

## Science for Environment Policy

## THEMATIC ISSUE: Nanomaterials' functionality



## **Science for Environment Policy**

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## Ultra-fine particles emitted by commercial desktop 3D printers

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## **Images**

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Figure 1: Library of anisotropic gold nanoparticles: Transmission Electron Microscopy (TEM) micrographs by Dr Željka Krpetić, Qi Cai and Jennifer Cookman (CBNI, UCD).

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## **EDITORIAL**

## Nanomaterials: addressing the challenges, benefiting from the opportunities

Some of the deepest challenges we will face in the coming decades derive from the opportunities offered by emerging technological advances. Many of these will improve our quality of life, and develop our economies, but all will be measured against the overarching principle that we do not make some error, and harm ourselves and our environment by exposure to new forms of hazard. Scientific and technological progress has increased both the duration and quality of our lives, throughout much of our history, but by virtue of previous mistakes we have learned to value innovation balanced with caution and safety.

The capacity to create features of the scale of one thousand times smaller than a millimetre (a nanometer) now offers the promise of radical technological development. After a slow start, one can begin to see the pace of real development and outcomes quicken. Some of this is reflected in the papers selected here.

Engineering at the nanoscale already improves the efficiency of clean energy harvesting and storage, lowering our dependence on polluting fossil fuels. It improves the efficiency of energy converted from sunlight, as well as the capacity and safety of batteries. As this develops we will see the different impacts, from faster, smaller and more energy efficient computers and mobile phones, to a new era of the environmentally clean electric car.

Several articles in this Thematic Issue illustrate how nanotechnology is likely to further revolutionise that arena, for example in capturing sunlight and turning it into usable electrical energy. The article 'Solar cell efficiency boosted with pine tree-like nanotube needle', describes how light collected from the sun can be bounced around many times inside a nanostructure to improve the chance of it exciting electrons, and 'Nanotechnology cuts costs and improves efficiency of photovoltaic cells' shows how electrons that are released can be captured by the large surface area of 'nano-tree like' anodes. Together these ensure that more of the sunlight is transformed to captured electrons and electrical power. The article 'New energy-efficient manufacture of perovskite solar cells' goes further, and suggests that the existing titanium dioxide that is currently used in solar cells could be replaced by perovskites, yielding quite dramatic improvements in energy conversion, at low device fabrication costs. The article 'Pomegranate-inspired battery design doubles stored energy' shows another interesting example suggesting that with nano-engineering the space around anodes will prolong the life, and safety, of batteries. The efficiencies and improvements implied by these examples are sufficient to illustrate how the design and engineering of structures on the nanometre scale could change markets, and make a better, cleaner and safer environment.

Few doubt that the advent of compact and cheap 3D printing, in which nanoparticle 'inks' are merged together by heat or light to form solid structures, will change our world. One will see much of what was produced in a factory, from furniture and decoration to the very structures of homes themselves, becoming personalised, individually designed, and made in small companies, or at home. Many of the new 'inks' necessary for metallic, ceramic and polymeric composites will be novel nanoparticles. Furthermore, the article 'New 3D printing technique for environmental nanodevices' is a good example of how processes also, such as the old-fashioned spinning mill from the previous century, are being transformed into an inexpensive and fast desk-top nano-scale 3D fabrication process.

The article 'New quantum dot process could lead to super-efficient light-producing technology' describes how anisotropic (elongated, non-spherical) indium-gallenium nitride quantum dots, or proximity to an anisotropic surface, can lead quantum dots to emit polarised light, potentially enabling 3D television screens, optical computers and other applications, at much lower cost. 'The potential of new building block-like nanomaterials: van der Waals heterostructures' and 'Graphene's health effects summarised in new guide' touch on the possibility of engineering 'building block-crystals' by arranging different 2D nanostructures such as graphene into low dimension crystals, which allows us, for example, to lower the loss of energy in transmitting electricity. There are also quite novel directions underpinning 'green nanochemistry' — illustrated by the potential of silk-based electron-beam resists (in the article 'Making nano-scale manufacturing eco-friendly with silk') — to be eco-friendly, and have new functionalities.

The article 'Low energy water purification enabled by nanomaterial-coated sponges' reports on structures at the nanoscale (a 'nanosponge'), capable of focusing an applied electric field to more readily puncture the membranes of bacteria that have contaminated water. The article is intriguing not just because of the science, but because it illustrates the point that nanotechnology can make disinfection both safer and less damaging to the environment.

However diverse, all the articles share a common theme – the key enabling properties are a result of the manipulation of structure at the nanoscale.

European institutions and organisations have been at the forefront of efforts to ensure safe and practical implementation of nanotechnology. Significant efforts have been made to address knowledge gaps through research, the financing of responsible innovation, and the upgrading of the regulatory framework to render it capable of addressing the new challenges. There are solid reasons for institutional attention to the issues. Succinctly put, the passing around and modification of natural nanoparticles and macromolecules (for example, proteins) within our bodies is the foundation of much of life. In doing so we regulate and send signals between cells and organs. It is therefore appropriate that questions should be asked about engineered nanoparticles and how they interact with us, and whether they could lead to unforeseen hazards. Those are substantive issues, and answering them well will support the creative drive towards real innovation for many decades to come, and honour our commitments to future generations.

History understood lights the path to the future, so it is worth pausing to understand how we reached this point, and reflect on two key lessons.

Progressive and incremental product development in industry required colloidal particles, one thousand times smaller than a millimetre, to be made even smaller. Thus did, almost accidently and imperceptibly, the evolution of nano-particles driven by product optimisation merge with the growing flood of highly innovative nanomaterials research. Thereby the concept of nanosafety in its broader context becomes almost synonymous with the safety of the evolved (and smaller) 'legacy' materials, many of them long in use. The future will view this accidental convergence as a temporary confusion in what nanotechnology is, and what it will become. Succinctly put, the recent past, derived mostly from experience with legacy materials, will not be a good guide to the future. This is well illustrated by the papers presented here, that go far beyond optimisation, and hint at changing markets.

A second set of confusions will also prove to be transient. The initial excitement about nano-innovation also stimulated unfocused fears of widespread 'nano-hazards', and these, combined with early poorly framed toxicological studies, left policymakers alert but with bewildering advice. These confusions are being resolved, at least partially. In fact, extensive experimental data now suggest that (most) nanomaterials in current use possess an acute toxicity no greater than might be expected from their bulk counterparts. Those that are toxic (or 'poisonous' in this acute sense) are easily identified, sometimes deriving their toxicity from being soluble.

There remain substantive longer-term questions to be understood in this arena of nanosafety, and it will be well to focus the energy, talent and resources on those.

Firstly, some may bioaccumulate, and their final degradation, fate and impact on the animate and inanimate environment is a key question yet to be extensively investigated. Secondly, we have only begun to

see the range and variety of materials that will one day enter markets. Indeed, history will barely notice the role of existing colloidal materials made smaller. All our knowledge and experience suggests (and the current papers hint) that it is really novel nano-structural objects (potentially even of similar materials) that, in future, will constitute a nano-enabled technology market. Within the plethora of what is to come, there could exist the potential for novel hazards, both acute and long-term. We will need to guard against that.

