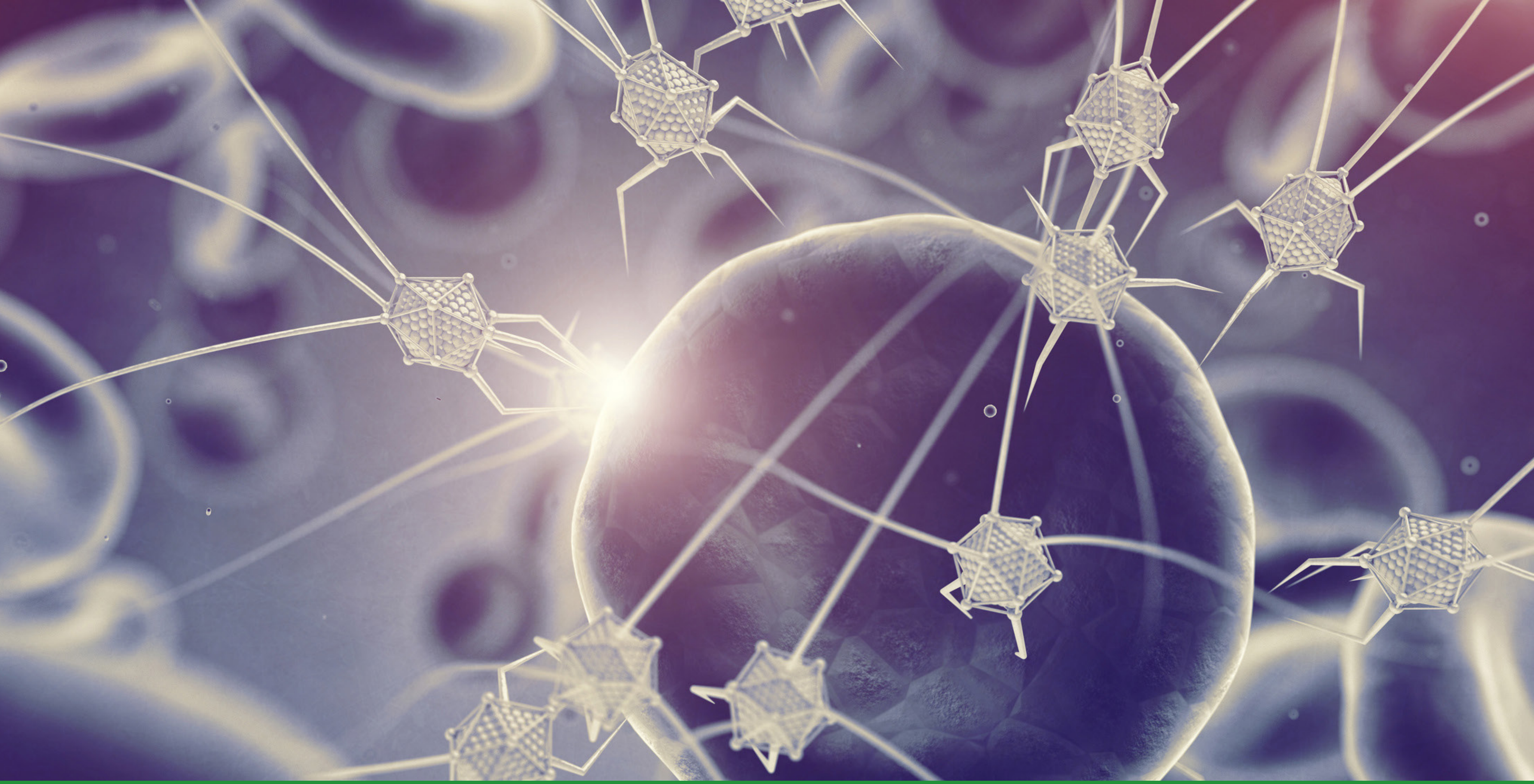

ENGINEERED NANOTECHNOLOGY – ENVIRONMENTAL PROBLEM OR SOLUTION?

When I first saw the title "Future Perspectives on Environmental Nano Technology" for a one day symposium at the Royal Society of Chemistry (RSC) in London I was intrigued to find out more. The "all things nano will change the world" scenario of several years ago was quickly followed by the health and environmental scares, so what was the current situation?

