of carbon nanotubes and titania nanostructures on human lung epithelial cells", Journal of Hazardous Materials, 2011, 191, 56–61.
[R5] P. Papakonstantinou, N. Shang "Process for the preparation of graphene" US9139439 (filed March 2012)
[R6] Shang, N.G., **Papakonstantinou, P**., Sharma, S., Lubarsky, G., Li, M., McNeill, D.W., Quinn, A.J., Zhou, W., Blackley, R., "Controllable selective exfoliation of high-quality graphene nanosheets and nanodots by ionic liquid assisted grinding", Chemical Communications, 48 (2012) 1877-1879 DOI: 10.1039/c2cc17185f
The journal articles have been subject to blind peer review practice by internationally-based editorial boards.

Relevant Grant Awards

G1: Nanoparticle Research Laboratory, D.E.L. – RCIF, 01/04/2009 - 31/07/2011; GBP1,067,901 **Prof JA Byrne**, Dr PSM Dunlop, Dr D Dixon, **Prof JAD McLaughlin**, Prof PD Maguire, Dr **PN Lemoine, Prof P Papakonstantinou**, Dr JWJ Hamilton

G2: The optimisation and understanding of the role of new nanoparticle ceramics for use in high frequency capacitors, Invest NI/AVX 01/09/2008 - 31/03/2014, GBP874,259, **Prof JAD McLaughlin, Prof JA Byrne**, Prof PD Maguire, Mrs Strawhorne - AVX
G3: Development of an Innovative Nickel Electrode System to Manufacture Improved Performance Next Generation Capacitors, Invest NI, 01/01/2012 - 30/09/2014, GBP151,086, **Prof JA Byrne, Prof JAD McLaughlin, Dr PN Lemoine**
G4: To develop novel dielectrics and processes which extend the capacitor range for automotive applications, Invest NI, 01/05/2014 - 30/09/2019, GBP1,979,702, **Prof JA Byrne, Prof JAD McLaughlin, Dr PN Lemoine,** Dr AR Boyd,
G5: SiSafe for topical delivery of active compounds, Invest NI, 01/05/2009 - 31/10/2010, GBP41,660, **Prof JAD McLaughlin,** Prof PD Maguire, **Prof JA Byrne,** Dr RS Saffie-Siebert (SiSaf)
G6: Production of transparent and conductive graphene ultrathin films using an environmentally friendly procedure, Invest Northern Ireland - Proof of Concept, 01/01/2010 - 31/03/2011, GBP100,736, **Prof P Papakonstantinou**

4. Details of the impact

[I1] AVX Limited is a wholly owned subsidiary of AVX Corporation which is a wholly owned subsidiary of Kyocera Corporation, Japan. AVX has 33 research, design, manufacturing, and customer support facilities in 16 countries around the world with fiscal 2020 sales reported as USD1.9Bn (17.02.21). AVX has established plants and distribution centres in Europe, Asia, and the Americas. In 1990 AVX became part of the Kyocera Group of Companies headquartered in Japan. The Corporation comprises 5 main product groups i.e., Ceramic, Tantalum, Advanced, KED (Kyocera Electronic Devices) and Interconnect. The European Ceramic operation is based at AVX Coleraine, Northern Ireland. **AVX Coleraine** is engaged in the marketing, development, and manufacture of Multi-Layer Ceramic Capacitors (MLCCs) for the Global Market. To remain competitive, AVX Coleraine moved the manufacturing of commodity products, using older technology, to low-cost economies, and re-invented itself as a supplier of semi-customised, higher value-added products to the high reliability sectors such as automotive, aerospace and space. The Coleraine, NI operation has achieved significant advances in the development of novel dielectric systems, which have delivered improved capacitor ranges.

