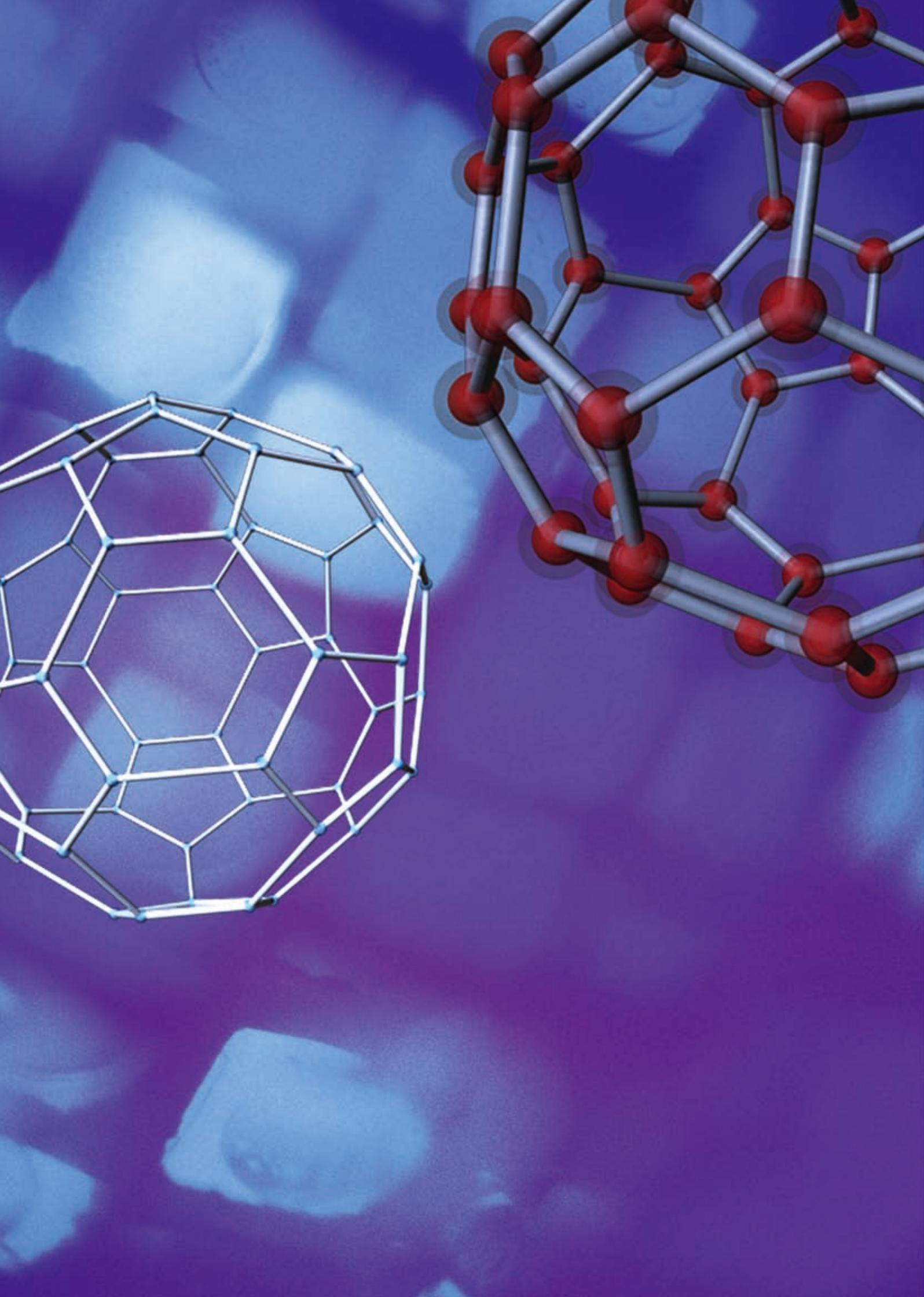
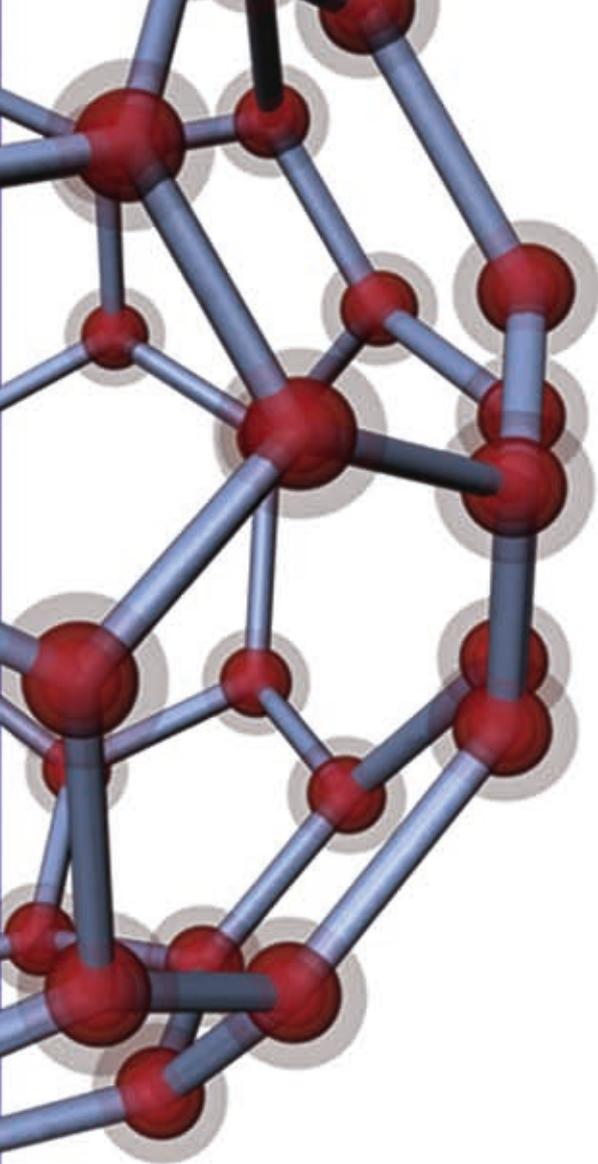


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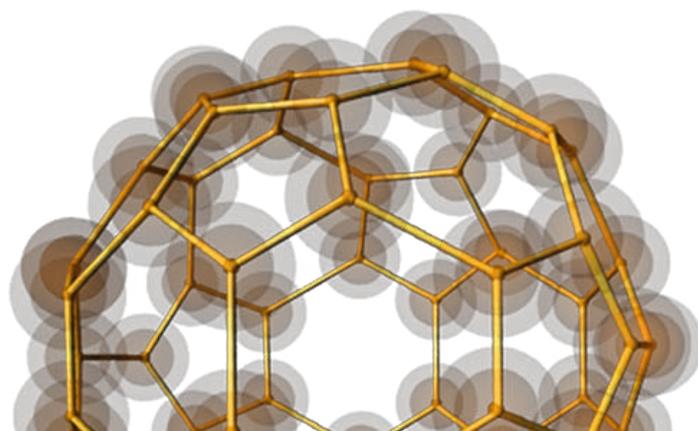
Environmental
Nanoscience Initiative