In its 2014 Strategic plan (1) the US National Nanotechnology Initiative (NNI) stated: "Nanotechnology—the science of the very small—is a relatively young field, ripe for new discoveries and understanding. But nanotechnology is already changing the world. Nanotechnology underpin a wide variety of applications and products on the market today, including electronic circuitry, displays, sensors, battery technology, disease therapeutics, and wear-resistant coatings". However, it also stated "In recent years there has been growing activity in environmental, health, and safety research; cooperation among regulatory agencies; and commercialisation and advanced manufacturing at the nanoscale" and featured nanotechnology product lifecycle schematic showing points for Environmental, Health and Safety evaluation and risk assessments (Figure 1)

So, I was interested to find out whether this symposium, organised by the RSC Journal Environmental Science:Nano and the RSC's Environmental Chemistry Interest Group, would focus on health, safety and environmental concerns or on environmental applications of engineered nanotechnology. The symposium was organised to coincide with the meeting of the international editorial board of the journal and so many of the presentations were given by its members, who are all recognised experts in the field of environmental nanotechnology, and in this article, we summarise some of the key presentations from the day.

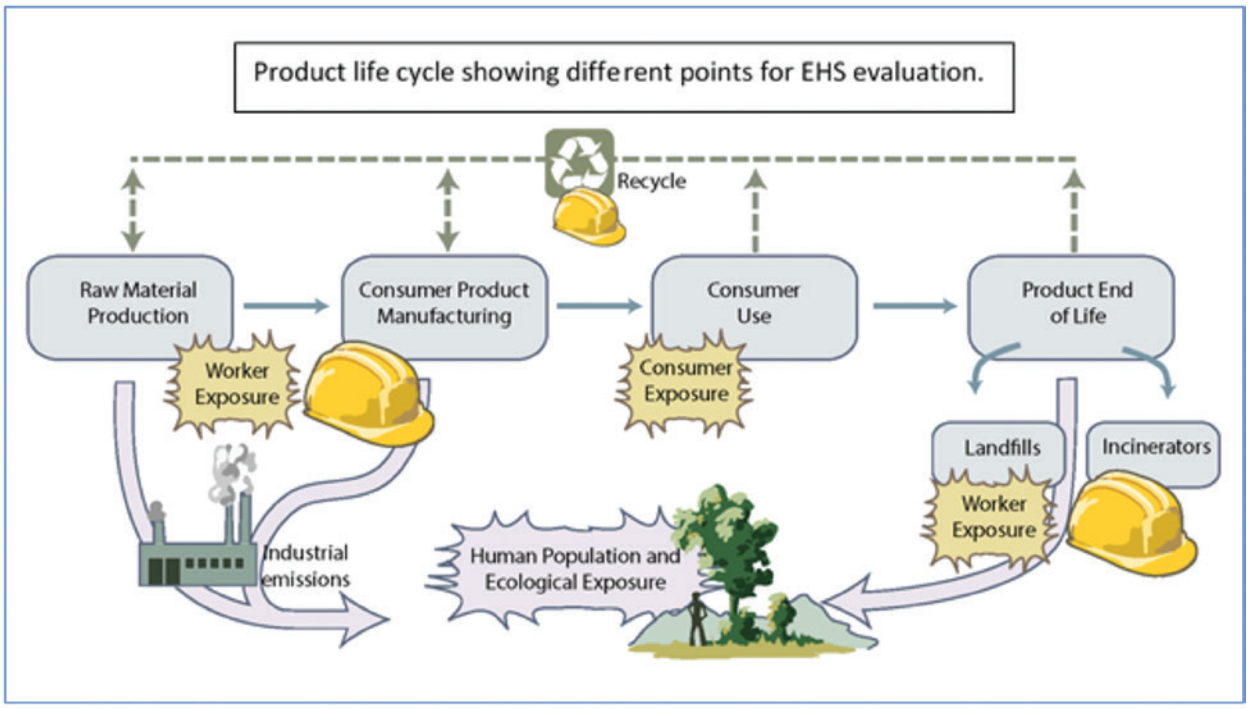

Figure 1: US National Nanotechnology Initiative Product Lifecycle showing points for Environmental, Health and Safety evaluation and risk assessments (www.nano.gov)

A Reminder: What is Nanotechnology?

Nanotechnology—the science of the very small—is a relatively young field, ripe for new discoveries and understanding.

"Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometres (nm), where unique phenomena enable novel applications. Encompassing nanoscale science, engineering, and technology, nanotechnology involves imaging, measuring, modelling, and manipulating matter at this length scale. A nanometre is one-billionth of a meter. A sheet of paper is about 100,000 nanometres thick; a single gold atom is about a third of a nanometre in diameter. Dimensions between approximately 1 and 100 nm are known as the nanoscale. Unusual physical, chemical, and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules." (1) This definition was established by the US NNI at its inception in 2001 for identifying and coordinating nanotechnology research and development as well as for facilitating communication and has largely been adopted globally.

Nanomaterials classification in the environment

Manufactured or engineered nanomaterials are used in a wide range of consumer products, manufacturing processes and medical applications. Products include cosmetics, sunscreens, paints, bandages and clothing. Examples of manufactured nanomaterials include silver (Ag), titania (TiO_2), ceria (CeO_2), fullerenes and carbon nanotubes.

Incidental nanomaterials arise because of human activity. e.g. diesel exhaust particulates, tyre wear debris and mineral extraction wastes.

Natural nanoscale objects, including minerals and organic nanoparticles, occur in the environment. e.g. ash clouds and natural decomposition products in water.

Following a brief introduction from Simon Neal, Executive Editor of the journal, Prof Peter Vikesland from Virginia Tech, USA who is also Editor -in-Chief of Environmental Science:Nano opened the scientific presentations.

The application of nanotechnology to better understand the chemistry of confined spaces

Prof Vikesland specialises in the use of nanotechnology for the detection and remediation of environmental contaminants and carries out ongoing studies to examine the potentially damaging impacts of nanotechnology on environmental systems. His research includes the development of nano-enabled sensors for the tracking of pathogens and their DNA; determining the environmental impacts of nanoparticles as contaminants; determining the triggers and kinetics of disinfection by-product formation; and characterising the chemical properties of aerosols. His presentation focussed on understanding the chemistry of confined spaces and specifically the application of Surface Enhanced Raman Spectroscopy (SERS) for the measurement of the pH of suspended aqueous droplets and aerosols such as smog, clouds, salt spray and exhaled breath. Aerosols play a major role in many environmental processes, as does pH, and therefore understanding the pH profiles of individual aerosol droplets is very important for a wide range of environmental issues. Conventional techniques collect and bulk the droplets prior to pH measurement, but this only provides an average value for all collected droplets and assumes all droplets are the same. 4-Mercaptobenzoic acid (4MBA) in conjunction with gold nano particles is well known as a model analyte for SERS study but 4MBA deprotonates at high pH (showing bands for COOH at 1710cm-1, and COO- at 1410cm-1) and this can be used to measure pH in the range 5-11 using SERS.

Aerosols are created containing the components of interest, 4MBA and gold nanoparticles. The resulting individual droplets are collected on hydrophobic filters which can then be analysed using SERS. Using this approach, the pH in the centre of droplets was determined to be between 8 and 13 which differs from the bulk solution measured pH of 7.4. Further analysis using confocal imaging shows a pH gradient between the droplet edge and the core and that the droplet air water interface is acidic with a highly basic core and this knowledge will be key in future aerosol studies in environmental systems. Prof Vikesland then briefly described how this work was now being extended, including the use of other complexing reagents with nanoparticles, to study the chemistry of other 'confined space' systems such as biofilms, plants, cancer cells and other environmentally relevant materials.

Multifunctional nanoscale material platforms for advanced environmental applications

This topic was presented by Prof John Fortner from Washington University in St Louis, USA, who is an Associate Editor of Environmental Science:Nano. He began by discussing graphene and how it can be easily derivatised with oxygen to form graphene oxides which have been employed in composite membranes for advanced water treatment. However, traditional membrane constructions can have tortuous flow paths and low permeability and Prof Fortner described the development of multifunctional, crumpled graphene oxide (CGO) porous nanocomposites that are assembled as advanced, reactive water treatment membranes.