Thus, it is worth stressing that nanostructures of a single material with different shapes and geometry may have very different properties. Look at Figure 1 below. Even a single simple material (gold in this case) can be made into an enormous variety of sizes, shapes, topologies, surface modifications and other aspects. The resulting nano-objects (as illustrated also by some of the papers in this collection) may have different electronic, optical, chemical reactivity, and many other properties. This is good news, for it reinforces just how much room there is for the technology to grow. Still, it illustrates the challenge for those studying the safety implications.

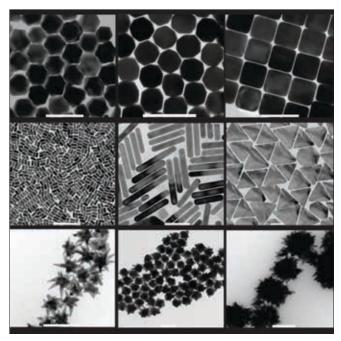


Figure 1. From top left: nano-trisoctahedra, faceted gold nanorods (top view), nanocubes, nanorods, nanoprisms and nanostars. Scale bars are 100 nm.

One way of focusing the research is along the lines of likely value chains, defining which particular manifestations of the materials are most likely to enter the market. One way of approaching the whole issue then, is to survey key recent scientific outputs to identify those nanomaterials with the highest potential, possibly disruptive application in technology, and support their safe implementation. A concrete example worth thinking about in understanding how research in nanosafety is conceived is suggested in the article 'Ultrafine particles emitted by commercial desktop 3D printers'. Many common processes where two materials rub against each other release dusts (including 'nano-dusts') and our lungs have evolved to deal

with this very effectively. As expected, the process of 3D printing itself will release billions of nanoscale particles per minute, and when not managed these may be inhaled into the lungs. Furthermore, the process of forming the ink may involve sufficient heat or other energy such that the surface of the inks may not be as simple as one expects. Ensuring we have clear understanding of the real-life impact of such new dusts, which might differ from (say) domestic nanoparticles generated by cooking, will be the basis for the informed and adequate risk management, and safe use of the product.

It will be important for scientists to learn from the recent past. Prudence suggests that we conserve our energy and resources by focusing both on the key unresolved issues from existing nanomaterials, and also on thoughtfully designed scientific studies of new materials to be relevant in realistic usage or exposure scenarios. In that regard, the article 'Potential health risk from nanosized cellulose crystals' is significant, for it raises significant and subtle questions about how we think about safety. Cellulose is one of the most abundant biopolymers on earth. Unsurprisingly, nature has discovered the benefits of engineering on the nanoscale in this arena long before us, and therefore many aspects of plants, from structural integrity to fluid transport, involve nanocellulose. Latterly great interest has emerged in the potential to apply nanocellulose as a structural additive in everything from building materials and car parts, to nanoporous filters to improve water quality, and far beyond. Indeed, many have seen this as an 'ideal' nanomaterial: 'natural', biodegradable, and ultimately without long-term effects on our environment in much the same way as fallen trees are ultimately consumed by the environment from which they are born. That these materials could, for example, raise new significant inflammatory effects is therefore surprising, possibly even disappointing. And yet, this is an illustration of just how cautious one has to be in interpreting what are, without doubt, correct scientific data. For example, there could be two competing interpretations of these data on nanocellulose.

The first is that the inflammatory effects observed may be an effect of 'dust overload', as the surface areas exposed by such materials, being large, could, if we are exposed to large amounts, adsorb, exhaust and overcome the natural protective biomolecules and processes in our lungs. Such overload is a rule rather than an exception when it comes to dust (and applies in a similar manner to mine dust, industrial processes, such as welding, and fruit waste, as well as bedbugs or sandstorms). Regulation, in particular on occupational safety, effectively handles such difficulties by setting occupational exposure limits. Investigations by the nanosafety community (in distinction to traditional occupational exposure research) into those issues will have limited additional impact. The second interpretation, which would be quite surprising for a natural and biodegradable material such as nanocellulose, is that (for example, due to its shape) there arises an exceptional and persistent pro-inflammatory effect that would require specific regulatory restrictions beyond those typical of (say) comparable dusts. Such discoveries are of capital importance, and the nanosafety scientific community can play a key role there. Where feasible, we should in future make efforts to design scientific investigations to differentiate between these scenarios, and clearly signal to the broader community to which category the outcome belongs.

For scientists working in this arena, the challenge will be more than scientific, but to exercise good judgement, remain unmoved by unfounded fears, certainly to have a clear guiding vision of the key issues, but never to grow so confident as to miss what could be radically new, and potentially critical.

From a policy perspective, one could say that scientific understanding of nanomaterials, and their safety, is rapidly developing, and some aspects (particularly in arenas such as acute toxicity) are essentially clarified. There are still significant unknowns particularly in their long-term fate and impact. Therefore, identifying materials, or better, material properties, that have the potential for adverse long-term effects is clearly a priority. However, there is already sufficient general scientific insight that could be implemented within existing regulatory tools, ensuring that sound contemporary science is applied in generation and interpretation of data for safety.

Also, we have every reason to suppose that practical developments will lead to quite new manifestations of materials, with properties as yet poorly explored. Notably, experience derived from legacy materials may not be a good guide to the future. In particular, the differences between materials, brought about by the manipulation of their shape, structure and surface at nanoscale, and their impact in provoking different biological responses is still being clarified. While the breadth of issues may appear to be daunting there is every reason to suppose that a thorough and deep understanding of the principles is possible. In facilitating responsible uptake of the promising technology, research can further support regulation by identifying likely value chains and supporting thorough understanding of the specific nanomaterial required to drive them.

Still, there is no room for complacency, for we are truly at a scientific frontier, and there may yet be surprises; in safety, failure has a high price. We do not doubt that that nanotechnology truly does have the power to make, and indeed is in the process of, making a better world. And translation into economic benefit, both in terms of making novel products and ensuring that safety, will continue to be a partner. But success will require from innovators, scientists, regulators, policymakers, and all concerned, not just resources, but perhaps even more, depth of thought, commitment, focus and persistence.

Professor Kenneth Dawson, Director, Centre For BioNano Interactions (CBNI) School of Chemistry and Chemical Biology University College Dublin, Ireland

## Pomegranate-inspired battery design doubles stored energy

A new pomegranate-inspired design is the basis of a longer-lasting lithium-ion battery created by US researchers. They designed a battery with an anode made from 'silicon pomegranates', which doubles the amount of energy that can be stored compared to a standard carbon anode.

"In tests, the new siliconbased anode was capable of storing more than twice as much energy as an ordinary graphite anode." Lithium-ion batteries are the rechargeable batteries that many of us use to charge our phones, tablets and laptop computers. Like most batteries, they have two electrodes — a cathode and an anode. The anode is the part that absorbs the lithium ions to store the charge during recharging.

There is significant interest in making more efficient lithium-ion batteries — for commercial as well as sustainability reasons. For example, the European Commission (EC) is currently seeking proposals for research projects focusing on a new generation of batteries that would be cheaper, longer-lasting and quicker to charge¹. Its main motivation is for batteries to be developed that could be used in electric cars.