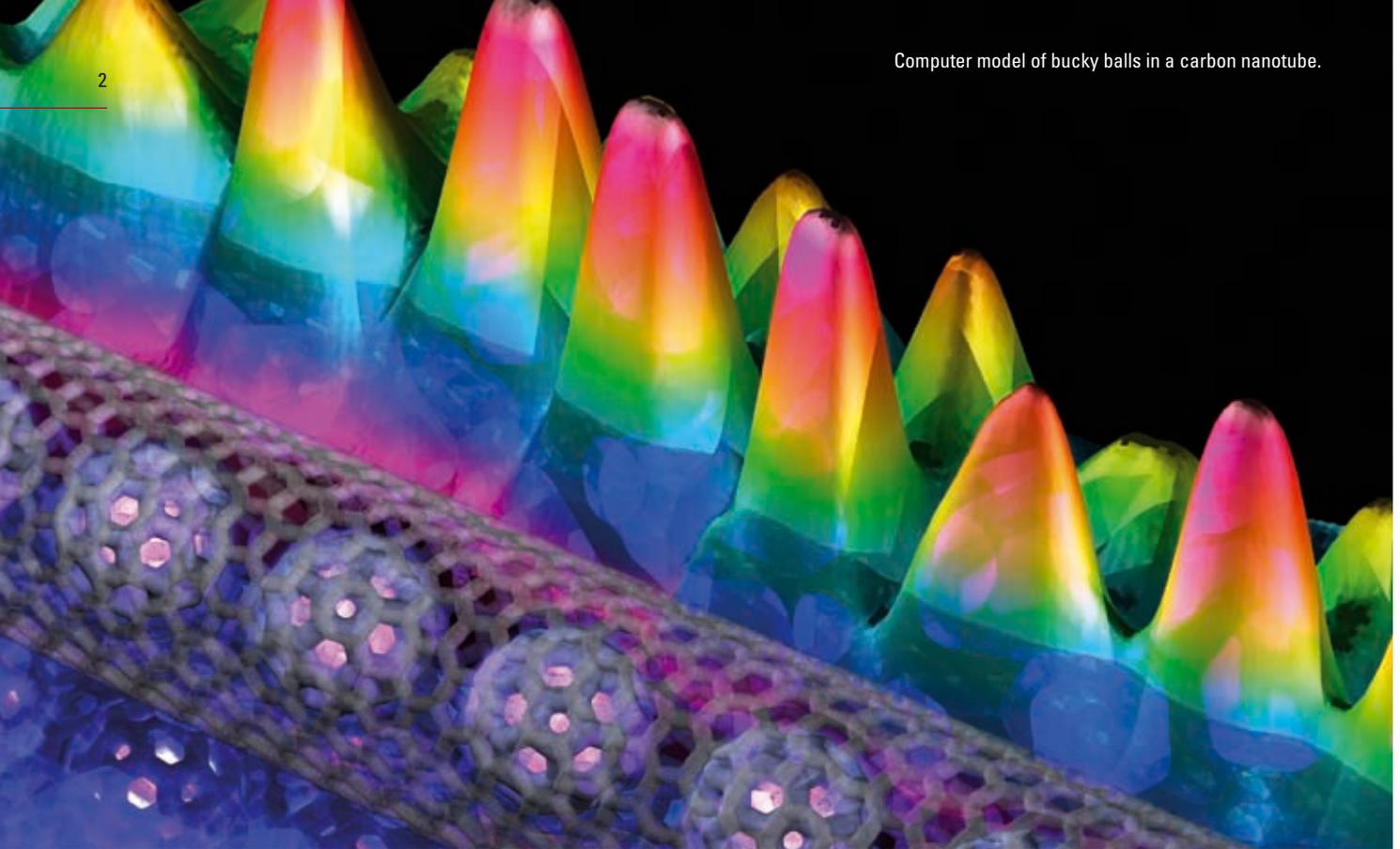




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Executive summary

Nanoscience, the science of the very small (a billionth of a metre), is supporting the growth of a technology predicted to be worth many billions of pounds within a decade.

Nanotechnology has been described as the first technological revolution of the 21st century, supporting economic growth and helping to meet some of the greatest challenges we face as a society, from addressing climate change to improving human health.

Nanotechnology could provide novel solutions for renewable energy and efficient carbon capture from power stations. In the healthcare sector there is the potential for better diagnostics and drug delivery. It can help improve the environment: from cleaner and more efficient fuels to better water treatment and environmental clean-up. We may see smart materials that are lighter but stronger and new antifouling surfaces that could enhance fuel efficiencies for vehicles and ships, and reduce environmental impacts. Sensors for environmental and health monitoring could incorporate nanotechnology in the coming years.

The technology uses fundamental changes in the properties of materials at the nanoscale to open up new avenues for innovation. Carbon nanotubes, described as the 'hottest thing in physics', may resemble rolled up sheets of graphite but they have fundamentally different properties. But do changed properties mean greater risks to the environment and human health? Do they behave in the same way in the environment; are they more persistent; are they more easily taken up by organisms and able to move and accumulate in them?

In 2004, the Royal Society and Royal Academy of Engineering report on the opportunities and uncertainties posed by nanotechnologies showed major gaps in our understanding of the environmental fate, behaviour and effects of nanomaterials, in particular, manufactured nanoparticles. While there were some scientists researching what are described as 'incidental nanoparticles' in atmospheric pollution, coal dusts and so on, few were working on intentionally-produced, manufactured nanoparticles. In

A growing and internationally-recognised community of scientists in environmental nanosciences.

2006, the Natural Environment Research Council (NERC), the Department for Environment, Food and Rural Affairs (Defra), the Environment Agency and the Engineering and Physical Sciences Research Council (EPSRC) launched the UK Environmental Nanoscience Initiative (ENI). This would begin to address some of the key questions about the environmental fate, behaviour and effects of manufactured nanoparticles. It would also build a community of scientists with relevant expertise and provide the evidence to support policy development in this area.

As part of a capacity-building strategy, ENI made two research calls to complement responsive mode research activities. Three years later we now have a growing and internationally-recognised community of scientists from institutions across the UK. Their research is highlighted here.

Research highlights

- Development of exciting techniques for visualising and characterising nanomaterials in the environment. Recognising this as a key need, NERC has recently established a Facility for Environmental Nanoparticles Analysis and Chemistry to support the research community.
- Investigating the environmental fate and behaviour of a number of manufactured nanoparticles in groundwaters, rivers, soils and sediments.
- Identifying the effects of nanoparticles on fish, invertebrates and microbes.

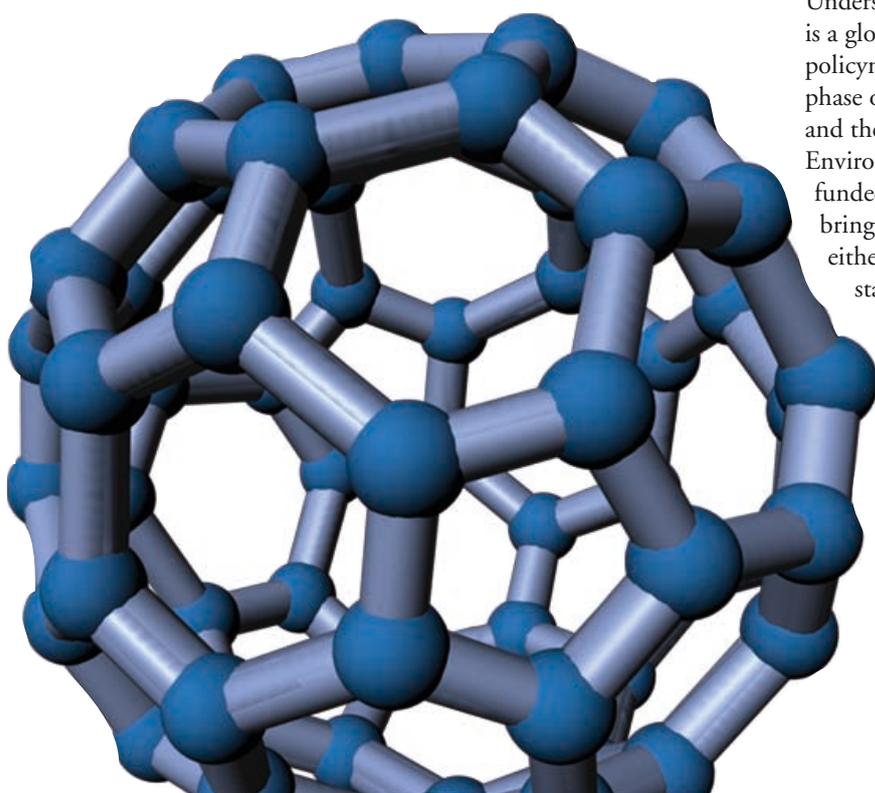
The research tells us that some nanoparticles can have effects on organisms, and they can also influence the behaviour and effects of other chemicals they might come into contact with. But it is hard to make generalisations; it depends on the nanomaterial concerned, the environment in which it occurs and the organism exposed.

The research also shows the environmental chemistry of nanoparticles can be complex and is often altered by the natural environment. As a result, we understand that key uncertainties lie around the nature and extent of environmental exposure. Developing validated models of fate, behaviour and bioavailability are important for making more confident statements about the level of exposure and risk these materials pose. This will be the main objective of the second, and much larger phase of ENI.

