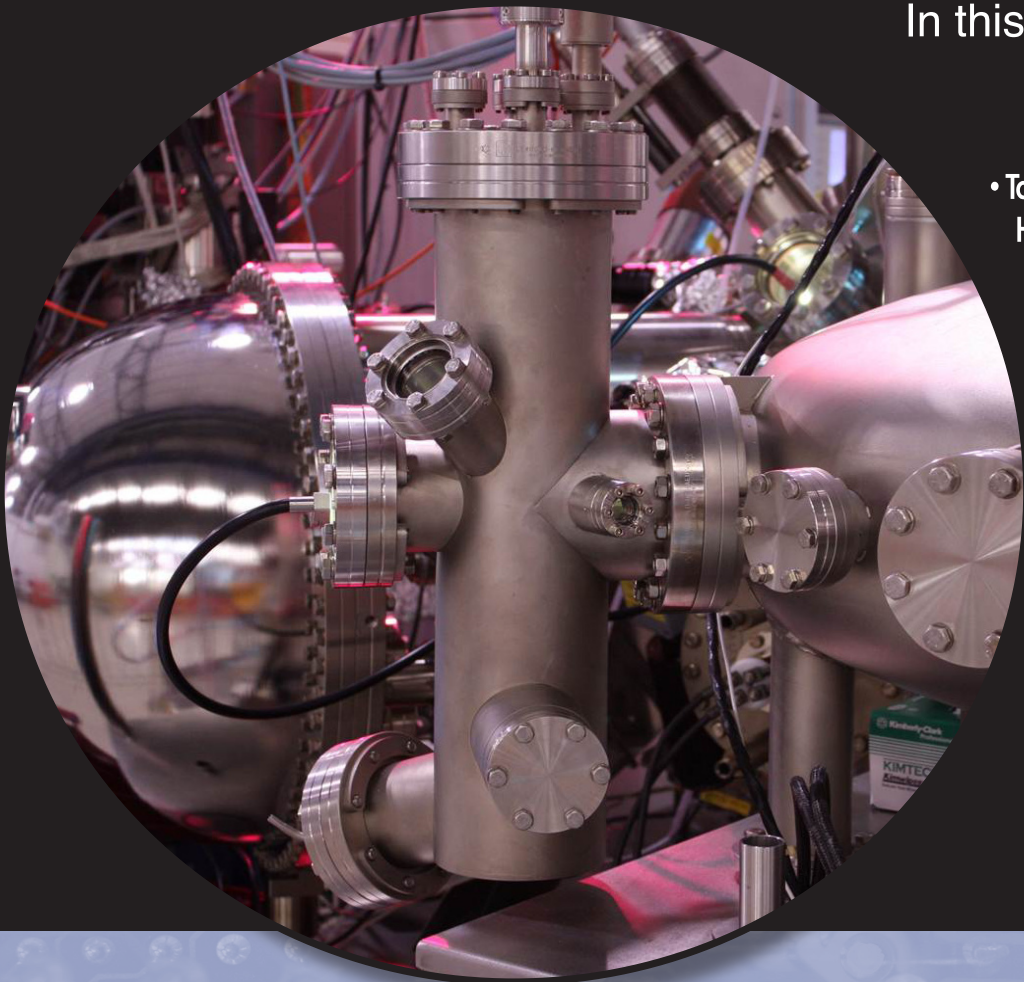
NANO Q

BIG SCIENCE MEETS THE VERY SMALL



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Issue 4

Australian Nanotechnology Network

Australian Government
Department of Innovation Industry, Science and Research

Welcome

by Professor Chennupati Jagadish

Convenor of Australian Nanotechnology Network

Welcome to the fourth issue of Nano Quest (NanoQ). The purpose of NanoQ (two issues per year) is to highlight recent developments in the field in Australia and also to provide information of interest to policy makers and the public. There has been a significant amount of public interest in nanotechnology with reports in the media creating hype as well as scare. Enhancing public awareness of nanotechnology is important for the acceptance of the technology by the wider community while addressing issues of public concern in terms of health, safety and environment.

The Australian Nanotechnology Network (formerly ARC Nanotechnology Network) is continuing its operations with support from Australian Government Department of Innovation, Industry, Science and Research. Network name is changed to reflect this change of funding source and also to encourage participation of industry in the Australian Nanotechnology Network (ANN) activities in addition to participation of the research community. ANN's flagship conference, International Conference on Nanoscience and Nanotechnology (ICONN), will address various issues including manufacturing, occupational health and safety, standards, regulation, ethics, social impact, environmental effects etc. ICONN 2012 will be held in Perth during Feb 5-9, 2012.