The new battery design replaces the graphite (solid carbon) anodes of ordinary lithium-ion batteries with anodes made from silicon and carbon nanomaterials. They should theoretically last longer because they can store more energy. Silicon nanoparticles form the 'seeds' of the pomegranates, which are encased in a thin carbon framework. Each silicon seed is housed in its own carbon bubble, with room to rattle around. Practically, the pomegranates exist in powder form, with the pomegranate structure only visible under a microscope.

This structure solves two main problems with silicon anodes. First, silicon anodes expand during charging so that after repeated charging cycles they disintegrate. The seed casings in the new design provide room for growth. Secondly, the outer casing keeps the silicon away from the electrolyte in the battery. Without this casing, the silicon would react with the electrolyte to form a substance that would clog up the battery.

In tests, the new silicon-based anode was capable of storing more than twice as much energy as an ordinary graphite anode. It was also very stable. After charging the pomegranate-inspired battery 1 000 times, the researchers found that it maintained 97% of its charge capacity. They also noted that no complex equipment or chemical processing was required to make their pomegranates.

In a previous study, the researchers showed that the silicon for their battery anodes could be extracted from rice husks², a recycled resource. Rice husks are some of the most high-volume waste products from farming and other research teams have also used them to make battery anodes³. One ton of rice husks is produced for every five tons of rice, amounting to more than 100 million tons every year.

Such sustainable sources address the EC's call for production processes that consider 'the availability of raw materials'. Today, silicon is made from silicon dioxide (silica) in energy-intensive processes that need high temperatures<sup>4</sup>. The silica in rice husks would also have to be converted into silicon, and it is not yet known whether the production process would be commercially viable.

Source: Liu, N., Lu, Z., Zhao, J., et al. (2014). A pomegranate-inspired nanoscale design for large volume-change lithium battery anodes. *Nature Nanotechnology* 9(3): 187–92. DOI:10.1038/ nnano.2014.6

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### Themes:

Environmental technologies,

<u>Sustainable</u> <u>consumption and</u> <u>production</u>,

Climate change and energy,

Resource Efficiency

- 1 http://ec.europa.eu/research/participants/portal/desktop/en/opportunities/h2020/topics/2528-nmp-17-2014.html
- 2 http://www.nature.com/srep/2013/130529/srep01919/full/ srep01919.html#affil-auth
- 3 http://www.pnas.org/content/ early/2013/07/03/1305025110
- 4 http://www.nature.com/nature/journal/v446/n7132/abs/nature05570.html

## Making nano-scale manufacturing eco-friendly with silk

Nanolithography – a way of making finely detailed patterns or structures, such as those found in advanced computer microchips, uses toxic and corrosive chemicals. Researchers have now shown that these could be replaced with eco-friendly silk proteins and water, eliminating the need to use and dispose of hazardous chemicals, while achieving similar levels of detail to conventional methods.

"The results demonstrate that silk proteins may be a viable alternative to conventional techniques for nanolithography, avoiding the use of toxic chemicals and generation of environmentally hazardous toxic waste products."

In nanolithography, an underlying base, such as silicon, is coated with a polymer, called a 'resist'. A design is then 'drawn' on the resist, typically using a narrow beam of light or electrons. This changes the properties of the resist and reveals the design by allowing a solvent to either dissolve the drawn area (positive resists) or the area around it (negative resists).

Conventional nanolithography uses toxic resist materials and volatile organic compounds (VOCs) to create designs on the resists. The resulting toxic and VOC waste products are a hazard to both those handling them and the environment. As such, there is a growing need to develop safer, eco-friendly resists and solvents, especially as new production techniques move from small labs to large manufacturing plants.

Researchers are now turning to the natural world in search of green solutions, one of which may be silk. Silk proteins have a natural tendency to self-assemble into different structures under different conditions. Silk dissolves in water under some conditions, but is insoluble under other conditions. This suggests it may be possible to produce both positive and negative silk resists by controlling how they are made.

Additionally, without using harsh chemicals it may be possible to produce resists with enhanced properties. Biological components, such as enzymes, could be added to form biosensors, for example.

The researchers in this study coated silicon and quartz slides with silk proteins to produce both positive and negative resist types. They then used an electron beam, at different strengths, to draw a design on to the resists. They found that areas of water insoluble silk proteins (the positive resists) were degraded when exposed to electron beams, making them soluble. Higher strengths of electron beams could also change the soluble silk proteins of the negative resists into water insoluble forms.

This allowed them to create positive and negative resists, respectively. Using this approach, the researchers found they could produce structures with a resolution of 30 nanometres (nm), which is similar to existing techniques. They believe that this resolution could be improved with further development and optimisation.

The researchers also added chemical and biochemical substances, such as 'quantum dots' and enzymes, to silk solutions. They found that silk proteins can preserve the function of these substances, such as the ability of an enzyme to trigger a colour changing reaction in the presence of a chemical.

The results demonstrate that silk proteins may be a viable alternative to conventional techniques for nanolithography, avoiding the use of toxic chemicals and generation of environmentally hazardous toxic waste products. The researchers note that their technique did require higher strengths of electron beam than is typical in conventional approaches.

Importantly, the results have also shown that it is possible to encapsulate functional molecules in silk protein resists. This could potentially benefit a wide range of different applications. For example, it could lead to biosensors capable of identifying and measuring environmental contaminants, or in diagnosing disease using extremely small samples of blood or other biological fluids.

Source: Kim, S., Marelli, B., Brenckle, M. et al. (2014). Allwater-based electronbeam lithography using silk as a resist. *Nature Nanotechnology* 9(4): 306–10. DOI:10.1038/ nnano.2014.47

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## Themes:

Environmental technologies,

<u>Chemicals, Sustainable</u> <u>consumption and</u> <u>production</u>

# Low energy water purification enabled by nanomaterial-coated sponges

A low cost, low energy method to disinfect water using electricity has been developed by researchers by combining carbon nanotubes (CNTs) and silver nano-wires with existing materials. The technology has the potential to be used in portable disinfection devices in developing countries.

"There are a number of treatment methods for disinfecting drinking water, such as membrane filtration and UV disinfection. However, these methods have a number of disadvantages, such as high maintenance costs and energy consumption."

Source: Liu, C., Xie, X., Zhao, W., et al. (2013). Conducting nanosponge electroporation for affordable and highefficiency disinfection of bacteria and viruses in water. Nano Letters 13(9): 4288–93. DOI:10.1021/nl402053z.

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## Themes:

Environmental technologies,

Environment and health,

Water,

Resource efficiency

Globally, an estimated 1.3 million children under five die every year from diarrhoeal diseases. Many of these deaths are caused by drinking water contaminated with microorganisms. In order to improve global access to safe drinking water and sanitation, the EU, and its Member States, have provided around €200 million per year to water supply, sanitation and hygiene ('WASH')¹ programmes in developing countries, and is the largest such donor in the world.

There are a number of treatment methods for disinfecting drinking water, such as membrane filtration and UV disinfection. However, these methods have a number of disadvantages, such as high maintenance costs and energy consumption. Chlorine disinfection is cheaper and more common, but can generate carcinogenic byproducts. As such, more efficient, affordable and low energy water disinfection treatments are needed.