International collaboration

Understanding the risks posed by manufactured nanomaterials is a global challenge, one that is best tackled by scientists and policymakers working together internationally. The second phase of ENI will reflect this, with NERC, EPSRC, Defra and the Environment Agency collaborating with the US Environmental Protection Agency. A £6 million call, equally funded by the US and UK and launched in April 2009, will bring scientists with complementary strengths together from either side of the Atlantic. This will place ENI on a global stage in what will be the first truly international research programme in environmental nanosciences.

Richard Owen
*Environmental Nanoscience Initiative
Coordinator*





The lotus leaf repels water and keeps clean by using nanoscale hair-like tubes on its surface. Scientists can now mimic this feature to produce waterproof clothing and self-cleaning paints, roofs and glass.

Background

Nanotechnology: great opportunities and uncertain risks

Exploiting new or enhanced properties at the nanoscale has become big business: manufactured nanoparticles, such as those made of silver and carbon 'bucky balls', are now used in a range of applications, from healthcare and renewable energy to environmental remediation and clean water.

The variety of consumer products containing manufactured nanoparticles is growing daily¹. A major enabling and disruptive industry, nanotechnology has a projected market value of a trillion dollars in the next decade, with potentially huge socio-economic benefits.

But nanoparticles are far from new. They occur widely, from volcanic ash to atmospheric pollution. What is new is the intentional production of nanoparticles and other nanomaterials engineered to have novel properties. There are concerns that the changed or novel properties of these materials may also mean enhanced or novel risks to environment and human health.

Assessing the opportunities and risks

Recognising the important future benefits of nanotechnologies, in 2003 the government commissioned the Royal Society and Royal Academy of Engineering to assess the opportunities and risks posed by this fast-growing area of innovation.

Their 2004 report *Nanoscience and Nanotechnologies: Opportunities and uncertainties*² concluded that most nanotechnologies probably posed few risks, but that intentionally-

1. www.nanotechproject.org/inventories/consumer/
2. www.nanotec.org.uk/finalReport.htm



manufactured nanoparticles required closer investigation. A good deal of the evidence for this came from the wide body of research on incidentally produced nanoparticles and human health, for example in atmospheric pollution ('ultrafines'), coal dust and asbestos.

Importantly, the report highlighted an almost complete absence of scientific data on environmental exposure, effects and risks of manufactured nanoparticles. It recommended an immediate programme of research into the environmental, health and safety aspects of manufactured nanoparticles.

In February 2005, the government responded to the report, accepting many of its recommendations and committing to a programme of research that would provide the evidence base for developing policy and regulatory controls where needed.

Birth of the Environmental Nanoscience Initiative

In response to the *Nanoscience and Nanotechnologies* report the government established a body to coordinate research into the environmental, health and safety aspects of nanomaterials, the Nanotechnologies Research Co-ordination Group (NRCG). In November 2005, NRCG published its research strategy. Two of the major recommendations focused on the need for basic data on environmental fate, behaviour and ecotoxicology of manufactured nanoparticles, about which there was little or no information.

It became immediately apparent that very few environmental researchers in the UK were working in this area and that there was an urgent need to develop capacity, knowledge transfer and interdisciplinary working in the research community. In May 2006, the Natural Environment Research Council (NERC), Defra and the Environment Agency established the Environmental Nanoscience Initiative (ENI) to facilitate this. ENI would be a fundamental science programme with a clear line of sight between the research community and policy-makers (www.nerc.ac.uk/research/programmes/nanoscience).

Research within the EPSRC Grand Challenges is funding research on nanotechnology for renewable energies, nanomedicine and environmental solutions.



Simon Fraser/Science Photo Library

ENI launched its first joint call in September 2006. The focus was on small, exploratory research proposals that addressed generic aspects relating to environmental risks of nanoparticles. It was designed to be a capacity-building, pump-priming activity to enable researchers to generate initial datasets that could support high-quality submissions through responsive mode routes to the research councils and others.

The response to the first call was overwhelming with 37 submissions from institutions across the UK. ENI awarded ten grants in April 2007 to a number of UK academic institutions investigating a number of exciting areas. These included:

- How nanoparticles move and behave in surface and groundwaters.
- Innovative methods for visualising nanoparticles in plants.
- How nanoparticles affect fish and invertebrates in aquatic and soil ecosystems.

Following the success of the first call, a second call was launched in May 2007, specifically addressing impacts of nanoparticles on environmental microbial communities in water, soils and sediments. Again the call was extremely well subscribed, with 23 expressions of interest received and seven awards made.

The findings of the research are highlighted in the following sections of this brochure, with full award details given on pages 17 to 18.

These grants are complemented by work on the human-health impacts of incidental and manufactured nanoparticles made through the joint Environment and Human Health Programme, also administered by NERC, and a number of standard, small and Knowledge Exchange responsive mode awards in the area. The findings are highlighted in the pages that follow and detailed on pages 18 to 19.

In April 2009, NERC and its other partners, Defra, the Environment Agency and the Engineering and Physical Science Research Council (EPSRC) built on the success of the first phase of ENI by launching phase two, a major international programme of research, collaborating with the US Environmental Protection Agency.

Having developed a research community in the UK in this area, we are looking to build on this to develop the first generation of validated models that allow confident predictions of environmental exposure, bioavailability (whether nanomaterials in the environment occur in forms that can be taken up by organisms) and effects for key nanoparticles of current concern.

We conclude the brochure with more details about this exciting new direction for ENI and discuss the implications of the research done so far for policy-makers and other stakeholders.



6

Nanoparticles

Understanding the environmental fate and behaviour of nanoparticles

Will manufactured nanoparticles from industry and other sources enter the atmosphere, soils, sediments or water? If so how persistent will they be, in what concentrations will they occur and what form will they take?

To understand the fate and behaviour of nanoparticles, we need to understand their structure, chemistry, size, surface area, how they aggregate and what influences this.

How do they behave in typical environmental conditions – with changing pH or salinity, or when organic matter and other naturally-occurring substances are present?

ENI research and other studies are showing that manufactured nanoparticles are perhaps unique chemicals in terms of the complexity of their behaviour in the environment. Understanding and quantifying exposure is not simple, but addressing this is central to characterising the risks they pose to environment and human health.

There remain significant challenges for the scientific community: understanding which properties of nanoparticles govern their environmental fate and behaviour; developing analytical procedures to detect them; and understanding bioavailability.

NERC has funded a range of projects in this area within ENI and more widely through both responsive mode and Knowledge Exchange grants.

1. Johnston et al., submitted, 2009
2. Jarvie et al., submitted, 2009
3. Baalousha et al., *Environmental Toxicology and Chemistry*, 2008

Detecting and characterising nanomaterials

One of the fundamental gaps identified is the need to optimise and develop analytical methods that allow researchers to detect and characterise nanomaterials in complex environments like surface waters, soils and sediments and in the tissues of organisms.

An ENI grant awarded to Lancaster University has allowed an innovative method using Two-Photon Excitation Microscopy (TPEM) coupled with autofluorescence to be developed. This has enabled nanoparticles to be imaged on living biological surfaces, like leaves and roots and within cells (Figure 1). Work at Sheffield and Oxford universities has similarly applied Raman microspectroscopy to image a variety of nanoparticles on bacterial biofilms and in cells. Researchers at the University of Reading are assessing the potential of novel small-angle-neutron-scattering (SANS) approaches to study the behaviour of nanoparticles in soils. Optimisation of a method called Coherent Anti-Stokes Raman Scattering or CARS at the University of Exeter means researchers can now visualise manufactured nanoparticles on the surfaces of fish gills (Figure 2). And researchers at the Natural History Museum have developed stable isotope tracer approaches to detect metal nanoparticles in laboratory studies of fate, behaviour and ecotoxicity.

