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Nanosurfaces 2019

Commercialised techniques involving plasma, surface coatings and graphene

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Introduction

Nanosurfaces 2019 took place on 15th October 2019 at the Institute of Materials, Minerals & Mining (IOM3), London, UK. This event included commercialised techniques featuring plasma, surface coatings and graphene. Applications ranged from anticorrosion and waterproofing of electronics to battery materials and biomedical applications. Scalability, reproducibility, economics and sustainability were considered by many of the speakers.

Plasma Applications

The Keynote 'Water Protection Technologies for Smartphones and Beyond' was presented by Angeliki Elina Siokou, P2i Ltd, UK. P2i originated as a spinoff from Durham University, UK. The original product was an oil repellent coating for textiles created in 2004. They then developed a hydrophobic coating for electronics. Initial applications were in hearing aids then, around 2011, the company moved into water protection for smartphones. They are now coating half a billion smartphones per year. Customers include Samsung, Apple, Bose, Huawei and ASUS. Around 18% of smartphones are thought to be damaged by water ingress every year. P2i's technology uses a radio frequency (rf) plasma attachment and polymerisation of surface molecules to provide a very thin hydrophobic conformal coating. This is suitable for mass production with good quality control. If a direct current (DC) plasma is used, the molecular structure is disrupted whereas pulsed DC retains coherent molecular structure and the best liquid repellence. Photoelectron spectroscopy analysis was used to analyse bond structure. The original product coating was splash proof but not completely waterproof, so a new coating was developed which is thicker (~100 nm) and has increased crosslinking. Thickness alone does not determine the level of water repellence (standards from IPX2 to IPX8), the process parameters affect porosity and film defects (1, 2). The coating was further improved by ensuring all product pieces are placed close to a plasma electrode. The coating was claimed to be durable and is tested with methods including the adhesive tape test, thermal, chemical and abrasion. It is economic for high-value items. The maximum temperature for the coating is 200ºC, determined by the maximum temperature for the items to be coated.

'Enhancement in the Reactive Deposition Process Using Remote Plasma Spluttering' by James Dutson, Plasma Quest Ltd, UK, presented the use of a remote plasma to generate ions whose path when accelerated is curved by magnets and focussed onto the sputter target. Key advantages of this technology are: high target usage, control over energy of sputter ions, low temperature at the substrate. They have had good success with aluminium doped zinc oxide as an indium tin oxide (ITO) replacement. Substrate heating is not required to control the phase or crystallinity of deposited material as this can be done *via* sputter ions energy control. Deposition rates are typically 1–6 μm h^{-1}, and 1 μm h^{-1} for the ZnO:Al materials. Plasma Quest is working with CSEM, Neuchâtel, Switzerland, on photovoltaics and transistors. The process can be carried out at ambient temperature so is suitable for coating plastics or sensitive substrates. Reactive deposition is possible, i.e. to incorporate an oxide or nitride from a metal target. The main driver is replacement of ITO for transparent conductive coatings and there is a Horizon 2020 European Union (EU) project: INREP, Towards Indium Free TCOs. The company is currently scaling up to large surface areas ≥50 cm^2. The process does not require a clean room.

'Molecular Plasma Technology' was presented by Britta Kleinsorge, Molecular Plasma Group, Luxembourg. This company offers atmospheric plasma (50 kHz) processes for surface modification. It is lower temperature compared to corona like arc plasma processes. Organic precursors could be functionalised and adhere to a surface at low temperature. Some interesting work on biological non-specific binding and antibody immobilisation was carried out with KU Leuven, Belgium, in which the process time was reduced from 24–72 h to 10 s. Superhydrophobic barriers have been developed for anticorrosion applications, waterproofing and adhesion. They presented a case study of a process they developed for a German automotive original equipment manufacturer that could be automated with reduced chemical usage.