"A key part of the research and development at AVX Coleraine involves collaboration with the Nanotechnology and Integrated BioEngineering Centre at Ulster University." **[C1]**

The company has a strong relationship with Ulster going back over 30 years and has directly funded collaborative R&D research projects, PhD studentships and offers placement opportunities for undergraduates in a range of disciplines. [redacted]

"… the knowledge gained through our recent collaborative activities has allowed AVX Coleraine to gain substantial credibility with customers such as NASA, BMW, Ford, and the European Space Agency. New device characterisation and fabrication capabilities introduced by NIBEC, including Electrical Impedance Spectroscopy, TEM techniques, Surface Science Characterisation, Zeta Mill Technology, and a Rare Earth Dopant Programme have all impacted on sales, growth, market penetration and job sustainability. Joint publications, publicity and sponsored PhD programmes have evolved leading a strong and fruitful relationship. [redacted]

Other impact includes one PDRA being employed by AVX as a Development Engineer, one Research Engineer being awarded a PhD by Ulster, and several other researchers progressing in their careers including to lectureships at Liverpool and Queens University Belfast, and senior roles at Ulster (Research Fellow, Athena SWAN Officer).

[I2] SiSaf Ltd was a spin-in company to NIBEC developing drug delivery formulations that use patented bioactive and non-toxic silicon nanoparticles (≤ 50nm). NIBEC assisted the company to develop improved fabrication and characterisation techniques and was represented on the SiSaf board by McLaughlin as CSO & Director until 2017. NIBEC and SiSaf jointly developed a wide range of capabilities in silicon nanoparticle production and characterisation. This led to an expansion of the SiSaf work force to seven staff, increased laboratory space and enhancement of their patent, IP and knowledge assets. SiSaf agreed a commercial arrangement with a British speciality drugs company Croda in 2018 to allow it to use and further develop its patented bio-courier technology known as ProSilic. As part of the deal, Croda took a minority stake in the company. ProSilic, which is based on a patented hybrid of porous silicon and liposomes, is a transdermal drug delivery system with applications in the treatment of skin conditions. Based on this expansion SiSaf expanded its activities at the Ulster University Jordanstown campus in 2014 and leased a suite of dedicated research laboratories. [redacted] With a strong investment profile to date and Human Clinical trials nearing completion, the CEO has stated “We are keen to sustain a long and lasting relationship with the NIBEC team. Their impact on the company has been critical at key stages and …NIBEC’s underpinning Engineering and Science capability is proving to be a highly important asset.” **[C2].**

[I3] 2-DTech Ltd, a spin-off company from University of Manchester, is now owned by Versarien plc. Collaboration with Papakonstantinou and the NIBEC team has improved 2-DTech’s understanding on a number of technical issues that were applied to various applications. In turn this helped 2-DTech to acquire a leading position in the production of 2D materials market on a global scale, particularly in the growing area of polymer composites. The partnership has helped 2-DTech to secure a number of grants including a SMART grant from Innovate UK **[C3]** on anti-corrosive coatings **[C4]**. A patent from Ulster was licensed to 2-DTech Ltd. **[R5]**. The company continues to have a spin-in presence within NIBEC under a service level agreement. The partnership has led to a new graphene product, named “nanene” as well as other 2D materials **[C5]**. In the last 7 years 2D-Tech has recruited one PhD student supervised by Papakonstantinou and has co-authored 6 papers on 2D materials for applications in energy storage and conversion, multifunctional composites and electrochemical sensors. Versarien plc. expect that Ulster’s process for graphene and 2D materials will grow their portfolio of products and contribute significantly to their revenue **[C6]**.

5. Sources to corroborate the impact

[redacted]

[C3] Insidermedia, “2-DTECH secures Innovate UK grants. https://www.insidermedia.com/news/north-west/127027-2-dtech-secures-innovateuk-grants

[C4] NanoWerk “2-DTech Endeavours to Create High Performance Corrosion Inhibiting Coatings Using Graphene”. https://www.nanowerk.com/nanotechnology-news/newsid=39093.php

[C5] Versarien PLC, “Major advance in scalable graphene production”. https://www.nanene.com/news/major-advance-scalable-graphene-production/

[redacted]