Similar analytical techniques are being developed at the universities of Manchester, Birmingham and Nottingham, Plymouth Marine Laboratory and the Rutherford Appleton Laboratory. Many involve technology transfer from other fields such as physics and the life sciences, emphasising the interdisciplinary nature of environmental nanosciences. For example, researchers at the University of Glasgow are transferring MRI – or magnetic resonance imaging – techniques used in medical sciences to see nanoparticles inside

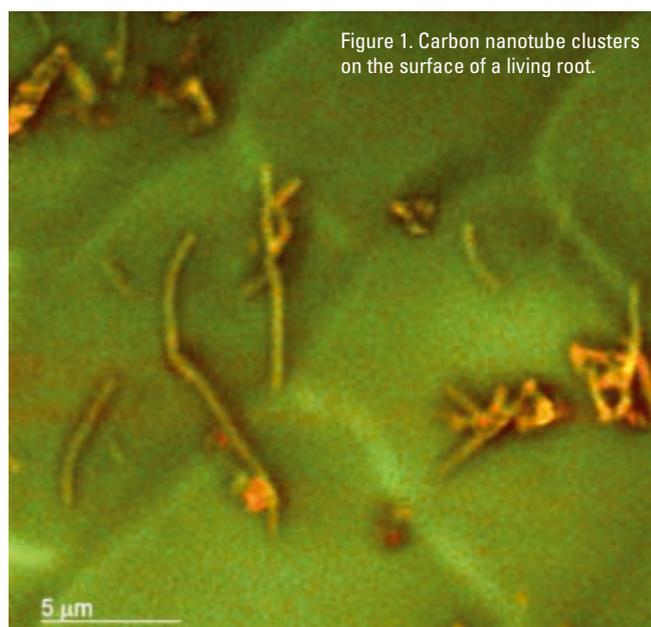


Figure 1. Carbon nanotube clusters on the surface of a living root.

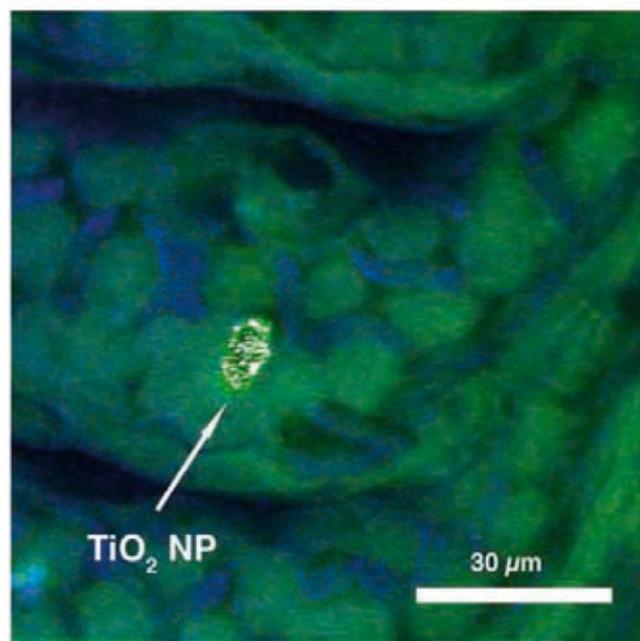
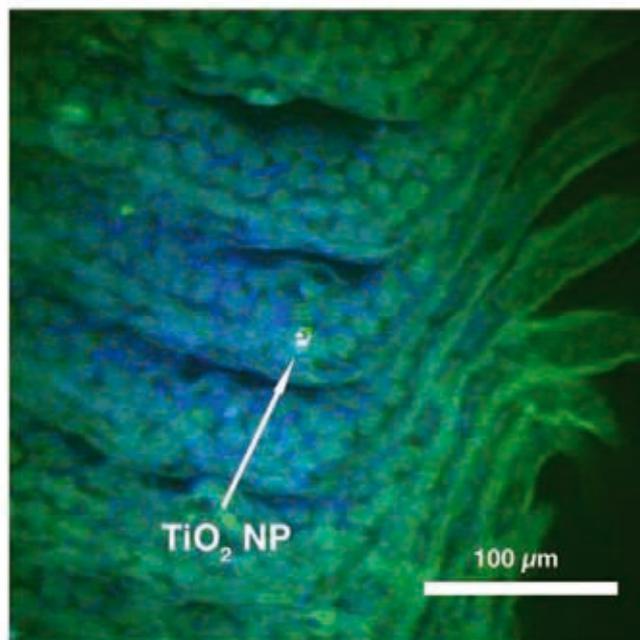


Figure 2. CARS images of gill tissue of rainbow trout following water-borne exposure to TiO_2 nanoparticles: A: Nanoparticle aggregate (TiO_2 NP) on gill lamellae, magnified $\times 3$ in B.¹

rocks. This allows them to investigate how nanoparticles move in pore waters. In the future we are likely to see further development of new methods specifically designed to cope with the particular demands of detection of manufactured nanoparticles in complex environmental matrices.

The UK's first environmental nanoscience facility

NERC launched the Facility for Environmental Nanoparticle Analysis and Characterisation (FENAC), based at the



Figure 3. Project scientists with the custom-built sample container for analysing neutron scattering from waste-water (raw sewage) samples spiked with engineered oxide nanoparticles. L-R: Dr Michael Bowes (Centre for Ecology & Hydrology), Dr Hisham Al-Obaidi (King's College London) and Dr Stephen King (Rutherford Appleton Laboratory).²

University of Birmingham, in March 2009. FENAC will provide analytical support over the whole range of environmental nanosciences, but is particularly focused on the physico-chemical analysis of manufactured nanoparticles, notably to support ecotoxicological studies (see page 9).

Environmental chemistry of nanoparticles

A number of NERC-funded studies have investigated the environmental chemistry of nanoparticles. Researchers at the University of Manchester aim to elucidate the surface chemistry of silver nanoparticles and its relevance to uptake and effects in bacteria and plants. A range of laboratory-based transport studies at the universities of Birmingham, Sheffield, Reading and Oxford are investigating the fate of nanoparticles in surface waters, groundwaters and soils, and how nanoparticles interact with and affect microbial communities in them.

One important question being addressed is what happens to manufactured nanoparticles widely used in high-tech cosmetics, household products and pharmaceuticals after they

are washed down the drain. What is their fate? And how do they behave in waste-water treatment plants? An ENI grant has enabled a cross-disciplinary team at King's College London, Rutherford Appleton Laboratory, the Centre for Ecology & Hydrology and the University of Oxford to investigate the fate of engineered oxide nanoparticles in waste-water (Figure 3).

The research team has used novel application of the SANS technique to show direct evidence that the surface characteristics of oxide nanoparticles control how they flocculate, influencing their sedimentation behaviour in waste-water treatment processes. This determines whether they pass through the effluent stream or are removed to sludge during primary waste treatment. The research is the first evidence that environmental pathways of nanoparticles could be manipulated by modifying their surface chemistry. Such innovative approaches could have wide-ranging implications for responsible environmental management of wastes from nanotechnology industries and consumer products.

Another question researchers at the University of Birmingham are investigating is whether manufactured nanoparticles are

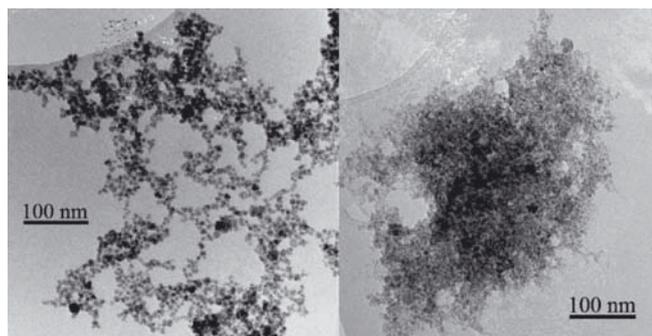


Figure 4. Transmission electron microscopy (TEM) image of aggregates of 7nm charge-stabilised iron oxide nanoparticles. The image on the right is in the presence of natural organic macromolecules called humic acids. The figure on the left is taken under identical circumstances but in the absence of humic acids.³

mobile in the matrix pore waters of rocks such as sandstones and limestones. This work will improve understanding of their potential to move within groundwaters. Preliminary results suggest that attenuation of a number of metal nanoparticles is high in fresh groundwater systems, in some cases leading to very efficient clogging, and that as a consequence mobility is very low in the pore waters of the rocks examined. However, there is also evidence that a small proportion of particles may be much more mobile.

Nanoparticle interactions in the environment

Do nanoparticles interact with naturally occurring substances and man-made chemicals already in the environment? If so, do they alter chemical behaviour or uptake into organisms?