'A Radically New Antimicrobial Nanosurface Formed by Plasma Processing' was presented by Alistair Kean, NikaWorks Ltd, Watlington, UK. There is a need for more environmentally friendly coatings, for example crisp packets which currently use 30–40 nm Al on plastic film. Tungsten carbide (WC) physical vapour deposition (PVD) coatings for surgical scissors need to be durable for decontamination cycles. The BeBionic prosthetic hand includes a titanium alloy coating on one surface. Three dimensional (3D) nanomaterials (metamaterials) are inspired by nature and nanosurfaces can have surface areas of the order of ~1000 $m^2 g^{-1}$. SOLAMON was a 7th Framework Programme for 'large' NP 20 nm, 30 nm or 40 nm scale. Gencoa Ltd is a PVD company in Liverpool, UK, which is developing antimicrobial coatings with NikaWorks.

'Virtual Cathode Deposition' was presented by Dmitry Yarmolich, Plasma App Ltd, UK. Plasma App is based at Harwell Oxford Science and Innovation Campus, UK. The speaker described a thin film battery project with the University of Cambridge, UK, which can deposit carbon as a combination of graphite and graphene immediately followed by the lithium cobalt oxide (LCO) cathode. It is a platform technology that can deposit a thick or thin film of almost anything from nanometre scale to 50 µm. Superior adhesion and solvent-free scalability were claimed. The speaker claimed that the technique can use two source virtual cathode deposition (VCD) to design materials in minutes, not hours.

Nanoparticles and Graphene

'Manufacture and Applications of Nanoclusters' was presented by Richard Palmer, Swansea University, UK. He set up Grove Nanomaterials to commercialise matrix assembly cluster source (MACS) technology (3) for the solvent-free synthesis of nanoparticles (NP) for catalysis, sensors and electrodes. Atomic nanoclusters can be created to mimic enzymes with formation of grooves and pockets. Size selected cluster beam deposition (CBD) of gold or molybdenum sulfide, which can be nickel or cobalt doped to replace platinum in water splitting, was carried out. The present plan is to scale up the research system to be able to produce 1 g h^{-1} and the technology has the potential to be scaled to mass production (tonne scale).

'Silica Nanoparticles for Super-Hydrophobic Ice-Repellant Coatings' was presented by Simon Haas, Promethean Particles Ltd, UK. Promethean Particles Ltd is a spinout from the University of Nottingham, UK. Using a continuous hydrothermal process, copper, silver, ZnO, barium titanate and silica NP can be produced as dispersion in liquid with no dry powders for safer handling. The liquids can be used in further processes and agglomeration is prevented. The dispersions are highly stable and the process is scalable. A production plant has been built which can produce 1000 tonnes per year based on dry weight equivalent. Conductive inks and printed electronics are currently being developed with partners. The speaker presented an Innovate UK funded programme, ICEMART, looking at SiO_2 NP to prevent icing of plane wings. The Welding Institute, Great Abington, UK, was part of this project and provided a process to functionalise the SiO_2 particles to render them hydrophobic. This technology is currently being commercialised *via* Sharc® Matter, an Opus Materials Technology Company, UK.

'Graphene Enhanced Products' was presented by Thanuja Galhena, Versarien plc, UK. Versarien acquired Cambridge Graphene Ltd, UK, in 2017 and supplies proprietary grades of two-dimensional materials. There are two main products: Nanene™ (graphene) and Hexotene™ (boron nitride). Both can be manufactured at a 3 tonnes per annum scale. The company has certification from the Graphene Council, New Bern, USA and the National