One possibility is the use of a process called 'electroporation', in which water is disinfected using an electric field. This kills harmful microorganisms by causing pores to form in their cell walls. Earlier studies have shown that the process works in principle, but needs high voltage electric fields, which use large amounts of energy, and is therefore costly.

However, this study shows how nanomaterials could be used to drive down the energy use and cost of electroporation disinfection.

The researchers coated commercially available polyurethane sponges with carbon nanotubes and silver nanowires. Together these turned the porous structure of the sponges into small conductive electrodes, with nanometer-sized tips that enhanced their local electric fields.

They tested the efficiency of the conducting 'nanosponge' in killing microorganisms using water 'contaminated'

with four diarrhoea-causing bacteria, including Escherichia coli and Salmonella enterica Typhimurium, as well an example virus that infects bacteria, called 'bacteriophage MS2'.

Nearly all — 99.9999% — of all bacterial species were removed from the contaminated water when it was passed through the nanosponge. This was achieved with a significant reduction in voltage, from the thousands of volts indicated in other studies, to around just 10 volts. The sponge inactivated 99.4% of the viral particles, which required around 20 volts. Using an electron microscope the researchers confirmed that the electroporation was the mechanism causing the antibacterial effect.

Silver nanoparticles are considered a potential health risk, and the researchers measured silver in the filter water effluent, finding levels of 70 to 94 parts per billion (ppb). This is however very close to US national standards of 100 ppb. There are currently no EU standards for silver concentrations in drinking water.

The flow rate of water used was 15 000 litres per hour per square metre of sponge. However, there was no optimisation of the flow rate, or analysis of variable flow rates, as may be seen if the technology is used as a portable device.

By combining CNTs and silver nanowires with existing materials, the researchers have significantly improved the energy efficiency of electroporation, without sacrificing effectiveness. They suggest that the low cost, low energy consumption and speed of treatment would make the technology useful as a portable decontamination device, as well as for use in larger water treatment systems.

1 <a href="http://ec.europa.eu/echo/en/what/humanitarian-aid/water-sanitation-hygiene">http://ec.europa.eu/echo/en/what/humanitarian-aid/water-sanitation-hygiene</a>

# New quantum dot process could lead to super-efficient light-producing technology

Polarised light forms the basis of many technologies, such as computer monitors. However, current approaches for making polarised light are inefficient, as they produce more than is ultimately used or needed. Researchers may now have found a way to directly produce polarised light using tiny nanostructures, called quantum dots, opening the way for more energy-efficient technologies.

"...the researchers found a way to force the light emitted from quantum dots to all take the same kind of polarisation." Most light sources, such as fluorescent light bulbs, produce light waves which scatter in all directions and orientations. However, this light can be 'polarised' using filters, which ensure that all light waves are of the same orientation. Like coins going through a slot, only light of the correct orientation can pass through a polarising filter, which blocks other orientations.

Polarisation forms the basis of many technologies, such as the LCD screens in computer monitors and hand held devices, including tablets and phones. It also has uses in more advanced applications, such as 'wiretapping-proof' quantum cryptography and medicine. However, because polarising filters block at least half of the light emitted, and therefore the energy used to produce it, many current technologies are far less energy-efficient than ideal.

One way to increase energy efficiency is to use materials that directly emit polarised light. 'Quantum dots' are one such material. Their shape and nano-size (around 10 000 could fit across the width of a single human hair) give them unique properties, allowing them to exploit quantum phenomena to produce light.

However, manufacturing quantum dots of only a single polarisation, rather than many different polarisations, is difficult. In an effort to overcome this challenge, the researchers found a way to force the light emitted from quantum dots to all take the same kind of polarisation.

They grew, layer by layer of atoms, tiny elongated sixsided nano-pyramids of the semiconductor material gallium nitride. This was done in a way that allowed the researchers to control the orientation of the pyramids, i.e. the pyramids were of the same basic structure, but rotated by different amounts. Thin layers of gallium nitride containing the metal indium were placed on top of each elongated pyramid and formed an asymmetrical quantum dot. The level of polarisation emitted from the quantum dots was then measured and analysed.

The researchers found that controlling the orientation of the individual pyramids — and therefore the asymmetry of the quantum dots — aligned the polarisation of light emitted from the quantum dots. Light of a specified polarisation was therefore produced. On average, 84% of the light produced was polarised, much higher than has been achieved using different approaches.

The study's authors believe this is the first reported example of a controllable method for producing multiple aligned quantum dots. Importantly, the method is compatible with existing materials and processing techniques, meaning that the equipment to construct these quantum dots already exists in many laboratories and manufacturing plants.

The researchers believe that they could improve the overall level of polarisation, above the 84% achieved in this research, by altering the amount of indium. If so, such quantum dots could form the light source of new super-efficient LCD screens. Quantum dots can also be controlled in such a way that they emit a single photon of light at a time, making them ideal for use in quantum cryptography.

Source: Lundskog, A., Hsu, C.-W., Fredrik Karlsson, K., et al. (2014). Direct generation of linearly polarized photon emission with designated orientations from site-controlled InGaN quantum dots. Light: Science & Applications 3(1), e139. DOI:10.1038/ lsa.2014.20

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Read more about:

Environmental Technologies,

Climate change and energy,

Resource efficiency

## Solar cell efficiency boosted with pine tree-like nanotube needle

'Dye-sensitised solar cells' (DSSCs) are an alternative to traditional silicon photovoltaic (PV) solar cells. They have a number of advantages over traditional PV cells, including greater flexibility and lower manufacturing cost, but they are less efficient at turning sunlight into electricity. Taking inspiration from nature, new research has doubled their efficiency using pine tree-shaped nanotubes.

"This study enhanced the design of a type of dyesensitised solar cell (DSSC) using nanotechnology so that they are more efficient at converting sunlight into electrical energy."

Averaged over the entire planet, each square metre of the Earth's surface receives energy worth about a barrel of oil, in the form of sunlight every year. As such, solar power is among the most promising sources of renewable energy.

The most common way of extracting energy from sunlight is through the use of silicon-based solar panels. Currently, these are around 20% efficient at converting light energy into electrical energy. However, while the costs of making this type of solar cell are coming down, they remain expensive to produce, both in terms of material cost and energy use.

This study enhanced the design of a type of DSSC using nanotechnology so that they are more efficient at converting sunlight into electrical energy. DSSCs are semi-transparent solar cells that use dye molecules to generate electricity. Electrons are knocked off the dye molecule by light and picked up by the 'photoanode': an electrode coated in nanoparticles of an electronabsorbing material, such as titanium dioxide (TiO<sub>2</sub>). A thin layer of liquid electrolyte between this layer and the negative electrode completes the circuit.

The main disadvantage of DSSCs is the use of liquid electrolytes. These typically contain volatile organic compounds (VOC), which are hazardous to health and the environment. Additionally, liquid electrolytes make DSSCs less durable, prone to electrode corrosion and electrolyte leakage.

Solid State DSSCs (ssDSSCs), where liquid electrolytes are replaced with more durable polymers or solid materials, were developed to overcome these disadvantages. However, they are currently only half as efficient at converting light energy into electrical energy as liquid-based DSSCs.