Researchers on the TPEM project at Lancaster University and researchers at the University of East Anglia are investigating the interactions of nanoparticles with pollutants such as polyaromatic hydrocarbons released from combustion processes, pesticides and other industrial chemicals. They want to know if nanoparticles alter uptake and toxicity of these pollutants. Early results suggest that interaction does occur, but that it is dependent on the nature of the pollutant, sometimes increasing uptake or toxicity of the chemical, but sometimes having the opposite effect. Several projects at the University of Birmingham have quantified the chemical behaviour of a range of nanoparticles with naturally-occurring organic macromolecules produced by weathering or microbial action. These studies have shown large effects on surface chemistry and aggregation, as shown in Figure 4.

These and other studies (see pages 17 to 19) are providing essential understanding of the likely environmental exposure pathways of nanoparticles and which organisms are likely to be exposed. It will help establish mathematical models and assessments of the environmental risks posed by nanoparticles, and even future 'green design' of these nanomaterials.

Dedicated UK environmental nanoscience facility

The Facility for Environmental Nanoparticle Analysis and Characterisation (FENAC) was launched in 2009. FENAC is designed to characterise the physical and chemical properties of nanomaterials in all areas of environmental nanoscience within NERC's remit, including characterisation of natural and incidental nanoparticles.

Facility director Professor Jamie Lead says, 'The environmental and human health impacts of manufactured nanoparticles are currently unknown but potentially serious. To gain full benefits from nanotechnology, these potential risks must be identified and minimised. FENAC concentrates on collaborating with members of the nanotoxicology community who are investigating the biological uptake and effects of these manufactured nanoparticles.'

This national facility, based at the University of Birmingham, brings together a wide range of physical and analytical detection methods including electron microscopy (TEM, SEM, ESEM, STEM), force and probe microscopy (AFM, STM), optical microscopy (NSOM, confocal microscopy), separation and sizing methods such as asymmetric and symmetric flow field-flow fraction (FIFFF), analytical ultracentrifugation and cross-flow ultracentrifugation.

Other chemical and spectroscopic methods are also part of the facility such as ICP-MS, EDS and PEELS. The facility will measure nanoparticle concentrations and physico-chemical properties in a range of abiotic and biotic media.

www.gees.bham.ac.uk/staff/leadjr.shtml



Impacts

Environmental effects of manufactured nanoparticles

If organisms are exposed to nanoparticles in the environment, will there be adverse effects? Will these effects be greater or less than those observed for the same substances in 'bulk' or dissolved form? Will there be any novel effects not previously seen before? If nanoparticles are found to have greater effects than their 'bulk' counterparts, is this because they are intrinsically more toxic, because they are more bioavailable, or because they can move more freely and extensively throughout the bodies of organisms?

The diversity of nanomaterials in production and the sheer diversity of organisms in the environment make it hard to make generalisations. As with fate and behaviour, understanding which properties of nanoparticles are important for influencing ecotoxicity is a significant challenge. So too is understanding how they are taken up by organisms and their acute and long-term effects.

Research both within and beyond ENI (for example through responsive mode grants awarded by NERC) is beginning to answer these questions. Grants awarded in the first ENI call considered general aspects of the environmental effects of nanoparticles in freshwater, marine and soil organisms. The second round focused more specifically on microbial impacts in groundwaters, soils and sediments. This reflected the functional importance of microbial communities in these and other ecosystems, and the potential

1. Federici et al., *Aquatic Toxicology*, 2007
2. Smith et al., *Aquatic Toxicology*, 2007
3. Moger et al., *Optics Express*, 2008
4. Mubling et al., *Environmental Science and Technology*, 2009



for deliberately introducing manufactured nanoparticles in significant quantities for clean-up of contaminated aquifers and soils.

These awards have shown that while in some cases manufactured nanoparticles can have adverse effects, in other cases they do not. The nature and magnitude of the effects depends on the type of nanoparticle, the environment where exposure occurs and the nature of the organism exposed. And while there is evidence that some nanoparticles can be hazardous under laboratory conditions, there is as yet little evidence that actual exposure of these nanoparticles occurs in the natural environment.

Laboratory studies on the impacts of nanoparticles

Some of the first laboratory studies funded by NERC and undertaken by the University of Plymouth have shown that nanoparticles of titanium dioxide (used in cosmetics and other applications) and single-walled carbon nanotubes are toxic to at least one species of fish (rainbow trout)¹ when exposure is via the water column. Further investigations² show that fish will eat diets contaminated with nanoparticles, and that the toxic effects are reminiscent of what we know about metals like cadmium, copper and mercury. These preliminary studies reveal limited effects on growth and food intake but important biochemical changes and pathologies in the internal organs, and effects on animal behaviour. The researchers found detectable levels of the nanoparticles studied in the internal organs – including the brain. In contrast, researchers at the University of Exeter found low bioavailability of titanium dioxide nanoparticles when fat head minnow and carp were exposed via the water column. The researchers used Coherent Anti-Stokes Raman Scattering (CARS) photon emission microscopy, a novel approach to visualise nanoparticles on the gills of exposed fish³.

Preliminary studies at the University of Birmingham have found distinct differences in gene expression in the brain and gills of fish (stickleback) exposed to carbon-based fullerenes, but no changes in gene expression in the liver, where much detoxification commonly occurs.

A number of studies are investigating the impacts of manufactured nanoparticles on invertebrates, bacteria and algae. Investigators at the University of East Anglia have developed a technique to fluorescently label synthetic polymer particles, making these easier to track in organisms. Studies with the freshwater flea *Daphnia magna* by this group have shown strong effects of particle size and chemistry on the ecotoxicity of these nanoparticles in this species, but in contrast low toxicity to algae and yeast.

Researchers at the Plymouth Marine Laboratory have done similar studies, using the common mussel *Mytilus edulis*, an important filter feeder in marine and estuarine environments.



Dr Liz Shaw (University of Reading) and PhD student Laurence Cullen examine the effect of nanoscale zerovalent iron (nZVI) on soil microbial communities using a denaturing gradient gel electrophoresis image.

The team found some harmful – but not lethal – effects, such as oxidative stress, when mussels were exposed to carbon-based fullerenes and nanotubes. In contrast, studies at the Centre for Ecology & Hydrology have found no effects on immunotoxicity, growth or reproduction for earthworms exposed to a number of nanoparticles, including zinc oxide, titanium dioxide and cadmium selenium quantum dots.

Research on bacterial communities also shows that toxicity is organism and nanoparticle specific. Researchers at Plymouth Marine Laboratory exposed bacterial populations in marine sediments to silver and titanium dioxide nanoparticles⁴. They monitored the diversity of the bacterial community using molecular techniques (DNA profiles). The emerging results show that while there are no dramatic changes in biodiversity with exposure to silver nanoparticles, there appear to be changes in antibiotic resistance.

The environmental chemistry of **nanoparticles** can be complex and is often altered by the natural environment.

Nanoparticles in remediation

Unlike silver nanoparticles, whose environmental presence is a side effect of their use as antimicrobial agents in medical and domestic applications, high concentrations of nanoscale zerovalent iron (nZVI) may be deliberately introduced into polluted soil and groundwaters as part of environmental remediation efforts. A research team at the University of Reading has been examining the impact of nZVI on the diversity and activity of microbial communities that themselves contribute to soil remediation through pollutant biodegradation. Data collected so far indicate a negative impact on the activity of biodegrading microbes over the short term. A second experiment is examining the longer term impact of nZVI both on biodegrading microbes and on microbial plant symbionts (rhizobia and arbuscular mycorrhizas) important for the final revegetation of the remediated site. Meanwhile, a project at Cranfield University has also been investigating the impact of iron-based nanoparticles on the structure and functional capabilities of the soil microbial community. Preliminary results suggest that there are subtle changes in community structure and function as a result of exposure to such particles, and further work aimed at elucidating the significance of these effects. In a parallel study, researchers at the University of Oxford have employed molecular profiling approaches to determine the impact of nZVI on the genetic diversity and community structure of river-water bacterial communities. These assessments suggest the impact on the bacterial community composition and key environmental parameters such as



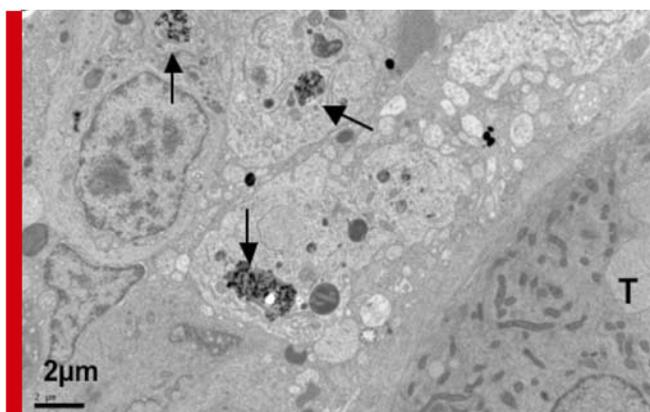
Matt Bain/NHFA

Some nanoparticles can have a harmful but not lethal effect on the common mussel *Mytilus edulis*.