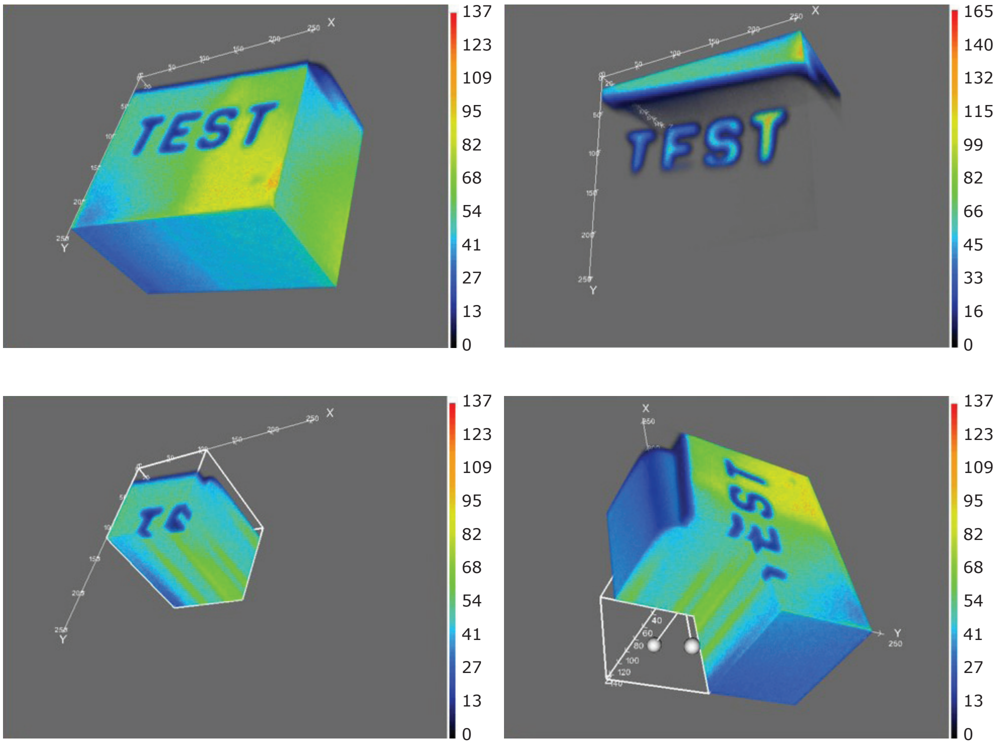

Fig. 1. SIMS images of 3D silicon/tantalum test object taken using the CAMECA SIMS instruments. Image courtesy of Mike Petty, Loughborough Surface Analysis Ltd, UK

Physical Laboratory (NPL), Teddington, UK, European Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) registration in the EU and is applying for similar certifications in China. Potential applications are composites, fire retardants, barrier coatings, energy storage, filtration and heat dissipation. A fairly unusual product application was a railway arch supporting sensors, claiming that lighter weight reduces transport, installation time and personnel costs. Graphene based inks known as GRAPHINKS® have been developed (4). Another example is a graphene coated diaphragm for some earphones – apparently bass is clearer. FLEXIBAT is an Innovate UK funded project. The company is working on flexible batteries with Zinergy UK Ltd, Cambridge, UK, making graphene coated electrodes for corrosion resistance. There are also supercapacitors using graphene plus metal oxide NP. The speaker noted that the cost of graphene has reduced considerably, making it cost effective for many applications.

'Enhanced Surface-Analysis Capability' was presented by Mike Petty, Loughborough Surface Analysis Ltd, UK. Petty focussed on the new secondary ion mass spectrometry (SIMS) system (Cameca, France) which can do quite sophisticated analysis mainly on semiconductor materials. Data cubes are formed so one can go back and analyse specific coordinates within a scanned cube (**Figure 1**). This technique is sensitive to isotope identification.

'Photocatalytic Antimicrobial Surfaces' by Jeremy Ramsden, University of Buckingham, UK. Ramsden discussed the antimicrobial application of photocatalytic powders coated *via* spray from titanium dioxide powders in a water solution. He described the problem of hospital acquired infections, especially resistant infections such as methicillin-resistant *Staphylococcus aureus* (MRSA), and presented studies of deaths and disability-adjusted life year (DALY) statistics in Europe, USA and elsewhere dating from 1930s to the present. There are many vectors of microbial transfer in and around hospital environments, these are surprisingly little studied and there is much debate about the relative importance of air, walls, floors, shoes or wheels and ceilings in transmission of pathogens. In particular there are few or no controlled studies on hospital cleaning efficacy. Hand hygiene compliance seems to have peaked at ~40%. He studies non-sacrificial catalytic coatings, i.e. TiO_2 which can kill microbes even under ambient lighting with continuous effectiveness. Estimated 10 colony forming units (CFU) m^{-2} s^{-1} of bacteria arriving and 6000 s^{-1} oxidising equivalents forming. He carried out a trial in which a coating was applied after a hospital deep clean on the high-touch surfaces, for example bed rails, table and tubing. The surfaces were tested using Agar pads (selective for MRSA and general). The coating used a commercial sol of TiO_2 NP in a sol-gel process to form a hard coating within