Boosting the efficiencies of ssDSSCs has mainly focused on identifying improved dyes and electrolyte replacements. However, this research shows how efficiency can also be improved through changes to the nanoparticle-covered photoelectrode, common to many DSSCs and ssDSSCs.

The researchers found that they could capture more electrons from the dyes by boosting the surface area of nanotubes with the pine tree-like nanotubes, than when they used straight nanotubes. The pine tree-like nanotubes, around 19 micrometres long could double the efficiency of the ssDSSC from 4% to 8% compared to regular TiO<sub>2</sub> coatings.

DSSCs and ssDSSCs have a number of advantages, other than cost, over traditional silicon solar cells. They perform better in low light, meaning they can extract energy from the sun during the mornings and evenings, or even indoors. This leads to more consistent output. Additionally, they are relatively thin, flexible and can be produced to be semi-transparent. This means that windows could become a power source, supplementing conventional power usage with eco-friendly solar electricity.

It is an important finding that improved dyes and electrolyte substitutions can improve the efficiency of ssDSSCs to around 15%. It suggests that applying the pine tree-like nanostructured photoanodes, while unlikely to double efficiency in practice, could further boost it. This would make ssDSSCs even more cost-effective while improving their eco-friendliness compared to DSSCs.

Source: Roh, D. K., Chi, W. S., Jeon, H., et al. (2014). High Efficiency Solid-State Dye-Sensitized Solar Cells Assembled with Hierarchical Anatase Pine Tree-like TiO2 Nanotubes. Advanced Functional Materials 24(3), 379–386. DOI:10.1002/adfm.201301562

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## Nanotechnology cuts costs and improves efficiency of photovoltaic cells

Researchers have summarised the most effective ways that nanostructures can improve the efficiency and lower costs of photovoltaic (PV) solar cells in a recent analysis. Sculpting ultra-thin solar cell surfaces at the nano-scale has been found to effectively boost their efficiency.

"Silicon represents 10-20% of the cost of a solar cell, so a 100-fold reduction in silicon could significantly improve the cost-efficiency of such systems."

Making solar cells ultra-thin reduces their material costs, but often at the expense of their efficiency. These 'thin film PVs' (tfPVs) use silicon films that are between nanometres and tens of micrometres thick, whereas typical solar cells use silicon wafers around 200 micrometres thick. Silicon represents 10–20% of the cost of a solar cell, so a 100-fold reduction in silicon could significantly improve the cost-efficiency of such systems.

Most common PV systems are based on a high quality silicon crystal. When photons of light collide with electrons in the silicon, they are knocked loose, which generates an electric current. Commercial versions of such systems are currently around 22% efficient at converting sunlight into electricity.

However, tfPV systems are currently 7–13% less efficient than traditional systems. This is partly because, when PV cells become thinner, light interacts differently with their surface texture and collisions between photons and electrons are reduced (this is not an issue with thicker PVs).

The study reviews current attempts to improve 'light management' in tfPVs using nanostructures. It summarises some of the different ways that researchers are using nanostructures to boost the number of collisions between photons and electrons.

For instance, nanostructures can increase the amount of light entering a PV by reducing reflections from its surface. A polished silicon wafer reflects more than 30% of the light that it receives. Densely packed nanostructures can be used to create thin anti-reflective coatings, which work across a wide range of wavelengths and angles of light.

Varying the shape, height or width of nanostructures can alter a property called 'optical resonance'. Such structures can capture and guide light to the PV surface, or bounce light around inside the tfPV cell. This keeps light in the cell for longer, which increases the chances of colliding with an electron.

The review also explores how nanostructures can be used to 'trap light' depending on their location in a tfPV. Nanostructures on the front of the PV can guide light into the absorbing layer, or reduce reflection. Nanostructures on the back of a PV could be used as high-performance reflectors, bouncing otherwise lost light back into the PV. The light-absorbing layer itself can benefit from a sculpted nanostructure, which could change its ability to absorb light of different wavelengths, for instance. This would allow the cells to extract energy from a wider range of light wavelengths than traditional PV cells.

TfPVs also offer additional advantages, besides lower material costs. For example, they are flexible because they only use very thin silicon, whereas current non-thin-film PVs are rigid. This could make tfPVs easier to install; like paper, they could be spooled off a roll.

Source: Brongersma, M. L., Cui, Y., & Fan, S. (2014). Light management for photovoltaics using high-index nanostructures. *Nature Materials* 13(5), 451–60. DOI:10.1038/nmat3921

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1 <a href="http://ec.europa.eu/research/energy/eu/index\_en.cfm?pg=research-photovoltaics-support">http://ec.europa.eu/research/energy/eu/index\_en.cfm?pg=research-photovoltaics-support</a>

## New energy-efficient manufacture of perovskite solar cells that rivals silicon solar cells

'Perovskite solar cells' (PSCs) are less costly than conventional silicon solar cells, but one of their key components is energy-intensive to manufacture as high temperatures are needed. Now researchers have identified new alternative materials for this component which cut energy demands as they can be produced at low temperatures.

"One of the main advantages of perovskite solar cells is the lower energy and financial costs of their production compared with conventional solar cells." PSCs replace the energy intensive, expensive, conventional silicon solar cells with cheaper materials based on organic lead halide perovskites. PSCs share the advantages and applications of other thin film solar cell technologies, such as dye-sensitised solar cells, over conventional silicon cells. For instance, as they are flexible, they can be installed from rolls, or they can be used as semi-transparent coatings on buildings and windows to generate electricity.

One of the main advantages of PSCs is the lower energy and financial costs of their production compared with conventional solar cells. The perovskite and many of the other components can be produced using lowtemperature methods.

In a PSC, light is absorbed by the perovskite pigment, which generates electrons and their positive counterparts, holes. To prevent electrons and holes recombining, the perovskite is sandwiched between two layers: a nanoparticle layer, which quickly conducts electrons away, but not holes, and a layer which allows holes, but not electrons, to pass. This sets up an electric field that forces the electrons to flow in a single direction, through an electrical circuit, eventually recombining with holes at the positive cathode of the cell.

However, the nanoparticle electron-selective layer is typically made of titanium dioxide and has needed a high temperature step (of around 500°C) as part of their manufacture. Researchers have now developed a low temperature alternative to this.

The researchers identified two 'organic compounds' that could replace current hole and electron selective materials. PCBM ((6,6)-phenyl C61-butyric acid methyl ester) was used as an electron-selective material to replace titanium dioxide, while PolyTPD was used as a hole-selective layer.

These were added to the solar cell using a process called 'meniscus coating', at room temperature, which allows layers of just 10 nanometres (nm) thick of each material to be made. The electrical properties and efficiency of the cells were then measured.

The researchers produced a PSC cell 475 nm thick, which is less than a half of a millionth of a metre. Their measurements suggested that only a few electrons and holes were recombining, which indicated that the new hole and electron blocking layers were effective. The efficiency of the solar cell converting light energy into electrical energy was measured at over 13%.

The most commonly used silicon solar cells, first developed in the 1940s, took around 50 years to reach their current 25% efficiency, but such high efficiency cells are expensive to manufacture. Today, due to economies of manufacturing, a typical solar cell installation is around 15% efficient.