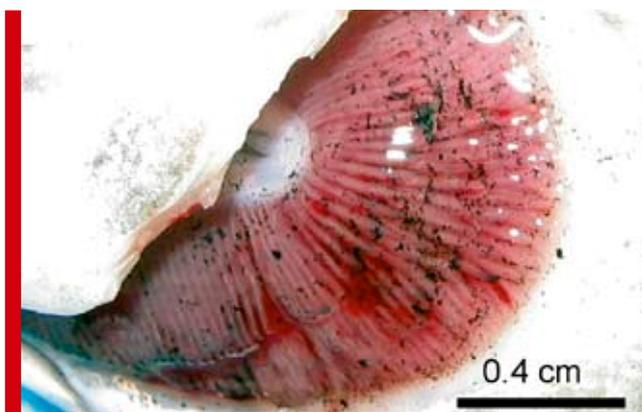


Nanoparticles of titanium dioxide (used in cosmetics and other applications) and single-walled carbon nanotubes are toxic to at least one species of fish, the rainbow trout.

Pat & Tom Lanson/Science Photo Library



TEM images of kidney tissues dissected from rainbow trout three weeks after intravenous injection of 100 μg TiO_2 nanoparticles (23nm) in 1ml trout ringer. Clusters of nanoparticles, indicated by arrows, are visible in tissue surrounding the kidney tubule T. (Modified from Scown *et al.*, 2009, in press *Tox. Sci.*)



Titanium dioxide nanoparticles on the gill surface of the trout.

Richard Handy

pH are moderate but short lived. The researchers are now extending their investigations to consider the impacts of other nanoparticles, such as nanoscale titanium dioxide on bacterial communities, and the uptake of nanoscale zinc oxide by plants.

Interdisciplinary research

It is clear that the magnitude and nature of effects is dependent on the nature of exposure, organism and type of nanoparticle exposed. However, a common theme emerging from all the biological effects research is the need to understand nanoparticle chemistry, behaviour and bioavailability in complex natural media, in the types of conditions where exposure occurs. This emphasises the truly

interdisciplinary nature of environmental nanosciences, where ecotoxicologists, environmental chemists and material scientists need to work together to understand both the chemistry and effects. Developing the expertise and analytical facilities needed to support biological effects studies – so that nanoparticles can be detected, measured and reported accurately – is recognised as a key priority. The initiation of the Facility for Environmental Nanoparticle Analysis and Characterisation has responded directly to this need. A strong interdisciplinary focus in the second phase of ENI will help develop a parallel evolution of our knowledge on both the physico-chemistry and the biology that is needed to push this field forward.





The future

Developing the evidence base for policy-making

A key role for the Environmental Nanoscience Initiative is to provide evidence for policy development. This is reflected by the make-up of the programme's funders: NERC and EPSRC (research councils), Defra (which leads on development of national policy), and the Environment Agency which, with others, develops and enforces environmental regulation.

The first phase of ENI specifically aimed to build research capacity and expertise in the area of environmental nanosciences. We believe we have made significant progress towards achieving this aim and that the UK now has a growing community of internationally-recognised researchers in this area. This community needs to be sustained and new researchers welcomed to it.

ENI second phase: international collaboration

ENI now enters an important and second phase, providing new funds to develop and validate models of environmental exposure, bioavailability and effects for nanoparticles. Working with international collaborators in the US (funded by the US Environmental Protection Agency) we hope to provide the first generation of such models. These will address key areas of uncertainty to allow more confident statements regarding levels of environmental exposure and risks.

In developing this second phase, we have carefully considered the recommendations made by the Royal Commission on Environmental Pollution in its 2008 *Novel Materials* study¹.

1. www.rcep.org.uk/novelmaterials.htm



The international focus of the programme reflects the common view that understanding the risks posed by nanomaterials is a global challenge best met through collaboration. The research funded under ENI will be complemented by research to be funded under the EPSRC's third Nanotechnologies Grand Challenge, which will focus on nanotechnology for environmental solutions and starts in 2010.

Implications for policy-makers

In November 2008, the Scottish Environment Protection Agency commissioned a workshop to understand the implications for policy-making of research funded so far within ENI and linked research*. A stakeholder workshop was facilitated by SNIFFER (the Scotland and Northern Ireland Forum for Environmental Research). This brought grantees and policy-makers together to consider the following questions:

- Do manufactured nanomaterials pose environmental risks and what is the evidence?
- Where are the key uncertainties and knowledge gaps?
- What should be the key messages for decision makers?

**For example, NERC responsive mode grants and NERC's Environment and Human Health programme.*

A key message emerging from both scientists and stakeholders is that uncertainties regarding the environmental risks posed by manufactured nanomaterials remain high. This is to be expected given the infancy of both domestic and international research programmes and the diversity of nanomaterials in production. However, research funded to date has provided understanding of where the major areas of environmental risk uncertainty lie, confirming the direction and content of the ENI's second phase:

- Some of the most important areas of uncertainty lie in understanding uses, sources and inputs of nanomaterials to the environment, behaviour, pathways, fate and persistence. Understanding environmental exposure and bioavailability is seen as an important priority. Although there are now some published studies that have begun to quantify potential exposure, there are high uncertainties associated with these, in part due to the need for more fundamental understanding of how nanomaterials behave in the environment. This includes interaction with other chemicals in the environment and how this influences their bioavailability.
- This is compounded by a lack of sufficiently sensitive and selective methods for detecting and characterising nanomaterials in complex environments, such as soils, sediments, estuaries and rivers. Recognising this, EPSRC is providing funds within the second phase of ENI to

POSTGRADUATE TRAINING

The big issue: the ecotoxicology of nanoparticles

Tessa Scown, fourth year PhD, University of Exeter

Four years ago I was looking for a research project for my post grad. My particular interests were in the field of ecotoxicology. At the time, NERC was searching for people to investigate the effects engineered nanoparticles may have on organisms in the aquatic environment. There was a specific focus on whether fish health may be at risk should nanoparticles enter freshwater systems. When I saw the opportunity to do a PhD in such a new and exciting field, I jumped at the chance and this led to my partnership with the Environment Agency.

I have been researching the effects of metal and metal-oxide nanoparticles on rainbow trout. I'm trying to identify target organs and the effects these nanoparticles may have on organ function.

My work has shown that metal and metal-oxide nanoparticles have the potential to enter the bodies of fish: liver and gills are the likely target organs. But there is still much to be learnt about the factors affecting behaviour of nanoparticles in aquatic systems which may influence their bioavailability.

In the next few years I hope to use the knowledge I have gained from my PhD either in further post-doctorate studies or through work within the environmental sector.



develop novel analytical methods complementing work within the Facility for Environmental Nanoparticle Analysis and Characterisation.