Crumpled 3D graphene oxide-based materials differ from 2D flat graphene oxide analogues in that they are highly resistant to aggregation and compression which allows for the incorporation of other multifunctional particles inside the 3D composite structure (2). He described how assemblies of nanoscale CGO with encapsulated Titanium Dioxide (TiO_2), Magnetite, Silver and Gold nanoparticles not only allow high water flux via vertically tortuous nanochannels outperforming comparable commercial ultrafiltration membranes, but also demonstrate excellent separation efficiencies for model organic and biological foulants. He also discussed performance improvements obtained with CGO based nanocomposite structures in terms of a 97% reduction in fouling, improved photocatalytic degradation of impurities and superior antimicrobial properties. Turning to cleaning and reuse he presented performance data generated from 5 in-situ recycles of a CGO-TiO_2-Magnetite composite membrane using back flush, magnetic particle removal and regeneration. He summarised by reinforcing the main benefits of CGO composite membranes of high permeability and multifunctionality.

What can we do when Nano meets Environmental Science?

This was the question posed by Dr Xianjin Cui, a research fellow at the University of Birmingham. He began by listing the wide range of potential application areas for engineered nanoparticles(NP) and materials before raising the question of safety and risk, which must consider not only toxicity and eco-toxicity of the nanomaterial, but also questions such as how much will be released through its life cycle, its fate after any release and how it may be converted in the release environment. He described some of the challenges in characterising nanoparticles in environmental complex media where they may be present at trace levels and may have changed shape and/or their chemical form in the sample. Sample homogeneity and issues with identifying and quantifying engineered nanoparticles in the presence of naturally occurring material were also highlighted. He then introduced the Facility for Environmental Nanoscience Analysis and Characterisation (FENAC) at Birmingham University which is funded by the UK Natural Environment Research Council (NERC) to support environmental nanoscience and nanotoxicology research. FENAC has access to, and expertise in, a full suite of characterisation techniques and employs separation methods alongside microscopic and spectroscopic techniques for nanoparticle characterisation.

Separation methods include symmetric and asymmetric flow field-flow fractionation, split-flow thin cell fractionation, dialysis and ultrafiltration devices including cross flow ultrafiltration which are all used for size fractionation. Thermo gravimetric analysis tandem coupled with fourier transfer infra-red and mass spectrometry (TGA-FTIR-MS) for the analysis of thermal desorption and degradation products was also available. Microscopy and imaging techniques include Scanning and Transmission Electron Microscopy with Energy Dispersive X-Ray Spectroscopy for elemental analysis, Atomic Force Microscopy, Confocal Microscopy and Nanoparticle Tracking Analysis. Trace elemental analysis was provided by ICP-MS.

Dr Cui described how combining this wide range of separation and measurement techniques allowed them to to overcome some of the challenges of complex media, trace levels and reproducibility.

Professor Greg Lowry introducing his presentation.

Engineering nanomaterial properties for increasing agrochemical utilisation efficiency

Professor Greg Lowry from Carnegie Mellon University, USA, is an Editorial Board Member of Environmental Science:Nano and he began by highlighting some of the challenges facing agriculture based industries while also having to meet demands for increasing yields. Agriculture requires high energy and water usage (>70% of global water withdrawal) and was responsible for >20% of global greenhouse gas emissions. Nanotechnology has an important role to play in the agriculture sector both through studying how plants work and also through improving crop performance. Nanomaterials can easily be taken up by plants and their tuneable surface chemistry and inherent slow release properties can be employed to deliver targeted benefits. He described how Ceria based nanoparticles had been shown to increase photosynthesis in plants exposed to high salinity and how metal oxide nanoparticles containing copper, manganese and zinc had all reduced the presence of disease and that copper also had increased crop yield for both tomatoes and eggplants. He described his work in studying the uptake and movement of leaf sprayed nanoparticles to all parts of plants including the roots and even the surrounding soil and how they have developed nanoparticle coatings which facilitate 100% entry of the particles to the plant. Using synchrotron XRF and XANES they could study nanoparticle uptake and trace it around the plant and found size based effects in that smaller ones could migrate out to the soil whereas larger ones remained in the leaf. He also discussed how positively charged particles tended to move to the roots while negative charged ones tended to stay in the leaves. Thus, by combining coating selectivity, size and particle charge parameters, targeted delivery for greatest efficacy can be achieved.

He concluded by reinforcing that there were tremendous application opportunities for engineered nanotechnology in agriculture and especially for the efficient and targeted delivery of micronutrients and crop protection chemicals to plants quoting the nano copper hydroxide based product Kocide 2000 as a current product in the market.