This issue of NanoQ features how the nanotechnology is used in the development of bio- fuel cells which convert directly chemical energy into electrical energy. Renewable energy sources are becoming increasingly important and an article is featured on low cost wet chemistry methods to obtain nanocrystal based solar cells. Nanoscale biological and chemical sensors are being developed for a broad range of sectors and an article on this subject is featured in this issue. Another article features how nuclear reactors could be used to study nanoscale materials. Finally, an article on an innovative book project showcasing Nanotechnology in Australia (published by Pan Stanford) with all authors being PhD students and early career researchers is featured developing valuable writing skills of our next generation of nanotechnology researchers. Book project was carried out under the mentorship of Deb Kane (MqU), Adam Micolich (UNSW) and James Rabeau (MqU).

If you would like to submit an article for consideration for publication in NanoQ, this needs to be written at a level which is easily accessible to the wider readership with no background in nanotechnology. Please submit these articles to Ms. Liz Micallef, Manager, Australian Nanotechnology Network. Also, if you are a reader interested in learning more about a particular area of nanotechnology and would like to see an article published in NanoQ, please contact Liz. We will do our best to feature articles of public interest. If you would like to receive a personal copy of NanoQ or would like to provide feedback on NanoQ, please contact Liz.

Enjoy the fourth issue of NanoQ

NANO NEWS

July 2012

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Australian Nanotechnology Network

Australian Government
Department of Innovation
Industry, Science and Research

The Australian National Fabrication Facility

Tackling National Challenges in Health

by Hayley Rafati

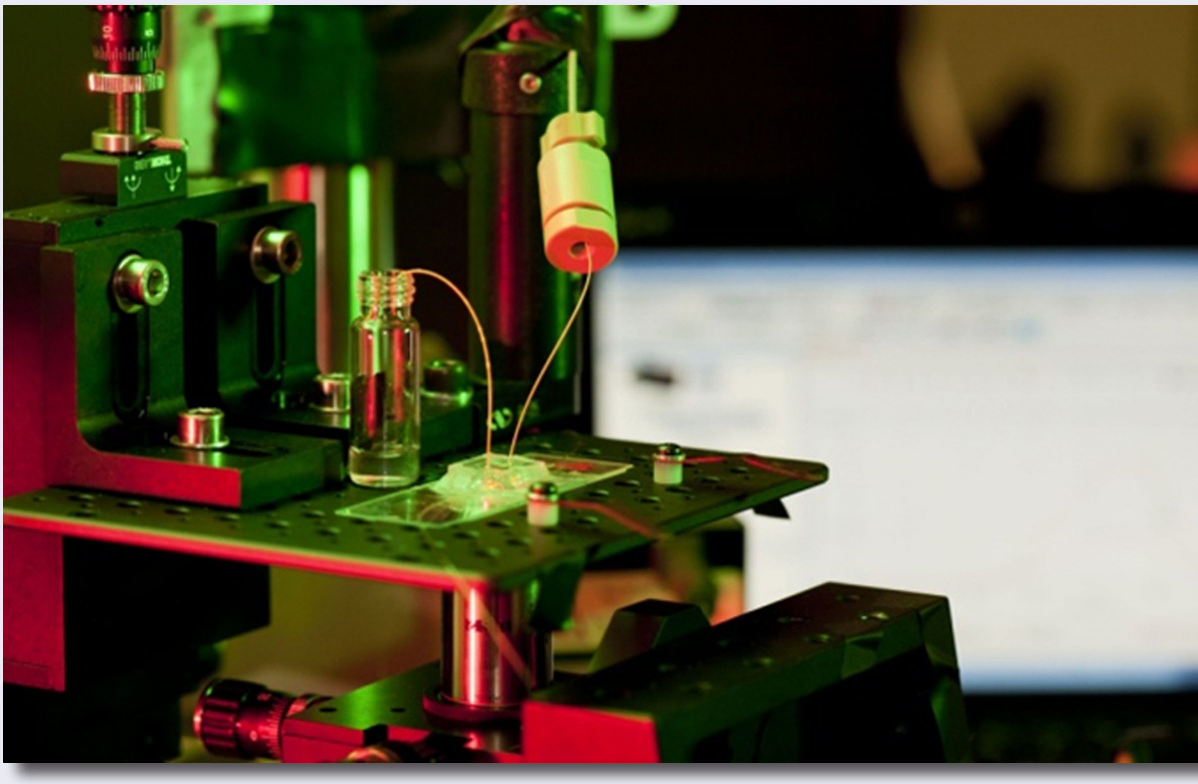
The Australian National Fabrication Facility (ANFF) is a national network that supports world-class academic and industrial research tackling many of the major challenges facing society today. Challenge in the fields of clean energy, healthy aging and national security are examples of national research priorities which ANFF scientists are delivering regular world leading advances.