- Some laboratory studies have shown that nanoparticles can exhibit toxicity to organisms in the environment. In some specific cases the hazardous properties exhibited by some nanomaterials have prompted regulators to take precautionary action. For example, the asbestos-like properties of some high aspect ratio, biopersistent carbon nanotubes prompted the Environment Agency to make an interim recommendation for these to be treated as hazardous waste when in a free form. However, for many manufactured nanoparticles the evidence, for example of whether there is a 'nano effect' when compared to the bulk or dissolved form, remains incomplete. Many hazard studies have been conducted at high concentrations of nanomaterials. More systematic evaluations of uptake and dose response have yet to be completed, as have studies that fully evaluate chronic effects.
- Understanding of which intrinsic properties of nanomaterials (eg surface charge, shape, size) govern environmental fate, bioavailability and effects, and how these are modified by the environment into which they are introduced, remains a key gap that will be addressed in the second phase of ENI. The value of developing and validating such predictive models for nanomaterials has been demonstrated by the fibre-pathogenicity model developed from work on asbestos. ENI will begin to develop these fundamental models for key nanomaterials

in production to support decision making in a similar way, in line with recommendations made by the Royal Commission on Environmental Pollution's 2008 report.

- Further areas of uncertainty remain: the fitness for purpose of methodologies and testing procedures used for environmental risk assessment is an area that continues to be considered through work funded by Defra, the European Commission and the Organisation for Economic Cooperation and Development (OECD), supported by basic research programmes such as ENI and projects such as the EPSRC PROSPeCT project. There is also a general awareness of the pace of nanotechnology development, from passive to active structures and a move towards convergent technologies (eg nano-bio). Vigilance of the changing landscape of nanotechnologies through horizon-scanning activities is seen as important.

Many stakeholders recognised the difficulties they faced in recommending precautionary action in the face of the uncertainties that remain when considering the environmental risks posed by nanomaterials. Integrated and coordinated research that reduces uncertainties is seen as important in this regard. Developing and validating robust models that allow better predictions of exposure, bioavailability and effects are key to supporting precautionary measures as needed, and this will be a primary focus of the next stage of ENI.

Richard Owen
Environmental Nanoscience Initiative Coordinator



Nanoscience facility director Professor Jamie Lead and Dr Gillian Spicer.

Projects

Environmental Nanoscience Initiative (ENI) directed funding

NERC project reference	Grant title/establishment	Total grant value £s	Period
NE/E014348/1	Dietary exposure to nanoparticles in fish: a pilot study University of Plymouth	55,383	2007-2008
NE/E014321/1	Effects of C-60 fullerenes and carbon nanotubes on marine mussels Plymouth Marine Laboratory	19,849	2007-2008
NE/E014836/1	Genomic and oxidation-related biological responses in fish exposed to fullerenes of different physicochemical characteristics University of Birmingham	28,827	2007-2008
NE/E015166/1	Manufactured nanoparticle migration in groundwaters University of Birmingham	57,981	2007-2008
NE/E01500X/1	Model nanoparticles for environmental risk studies The Natural History Museum, London	56,564	2007-2008
NE/E01495X/1	Nanoparticle immunotoxicity using an environmental sentinel as a model NERC Centre for Ecology & Hydrology	38,993	2007-2008
NE/E014585/1	Pharmaceutical and cosmetic silica nanoparticles: towards an understanding of their structure, fate and behaviour in aquatic systems King's College London	63,879	2007-2008
NE/E014933/1	Synthetic polymer nanoparticles: effects of composition and size on uptake, toxicity and interactions with environmental contaminants University of East Anglia	61,991	2007-2008
NE/E014496/1	Understanding the fate and behaviour of manufactured nanoparticles in natural waters University of Birmingham	48,327	2007-2008
NE/E015018/1	Visualisation of nanoparticles in the environment University of Lancaster	19,668	2007-2008
NE/F011784/1	Impact of manufactured nanoparticles on the catabolic capabilities and phenotypic structure of soil microbial communities University of Cranfield	56,857	2008-2009
NE/F011830/1	Biomembrane interactions in the toxicology of nanoparticles to microorganisms University of Leeds	20,015	2008
NE/F011881/1	Impact and recovery of groundwater microbial communities exposed to manufactured nanomaterials (MNM) University of Oxford	53,435	2008-2009
NE/F011911/1	A study of the effects of silver surface chemistry on bactericidal properties of silver nanoparticles University of Manchester	20,167	2008-2009
NE/F01192X/1	An investigation into the effects of nanoparticles on the bacterial diversity of freshwater and coastal marine sediments Plymouth Marine Laboratory	37,997	2008-2009

Continued overleaf



Environmental Nanoscience Initiative (ENI) directed funding cont.

NERC project reference	Grant title/establishment	Total grant value £s	Period
NE/F011938/1	Interaction of nanoparticles with microbial populations during particle transport University of Sheffield	48,316	2008-2009
NE/F011946/1	Nanoscale zerovalent iron (nZVI) impact on soil microbial communities University of Reading	64,682	2008-2009
Total	ENI directed funding	752,931	

Project summaries can be found at: www.nerc.ac.uk/research/programmes/nanoscience/facts.asp

Environment and Human Health projects (EHH) directed funding¹

NERC project reference	Grant title/establishment	Total grant value £s	Period
NE/E008860/1	A proof of concept study for a structure activity model for the toxicity of nanoparticles University of Edinburgh, Respiratory Medicine	109,844	2007-2008
NE/E008550/1	Assessing human exposure, uptake and toxicity of nanoparticles from contaminated environments Napier University, Life Sciences	121,078	2007-2009
NE/E009166/1	Hazards of nanoparticles to the environment and human health The Natural History Museum, Mineralogy	118,300	2007-2009
Total	Environment and Human Health programme	349,222	

Project summaries can be found at:
www.nerc.ac.uk/research/programmes/humanhealth/facts.asp



Responsive mode and knowledge transfer funding¹

NERC project reference	Grant title/establishment	Total grant value £s	Period
NER/S/J/2005/13991	The Big Issue: The ecotoxicology of nanoparticles	N/A Studentship	2005-2008
NE/D007267/1	Toxicology of nano materials to fish: a fact finding pilot study University of Plymouth	60,391	2006-2007
NE/D004942/1	Understanding the environmental behaviour and biological impacts of manufactured nanoparticles in natural aquatic systems University of Birmingham	441,615	2006-2010
NER/S/J/2005/13991	Trace metal interactions with manufactured and natural nanoparticles University of Birmingham	N/A Studentship	2006-2009
NE/E002889/1	Engineered nanoparticles in the natural aquatic environment (Nanonet) University of Birmingham	128,947	2007-2010
NE/F008368/1	Nanoparticles in the natural environment University of Birmingham	N/A Studentship	2007-2010
NE/G010269/1	Opening the black box: imaging nanoparticle transport with magnetic resonance imaging University of Glasgow	23,268	2009-2010
NE/G010641/1	Quantifying the physicochemical characteristics of cerium oxide nanoparticles; a preliminary for ecotoxicological investigations University of Birmingham	50,817	2009-2010
NE/G001812/1	Sub-lethal effects of manufactured nanoparticles on fish: bioenergetics, brain and behaviour University of Plymouth, Biological Sciences	419,464	2009-2012
Total Grand total	Responsive mode and knowledge transfer Directed funding and responsive mode	1,124,502 2,226,655	

Project summaries can be found at:

Grants and fellowships: <http://gotw.nerc.ac.uk/refno.asp>

Studentships: <http://sotw.nerc.ac.uk/refno.asp>

1. Only projects considering risks of manufactured nanoparticles are included here. There is also a large body of ongoing work on incidentally produced and naturally-occurring nanoparticles.



Glossary of terms

This glossary uses (where possible) the most recent terminology recommended by BSI for use in relation to nanotechnology.

Bioavailability

The ability of a substance to interact with the biosystem of an organism. Systemic bioavailability will depend on the chemical or physical reactivity of the substance and its ability to be absorbed through the gastrointestinal tract, respiratory tract or skin.

Ref: *Risk assessment of chemicals: an introduction*, ed. C.J. van Leeuwen and J. L. M. Hermens, Kluwer Academic Publishers, 1995

Carbon nanotube

Nanotube composed of carbon.

NOTE: Usually consisting of curved graphene layers, the most important classes of carbon nanotubes are singlewall carbon nanotubes and multiwall carbon nanotubes.

Ref: ISO/TS 11751

Fullerene

Molecule composed solely of an even number of carbon atoms, which form a closed cage-like fused-ring polycyclic system with twelve five-membered rings and the rest six-membered rings.

NOTE: Adapted from IUPAC Compendium of Chemical Terminology [6]. [6] IUPAC, *Compendium of Chemical Terminology*, Second Edition, 1997 (<http://goldbook.iupac.org/>)

Ref: ISO/TS 11751

Nanofibre

Nano-object with two similar external dimensions in the nanoscale and the third dimension significantly larger.