In comparison with silicon solar cells, PSCs have grown in efficiency from 4% in 2009 to in excess of 17.9% in just five years. These remarkable increases in efficiency in such a short time make them an increasingly viable commercial prospect.

This research has further improved the potential costeffectiveness of PSCs by showing that lower energy production methods can be used in their manufacture. Additionally, the methods used in this research could be transferred to existing production techniques, such as reel-to-reel production, when a reel of the base material is unrolled and coated with a functional material, such as PCMB or PolyTPD, before being rolled up on a second reel in a single step, bringing commercial realisation of low-power technologies a little closer.

**Source:** Malinkiewicz, O., Yella, A., Lee, Y. H., *et al.* (2013). Perovskite solar cells employing organic charge-transport layers. *Nature Photonics* 8(2), 128–132. DOI:10.1038/nphoton.2013.341

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## Graphene's health effects summarised in new guide

A guide has been published on the known and potential health and safety effects of human exposure to graphene. It is designed to help inform those working with graphene and graphene-based nanomaterials and could be especially useful as a growing number of industries begin to experiment with and use these materials.

"The extent and mechanism by which cells interact and uptake graphene is considered critically important, since once inside a living cell the material could interact with or disrupt cellular processes and cause damage."

Almost all carbon nanomaterials are based on variations of graphene, a one atom thick honeycomb-like arrangement of carbon atoms. Graphene can be stacked, wrapped or rolled, to form graphite, football-like 'buckyballs' or carbon nanotubes (CNTs), respectively.

These materials have unique properties which may make them useful in industrial processes and consumer technologies, such as flexible display screens, carbon-based microchips and medical applications. Additionally, graphene is also being investigated for environmental applications, such as cleaning up hazardous materials and pollutants in contaminated waters. These properties can be further modified by attaching different chemical groups to the graphene surface.

While the potential use and safety of CNTs has been investigated for some time, much less is known about graphene — partly because of early difficulties in increasing its production, and because it is in an early stage of development. Now, with increasing research, the adoption of different types of graphene materials in different industries will increase the likelihood of human exposure to this material.

In 2013, researchers published an overview on possible safety concerns for graphene. The paper summarises the physical and chemical characteristics of graphene and CNTs and the evidence of how they may affect health. Existing knowledge and experience from the safety studies using CNTs was used to speculate on the safety of graphene.

The possible effects of graphene on human health were examined at the cellular, tissue and whole body levels in comparison to CNTs. The extent and mechanism by which cells interact and uptake graphene is considered critically important, since once inside a living cell the material could interact with or disrupt cellular processes and cause damage. Exposing the body to carbon nanomaterials could result in either their accumulation in the tissues or elimination through excretion.

Accumulated nanomaterials could pose a risk to organ function, and therefore to health.

At the level of the whole body, the authors indicate that there are two main safety factors to consider regarding exposure to CNTs and graphene. The first is their ability to generate a response by the body's immune system; the second is their ability to cause inflammation and cancer.

The authors used the existing evidence to develop a set of three generalised guidelines, which if implemented, could reduce the overall health risk to a minimum for workers involved in developing graphene, and graphene-based technologies.

These can be summarised as follows:

- 1. Use individual graphene sheets that are small enough for immune cells to engulf and remove from the site where they were found in the body.
- Use stable, individual graphene sheets which are easily dispersed in water to minimise their clumping and aggregation in the body.
- 3. Use graphene, or chemically modified graphene material, that can be easily cleared from or biodegraded in the body, to prevent damage from chronic accumulation into tissues.

This study provides useful information to help guide the work of graphene research groups and could help raise awareness of graphene's potential health and safety effects.

The potential promise of graphene is such that in 2013 the European Commission announced<sup>1</sup> that a graphene initiative was a winner in the multi-billion euro 'Future and Emerging Technologies' competition. Furthermore, over 100 research groups will receive funding for up to seven years for graphene-related projects as part of the Horizon 2020 programme.

Source: Bussy, C., Ali-Boucetta, H., & Kostarelos, K. (2013). Safety considerations for graphene: lessons learnt from carbon nanotubes. *Accounts* of *Chemical Research* 46(3), 692–701. DOI:10.1021/ ar300199e

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Read more about: Environment and health,

Chemicals,

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1. http://europa.eu/rapid/press-release\_IP-13-54\_en.htm

## Ultra-fine particles emitted by commercial desktop 3D printers

Desktop three-dimensional (3D) printers, available for use in offices and homes, can release between 20 and 200 billion ultra-fine particles (UFPs) per minute, finds new research. UFPs may pose a risk to health, and the study's authors recommend caution when operating 3D printers inside unventilated or unfiltered indoor environments.

"While the actual risk to health remains unclear and further research is needed, on the balance of the evidence, the researchers conclude that because of the large emission of ultrafine particles (UFPs) by 3D printing instruments, users should be cautious when operating them inside unventilated or unfiltered indoor environments."

The advent of low-cost commercial desktop 3D printers, used to turn computer based designs into physical objects, has seen 3D printing move out of research laboratories and industrial applications into the home and office. Most desktop 3D printers work by feeding a solid plastic polymer into a computer-driven heated nozzle through a process called 'fused deposition modeling' (FDM), which lays down material in layers.

The nozzle deposits a thin layer of molten polymer on a surface. As the plastic hardens, the next layer is added, slowly building a solid 3D object. Two plastic polymers are commonly used for this: acrylonitrile butadiene styrene (ABS) or polylactic acid (PLA). ABS requires higher nozzle temperatures (220 °C) than the biodegradable form of PLA (180 °C).

Similar industrial processes have been shown to emit relatively high levels of gases, volatile organic compounds and fine particles. Nano-sized UFPs — particles smaller than 100 nanometres (nm) — may be of particular importance to health.

Most desktop 3D printers lack filter or ventilation accessories and are likely to be used in enclosed spaces, such as offices, with little additional ventilation. To date there has been no research on the UFP emissions of these printers.

The new study measured UFP emissions from FDM desktop 3D printers in a commercial office space. The researchers took UFP measurements in an enclosed office with two printers using PLA and two identical printers using ABS, each operating for about 20 minutes. They analysed the data and compared it to other domestic sources of UFPs.

The estimated emission rates for both PLA and ABS were high, with PLA emitting around 20 billion particles per minute, and 200 billion particles per minute for ABS.

Compared to other domestic sources of UFPs, the 3D printing using PLA had a similar UFP emission to cooking using an electric frying pan. Using ABS resulted

in UFP emissions similar to those from grilling food on a gas or electric stove at low power.

UFPs are able to deposit in the lungs and airways of the head, where they can travel through the olfactory nerve to the brain, and studies have shown that UFPs may be an important part of the toxicity emitted from melting plastics. A number of studies have also shown that high UFP concentrations, such as from traffic pollution, are associated with adverse health effects, such as asthma, stroke and even decreased lifespan due to heart and lung diseases.

The authors highlight that the chemical identity of the UFP itself is likely to be important with regards to safety. For example, while ABS has been shown to have toxic effects, PLA is considered safer, and PLA nanoparticles are widely used in drug delivery.