Fabrication of advanced materials and devices at the micro and nano scale underpin many of the advances that have been made within core areas of health research. Here we examine the application of advanced fabrication techniques in the health arena, specifically, new methods for drug delivery, diagnosis of disease, and ultimately, prevention.

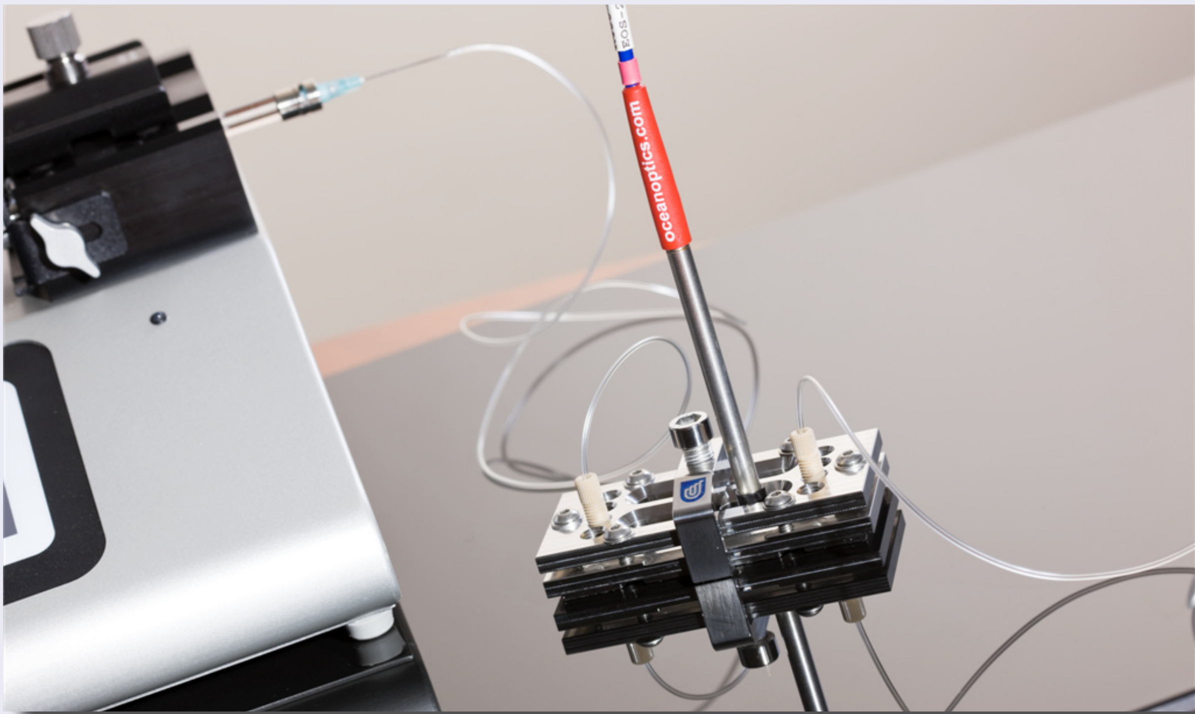
The following case studies have been supported by the Australian National Fabrication Facility; a national network of 8 nodes distributed across 20 institutions and the CSIRO, all of which provide open access to state-of-the-art fabrication capabilities.

Diagnosis of influenza

During the H1N1 pandemic of 2009, Australia reported over 36,900 confirmed cases of Human Swine Influenza, 186 of which resulted in death. Conservative estimates from the Department of Health and Aging report that, in the absence of pandemic conditions, Influenza affects over 25,000 Australians every year, a figure that has reached a staggering three to five million people worldwide.



Testing of the VESPR biosensor



Experimenting with Dr. Priest's microfluidic biosensor

With this in mind, the detection and treatment of communicable diseases such as Influenza has become a matter of national priority, and one that is echoed through the ANFF network.

Keeping in line with the Australian National Research Priority of promoting and maintaining good health, sensing and identifying deadly pathogens have become a focal point for the work conducted by the ANFF Optofab Node's Professor Tanya Monro and Dr. Alexandre Francois. Using photonics, the Adelaide-based team has developed a bio-sensing device that can detect pathogens such as viruses, bacteria or other organic biomarkers within a small sample.