NOTE 1: A nanofibre can be flexible or rigid.

NOTE 2: The two similar external dimensions are considered to differ in size by less than three times and the significantly larger external dimension is considered to differ from the other two by more than three times.

NOTE 3: The largest external dimension is not necessarily in the nanoscale.

Ref: ISO/TS 27687

Nano-object

Discrete piece of material with one or more external dimensions in the nanoscale.

NOTE: This is a generic term for all nanoscale objects.

Ref: ISO/TS 27687 (PAS 136:2007)

Nanoparticle

Nano-object with all three external dimensions in the nanoscale.

NOTE: If the lengths of the longest and the shortest axes of the nano-object differ significantly (typically by more than three times) the terms nanorod or nanoplate are intended to be used instead of the term nanoparticle.

Ref: ISO/TS 27687 (PAS 136:2007)

Nanoscale

Size range from approximately 1nm to 100nm.

NOTE 1: Properties that are not extrapolations from larger size will typically, but not exclusively, be exhibited in this size range.

NOTE 2: The lower limit in this definition (approximately 1nm) has no physical significance but is introduced to avoid single and small groups of atoms from being designated as nano-objects or elements of nanostructures, which might be implied by the absence of a lower limit.

Ref: ISO/TS 27687 (PAS 136:2007)

Nanoscience

The systematic study and understanding of matter, properties and phenomena related to the nanoscale.

Ref: ISO/TC 229 (working definition)

Nanotechnology

The application of scientific knowledge to control and utilise matter at the nanoscale, where size-related properties and phenomena can emerge.

Ref: ISO/TC 229 (working definition)

Nanotube

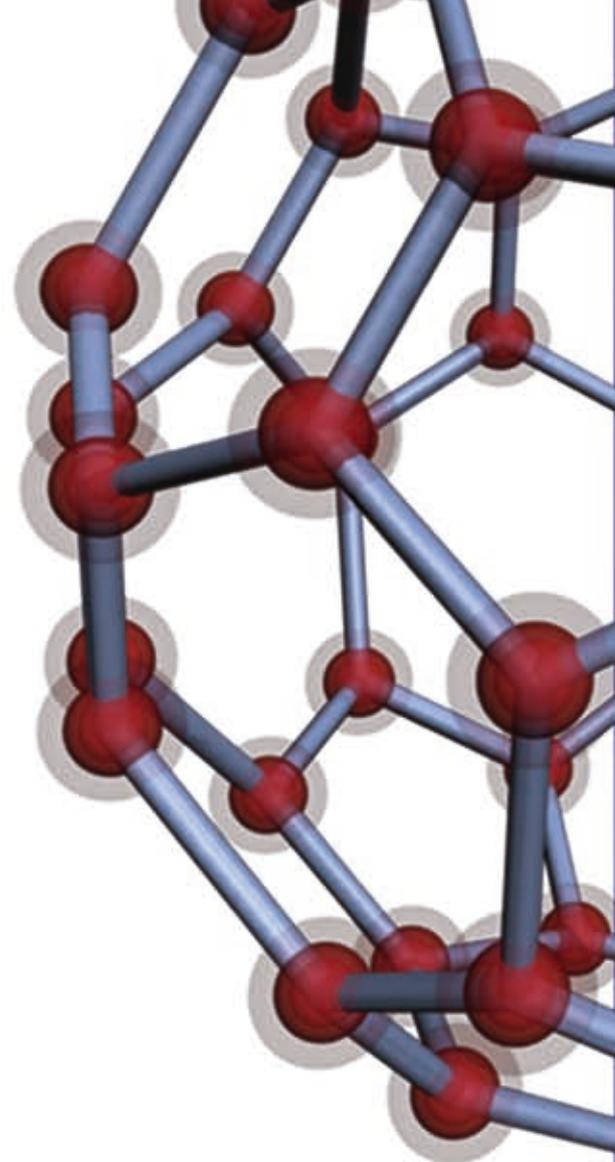
Hollow nanofibre.

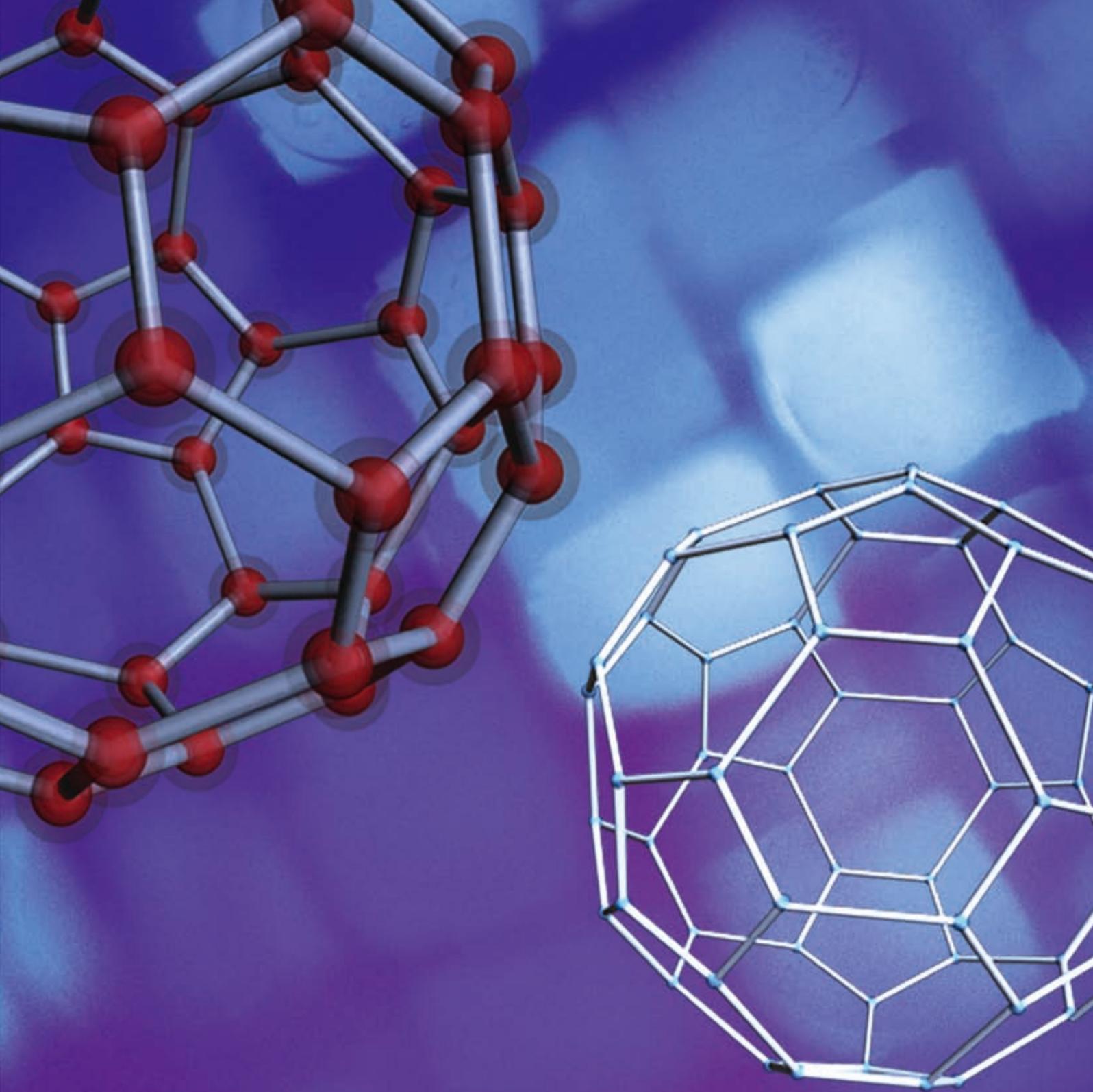
Ref: ISO/TS 27687

Quantum dot

Crystalline nanoparticle that exhibits size-dependent properties due to quantum confinement effects on the electronic states.

Ref: ISO/TS 27687





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FSC and NAPM certification.



Small World

Environmental Nanoscience Initiative

More information
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