They note a couple of limitations in their methodology. Firstly, they did not determine the chemical composition of the UFPs. This is important because small amounts of ABS and PLA can be broken down into other types of chemicals with different or unknown health risks when heated. Secondly, the effects of particles sticking together or growing by condensation were not accounted for, which could affect measurements.

While the actual risk to health remains unclear and further research is needed, on the balance of the evidence, the researchers conclude that because of the large emission of UFPs by 3D printing instruments, users should be cautious when operating them inside unventilated or unfiltered indoor environments. Under the General Product Safety Directive¹ manufacturers have a responsibility to provide consumers with information to assess a product's threat — especially when not obvious — and to take necessary measures to avoid such threats. In the case of 3D printers this could be by providing enclosed and filtered printers or ventilation equipment.

Source: Stephens, B., Azimi, P., El Orch, Z., et al (2013). Ultrafine particle emissions from desktop 3D printers. Atmospheric Environment 79, 334–339. DOI:10.1016/j. atmosenv.2013.06.050

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Environment and health,

Sustainable production and consumption,

Resource efficiency

1 http://europa.eu/legislation\_summaries/consumers/consumer\_information/l21253\_en.htm

## New 3D printing technique for environmental nanodevices

A nanoscale 3D printing technique could be useful for nanomanufacturing processes with environmental applications. The authors of a new study have found a way to control their printing process by incorporating a simple pattern into the printing surface. They say their technique could reduce costs for nanoscale printing.

"According to the researchers, their technique has the potential to reduce the cost of nanomanufacturing processes because it only requires a relatively basic set-up compared with techniques previously used to build nanowalls."

Nanoscale manufacturing methods are already being used in environmental applications, such as water purification, and nanoengineers have tested approaches to cleaning up oil spills based on nanomachines¹. 3D printing may be one way to speed up the manufacture of nanoscale objects and devices needed for these applications. The technology is becoming increasingly affordable and produces minimal waste, but it is more difficult when the objects being printed are very small.

One possible method is called 'dip pen nanolithography', which uses an atomic force microscope (AFM) tip coated in 'ink' molecules. An alternative is 'electrojetting', in which nanofibres are squirted from a liquid through a nozzle under an electric field. However, with both techniques the shape and arrangement of what is produced cannot be easily controlled.

The authors propose a new method for nanoscale 3D printing that uses nanofibres made by electrospinning. In electrospinning, a voltage is applied to the substance — in solution — being spun, giving it a charge. The electrified substance is spun onto a screen or plate with the opposite charge, where the liquid solvent evaporates immediately, leaving just the fibre.

Electrospun nanofibres have been considered for environmental applications, such as membranes to filter pollutants or toxins from water, as well as for biomedical applications, such as building artificial tissue scaffolds<sup>2</sup>.

Although electrospinning is an old technique that is already familiar to nanotechnologists, it has not been possible to control the fibres that are produced in this way. In their study, the researchers used a syringe as a spinner and spun their charged printing solution of poly(ethylene oxide) (PEO) onto a very thin strip of oppositely charged platinum on a glass printing surface.

The platinum functioned as a pattern and allowed them to control how the fibres are deposited. The jet was attracted to the platinum, and formed a 180-nanometre wide (less than a thousandth of a millimetre) thread along its length.

The researchers were able to move the spinner back and forth, building up a 220-micrometre long 'wall' of thread, stacked 25 fibres deep, in under two tenths of a second. As they added each new layer of fibre, it took on the same charge as the platinum, helping to attract the next layer from the oppositely charged oncoming nanofibre. They went on to stack up 300 fibres and found that longer walls were more stable.

According to the researchers, their technique has the potential to reduce the cost of nanomanufacturing processes because it only requires a relatively basic set-up compared with techniques previously used to build nanowalls. In addition, more complex metal patterns could be created on printing surfaces, making it possible to build more complicated structures using this technique.

Source: Lee, M., & Kim, H. (2014). Toward Nanoscale Three-Dimensional Printing: Nanowalls Built of Electrospun Nanofibers. *Langmuir* 30, 1210-1214. DOI: 10.1021/la404704z

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- 1 Guix et al. (2012) Superhydrophobic Alkanethiol-Coated Microsubmarines for Effective Removal of Oil. ACS Nano 6 (5) 4445-4451
- 2 Ramakrishna et al (2006) Electrospun nanofibers: solving global issues. Materials Today 9(3):40-50.

# The potential of new building block-like nanomaterials: van der Waals heterostructures

A new review examines the potential uses and scientific, technical and manufacturing problems facing 'van der Waals heterostructures' — an emerging science which uses building block-like nanomaterials. Van der Waals heterostructures are nanomaterials built by layering different materials, each one atom thick, on top of each other, to create materials with unique properties and uses.

"Scientific and industrial interest in van der Waals heterostructures continues to grow, mirroring that of graphene." Graphene, a honeycomb-like two-dimensional (2D) crystal, is just one atom thick. It has chemical, electrical and mechanical properties unlike its three-dimensional (3D) graphite form. There has been a boom in research to exploit these properties for various applications, which range from carbon-based computer chips and solar cells, to tissue engineering and drug delivery.

Researchers are now identifying and probing the properties of other 2D crystals and the ways they may be combined. The combined layers of different 2D crystals are called 'van der Waals heterostructures', named after the weak 'van der Waals' chemical bonds which hold the different layers together.

By swapping or changing the number and order of the different 2D-crystal layers, it is hoped that new materials, with properties not found in their component parts, could be made. As different layers of materials are stacked on one another their physical and quantum properties can, in effect, combine, interfere or cancel one another, to greater or lesser degrees depending on the materials, leading to the new properties. The authors of this study review this fledgling research area by discussing the potential of van der Waals heterostructures. Among the possible applications they consider are room temperature superconductors, which would allow new highly efficient electric motors and generators, and potentially power transmission without any loss of energy.

However, there are problems that must be overcome before van Der Waals heterostructures can be used in applications. For example, while there are many materials from which 2D crystals could be made, few are stable under ambient conditions. The surfaces of larger 3D crystals can undergo chemical reactions which

protect the rest of the crystal; however, for a single atom thick 2D layer of the same material, these reactions would destroy them. This limits the number of useful materials which could be used, or presents complex manufacturing hurdles to overcome.

So far, around 12 suitable 2D crystals, which are stable under ambient conditions, have been identified. The researchers developed three broad principles to help identify more. Firstly, 3D crystals with high melting temperatures are most likely to have stable 2D crystals. Secondly, parent crystals must be relatively chemically inert. Finally, insulating and semiconducting materials are likely to be more stable than metallic ones.

The researchers say that despite their complicated fabrication, van der Waals heterostructures can now be produced for laboratory purposes within a few days. In the future, the most likely manufacturing technique for use in industry will probably involve growing separate sheets of 2D crystals and then layering, rather than growing, one on top of another.

Scientific and industrial interest in van der Waals heterostructures continues to grow, mirroring that of graphene. As the number of materials and techniques expands, the authors suggest this could cause a snowball effect, with a potentially endless choice of possible van der Waals structures leading to as yet unimagined applications, benefiting a wide range of areas, from renewable energy to medicine. However, as with all new technologies, they may fall short of being able to realise current aspirations, such as super-efficient electric motors and generators.