The Versatile Enhanced Surface Plasmon Resonance or "VESPR" biosensor device is roughly the size of a credit card, easily fitting into one's pocket, lightweight and robust. The VESPR device comprises an array of silver coated optical fibres, on which highly specific antibodies are bound to silver nanoparticles.

Prior to being exposed to any pathogen, the combined silver particle-antibody structure reflects light that is characteristically unique in frequency and colour. Upon introducing the pathogen (such as the influenza virus) into the biosensing device, the emitted light is redshifted providing an easily detected signal through the optic fibre.

Preliminary trials, using an inactive flu virus, have revealed a positive result that can be detected by the sensor within 5 minutes of exposure. According to Prof. Monro's team, the rapid, real-time results obtained by the VESPR device represents a significant increase in efficiency compared to the results obtained by conventional methods of pathogen detection, which often require stringent temperature dependant incubation and may take hours, or even days to process.

Not only is the VESPR device incredibly compact, it is relatively inexpensive to manufacture, requires little or no training to use, and can potentially process samples in parallel, advantages that make it a crucial tool for personal or broad spectrum healthcare applications.

Real-time analysis of blood for infectious diseases

Less than 20 km away at the Ian Wark Research Institute, Dr. Craig Priest is helping the Monro team tackle a similar problem; detecting the presence of harmful pathogens using a highly sensitive microfluidic device. Using high-end lithography techniques funded by the ANFF network, the Wark team have managed to fabricate a tiny biosensor capable of mixing fluids, controlling reactions, analysing and separating material on a device no larger than a 50 cent piece.

The microfluidic biosensor uses microscale channels, much smaller than the width of a human hair, to sort and filter tiny liquid streams containing blood constituents such as DNA or proteins.

Similar to the VESPR biosensor, the microfluidic device can be used to detect viral DNA within biological samples, potentially giving physicians access to real-time analysis of blood constituents enabling rapid diagnosis. This is undoubtedly a huge step forward in the identification and containment of infectious diseases.

Devices such as VESPR or Dr Priest's microfluidic device can help to reduce the spread of communicable diseases and prevent the prescription of incorrect medications; however, these technologies do not assist in the treatment of infected individuals. ANFF is also investing in the next phase of health research; addressing the delivery and management of appropriate medications post-diagnosis.

In-vivo transport of therapeutics

Dr. Christina Cortez-Jugo, Technology Fellow at the Melbourne Centre for Nanofabrication (the Victorian Node of the ANFF network) is leading the charge, giving disease a taste of its own medicine. The ability to deliver large therapeutic biomolecules into cells without affecting healthy cells remains a largely unsolved technological challenge. According to Dr. Cortez-Jugo, the team is addressing this problem by developing sophisticated, nanoscale therapeutic carriers, with improved efficacy and specificity. The project is investigating the use of pore forming proteins, specifically Listeriolysin O (LLO); a small enzyme excreted by bacterium Listeria monocytogenes, as an instrument for therapeutic transport in vivo.

In nature, these pore-forming proteins are released into the host's blood stream by the invading bacterium, binding to and polymerising on healthy cell membranes. Although the precise mechanism by which membrane channels are formed remains elusive, cellular exposure to the LLO protein allows the bacterium to temporarily puncture and invade the cells.