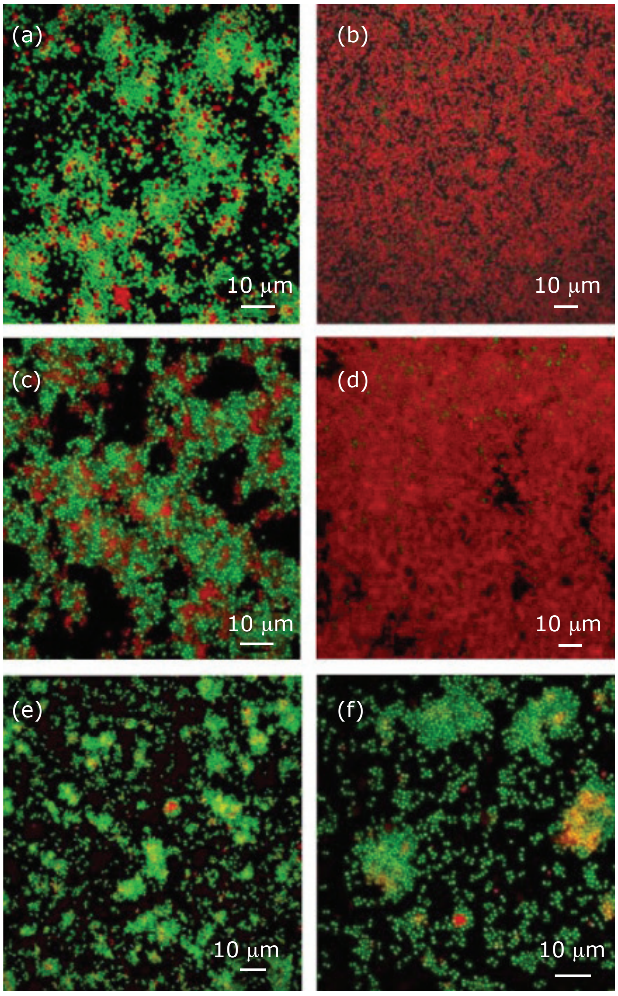

Fig. 2. Stained *Staphyloccocus epidermidis* within a biofilm (confocal laser scanning microscopy). Green fluorescence: live bacteria; red fluorescence: membrane-compromised bacteria. (a) 1.5 h exposure to UVA only; (b) 1.5 h exposure to photocatalytic treatment; (c) 3 h exposure to UVA only; (d) 3 h exposure to photocatalytic treatment; (e) 3 h exposure to TiO_2 in the dark; (f) 3 h no treatment control (no TiO_2, no UVA exposure). Reprinted from (5) with permission from Elsevier

20–30 mins. The coating is invisible (1 μm) and can be applied to mirrors and glass. Sampling was carried out for three months, the coating was durable in this timeframe. Evidence suggested the coating resulted in lower microbial growth (**Figure 2**) (5). Microbial resistance is unlikely as the microbial cell has no mechanism for defence against peroxide. The half-life of bacteria was ~6 h.

Conclusions

Martin Kemp, Chairman of the IOM3 Nanomaterials Conference organising committee, remarked how many of the presentations featured plasma techniques and was excited by the many examples of commercialised techniques. There will be another meeting in early 2020.

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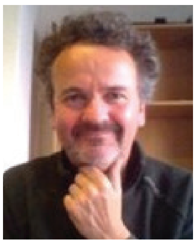

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