**Source:** Geim, a K., & Grigorieva, I. V. (2013). Van der Waals heterostructures. *Nature* 499(7459), 419–25. DOI:10.1038/nature12385

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# Potential health risks from different forms of nanosized cellulose crystals

A new study has found evidence for lung toxicity of different forms of 'cellulose nanocrystals' (CNCs) in mice. The study suggests that physical characteristics, such as length, of the CNC relates to the type of effect it has on the lung. These nanosized crystals, made from plant-derived materials, are increasingly being used in novel applications, such as cleaning up oil spills in water and flexible electronic displays, and consumer products, which raises concerns about their potential health impacts.

"Although results in animals, such as mice, do not always translate to identical effects in humans, this study suggests that the use of CNCs in industry could potentially cause lung damage in humans, and that precautions, such as respiratory protective equipment, may be prudent for those occupationally exposed to CNCs."

Source: Yanamala, N., Farcas, M., Hatfield, M.K. *et al.* (2014). In vivo Evaluation of the Pulmonary Toxicity of Cellulose Nanocrystals: A Renewable and Sustainable Nanomaterial of the Future. *ACS*Sustainable Chem.

Eng. 2(7): 1691–1698.

DOI: 10.1021/sc500153k

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Cellulose is the substance that makes the cells of trees and other plants rigid. It is the most abundant organic compound on Earth and can easily be extracted from wood/plant pulp. When cellulose is treated with an acid it can be broken down into CNCs, which are nanosized rod-like crystals around 100 to 1000 nanometres (nm) in length.

CNCs have better electrical, optical, and mechanical properties than their original non-nanosized form. These properties and some of their eco-friendly aspects — such as their sustainable method of production and biodegradability — have made CNCs attractive to industry. Applications range from electronics to cosmetics and pharmaceutical products.

However, the rod-like shape of CNCs suggests there may be a risk of toxicity, similar to other nanosized fibres. It is well known that inhalation of similar particles can cause lung inflammation, and recent studies have suggested that materials containing CNCs are associated with lung toxicity.

This new research examined the effects of two similar forms of CNCs on the lungs of mice. The first form was a dry powder CNC (CNCP), and the second was a gel-based CNC suspension (CNCS). Asbestos was also used as a control for lung damage. Mice were exposed to asbestos and both CNC forms at different concentrations and the effect on their lungs examined after 24 hours. The researchers inspected them for signs of tissue damage and inflammation, as well as changes in the numbers and types of immune cells. The physical dimensions of the two CNC formats were also examined.

The CNCs in the powder form were around three times longer (300 nm) than those of the gel form (88 nm). Inflammation biomarkers increased with greater concentrations of both CNCS and CNCP after 24 hours. There were some differences between CNCS and CNCP, both in type of damage to the mice and degree of increase in these biomarkers. Biomarker profiles, which differed from those of asbestos, were typically higher for both CNC types. The number of immune cells increased in both treatments, but was slightly higher in mice treated with CNCP. Both CNC types elicited higher cellular responses than the asbestos control.

Differences in the levels and types of biomarkers and immune cells between the two CNC preparations suggest that the physical characteristics, such as length, of the CNCs could result in different types of immune response. For example, longer-term or repeated exposure to one form could result in a more long-term allergic response, while another form may result in temporary, local, inflammatory tissue damage.

More research is needed to analyse the risks that CNCs may present to human health. They are increasingly used in industrial processes, which means that there is a growing risk of exposure, including through inhalation, to humans, and this study suggests that precautions, such as respiratory protective equipment, may be prudent for those occupationally exposed to CNCs. Results in animals, such as mice, do not always translate to identical effects in humans, and there are still other very significant questions on the interpretation of such data, as highlighted in the introduction: resolving these questions will also determine what the appropriate level of protection could be and relate it to types of protection required for different dusts during manufacturing.

## Further reading

You may also be interested in reading the following publications from Science for Environment Policy.

## News Alert articles Silver nanoparticles could pose risk to aquatic ecosystems (November, 2014)

Silver nanoparticles are toxic to common bacteria at concentrations found in many aquatic environments across the globe, new research has found. Bacteria often form a key part of ecosystems and these impacts may be felt by the entire system, the researchers warn.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/risk\_to\_aquatic\_ecosystems\_from\_silver\_nanoparticles\_394na1\_en.pdf

## Carbon nanotubes could be released by plastic as it degrades (May, 2014)

Carbon nanotubes (CNT) could be released into the environment as the plastic they are embedded in degrades, a new study suggests. The research found that general wear combined with exposure to UV light and moderate humidity would expose CNTs, posing a potential threat to human health.

 $\frac{http://ec.europa.eu/environment/integration/research/newsalert/}{pdf/372na3\_en.pdf}$ 

## Thematic issues

## Nanomaterials (April, 2009) Issue 12

Nanoparticles may be small, but they are at the centre of a huge debate. Nanotechnology has great potential for industry and society, but we need more awareness of the potential impact of manufactured or engineered nanoparticles on human health and the environment to ensure that its products are safe. Although nanotechnology is new, it is expanding quickly and research is needed to understand its associated risks. This Thematic Issue outlines some of this research and indicates areas for future investigation.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/12si\_en.pdf

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## Science for Environment Policy In-depth Reports

In-depth Reports are a series of publications from Science for Environment Policy, which take a comprehensive look at the latest science for key policy topics.

## **Environmental Citizen Science – December 2013**

Citizen science's value for science, society, education and environmental policymaking are considered in this In-depth Report, which explores academic research into citizen science practice and theory and outlines a number of case study projects. Overall, the report finds its potential value is high, but that this potential, particularly for citizens and policymakers, remains largely untapped.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/IR9\_en.pdf

## Sustainable Phosphorus Use – October 2013

We are facing a critical phosphorus challenge, as developments in industry, agriculture, waste handling and lifestyle have massively reduced the capacity for this important element to be cycled effectively by society and the environment via natural geological processes. The major source of phosphorus used in fertiliser is phosphate rock, which we mine in vast quantities, more than can be replaced by the slow geological cycle. This In-depth Report examines scientific knowledge on the phosphorus challenge and recent research into the sustainable use of the element.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/IR7\_en.pdf

## Nitrogen Pollution and the European Environment – September 2013

Nitrogen pollution's wide-ranging impacts include contributions to global warming, acid rain and eutrophication. This In-depth Report summarises scientific studies and research results on nitrogen pollution in the European environment.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/IR6\_en.pdf

## Soil Contamination – September 2013

After more than 200 years of industrialisation, soil pollution has become a widepread problem in Europe. This In-depth Report draws on current research and case studies from a number of scientific disciplines that investigate the interaction between contaminated soils and human health.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/IR5\_en.pdf

## Plastic Waste: Ecological and Human Health Impacts - November 2011

This In-depth Report summarises and collates current research on the ecological and human health impacts of plastic waste in the environment. Using the Drivers Pressures State Impact Response (DPSIR) framework, it highlights major issues and concerns, as well as outlining questions around existing responses and possible strategies for the future.

http://ec.europa.eu/environment/integration/research/newsalert/pdf/IR1 en.pdf

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