Nanostructured materials for water treatment: from lab study to village trial

Professor Weiguo Song from the Chinese Academy of Sciences and an Associate Editor of Environmental Science:Nano described how improved Chinese standards for drinking water in 2012 had driven work to reduce contaminants and particularly arsenates and fluoride in many areas. He described a trial site in Inner Mongolia where arsenic levels were 220ppb, fluroride was 3.3ppm and which also had potential issues from mercury, chromium, cadmium and lead contamination. He described how the high surface area for adsorption and or reaction with nanomaterials gives high capacity and fast kinetics making them ideally suited for use in water treatment. They employed XAFS, XPS and XANES to study the interaction of nanosphere metal oxides and their application to remove impurities in drinking water. Basic aluminium carbonate nanospheres had shown high adsorption for fluorides and arsenates and they had now scaled up production of the technology to produce drinking water treatment cartridges for household use. At the trial site in Inner Mongolia these had been running for 5 years and Prof Song quoted impurity removal figures of 97.8% for Arsenic, 84.8% for Fluoride and 90.9% for TOC (humic acids)

Prof Jerome Rose introducing the SERENADE project

From risk assessment to safer by design nanomaterials: lessons learned from the French funded SERENADE project

Prof Jerome Rose is research director at the Centre Europeen de Recherche et Denseignement de Geosciences de L'Environnement (CEREGE) and also an Editorial Board Member of Environmental Science:Nano. He began by giving a brief history of the emergence of engineered nanomaterials and the subsequent raising of concerns over toxicity and eco-toxicity and how many studies were started to look at these concerns around nanoparticles themselves. These limited studies soon moved to wider approaches where the whole life-cycle of the materials were considered including the effects on the workforce, the consumer and the environment and this then moved on to a 'safer by design' approach as in the SERENADE project. SERENADE is a French project which aims to develop and apply the 'safer by design' process to create safer nanoproducts. It achieves this goal by combining knowledge and scientific approaches from a range of disciplines and a tutorial review of its work was published in 2017 (3). This tutorial review presents the conceptual approach to 'Safer by Design' and provides examples of case studies primarily for TiO_2 in paints and cements to demonstrate how the approach can inform design decisions with particular attention to chronic low dose exposure scenarios. In their latest work they have developed a high energy X-ray imaging platform and employed nano-scale 3D computerised tomography to study nano CeO_2 aggregation in acrylic wood coatings and the release of TiO_2 in relation to the porosity network and volumes of cements.

The Nano-Bio interface: nanoparticle interactions with lipids and protein

Professor Joel Pederson from the University of Wisconsin Madison, USA, and an Associate Editor of Environmental Science:Nano began by discussing the strategy and principles behind sustainable nanomaterial design and green synthesis before moving on to his work on the interaction of nanoparticles with bio-membranes both for applications and environmental impact. The studies focus on how nanoparticles size, aspect ratio and surface chemistry influence attachment to, penetration of, and alteration of biological membranes by using a wide range of high-end techniques including quartz crystal microbalance with dissipation monitoring (QCM-D), sum frequency generation spectroscopy (SFG), stochastic optical reconstruction microscopy (STORM) together with more conventional techniques such as XPS, NMR, AFM and MS. He described studies with nanomaterials in ion channels and phase segregated domains showing accumulation at phase boundaries and microdomain formation. Prof Pedersen also discussed ways to design nanomaterials for 'end of life' and used the example of silanisation of cellulose nanofibres to facilitate incorporation into polymer matrices before closing with a summary of the challenges and opportunities for nanomaterial modes of action studies on living systems.

Overall this was a fascinating symposium and a chance to hear from some of the world leading experts on the impact of nanotechnology in the environment and it was clear that nanomaterial research into both beneficial applications for, and possible impacts on, the environment are still receiving widespread global interest and attention.

References

(1) National Nanotechnology Initiative Strategic Plan National Science and Technology Council Committee on Technology Subcommittee on Nanoscale Science, Engineering, and Technology, February 2014, https://www.nano.gov/node/1113

(2) Engineered Crumpled Graphene Oxide Nanocomposite Membrane Assemblies for Advanced Water Treatment Processes Yi Jiang et al, Environ. Sci. Technol. 2015, 49 (11), pp 6846–6854

(3) SERENADE: safer and ecodesign research and education applied to nanomaterial development, the new generation of materials safer by design. Bottero J. Y. et al, Environ. Sci.: Nano, 2017, 4, 526

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