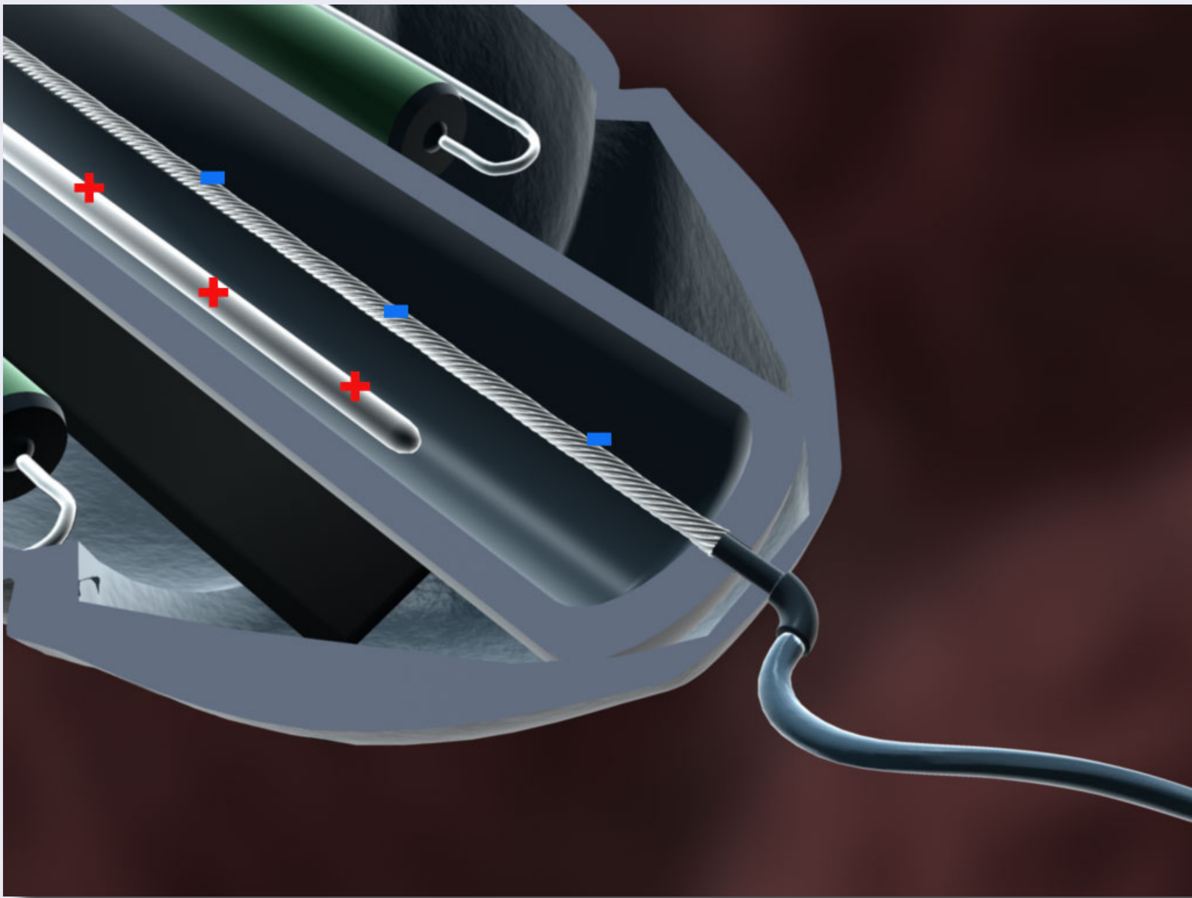
Did you know...

You can incorporate the cost of ANFF facility usage and services into your next NMRH and ARC grant?

A document is now available online to assist applicants and provide advice on how to incorporate the research costs that may be associated with ANFF usage. Using the online Research Management System, the how-to guide includes a sample proposal outlining how to complete each stage of the application, and additional contact details to facility managers.

To access the document, simply head to:

http://www.anff.org.au/arc-and-nhmrc-applicants.html or for project advice contact the relevant facility manager listed within the document.



Schematic of a device which could be propelled through a liquid using artificial twisting muscle

It is this concept that has propelled researchers to harness the natural power of pore-forming proteins as a potential carrier of beneficial molecules such as therapeutic drugs across the cell membrane. Using the PC2 laboratory and characterization techniques at the MCN, Dr. Cortez-Jugo and her team are conducting trials using LLO proteins to channel complex DNA-based molecules into red blood cells. Preliminary results using conjugated fluorescent markers show real-time movement of the LLO protein bypassing the membrane barrier and entering intracellular fluid with remarkable precision and specificity. Dr. Cortez-Jugo hopes that in the future, this technology could be used to deliver chemotherapy, gene therapies, vaccines or other treatments for communicable diseases.

Artificial twisting muscle

Across the country, scientists within the NSW based Materials node of ANFF at University of Wollongong are finding inspiration from the motility of bacteria, such as LLO-producing Listeria monocytogenes. Duplicating the mechanisms of natural bacterial motion, researchers are working towards developing their own artificial therapeutic carriers, giving rise to a new wave of drug delivery systems.

The Materials node team has developed tiny, twisting artificial muscle fibres comprised of carbon nanotube filaments. The motion of these artificial muscle fibres possess an uncanny resemblance to the helical propulsion observed in bacterial motility.

The team, headed by chief investigator Professor Geoff Spinks, fabricates highly flexible nanotube yarns that are twist-spun from forests of multiwalled carbon nanotubes. To test the effectiveness of the propulsion of these yarns, a single coiled helical length of the carbon nanotube yarn is placed within an electrolyte solution filled with electrically conductive ions. The other free end is affixed to a voltage supply. The fibres immersed within the solution absorb the ions, causing a subsequent swelling of the nanocarbon filaments. As the fibres aggregate and increase in volume, the unattached end rotates in a helical motion at the speed of nearly 600 rpm.

It is hoped that this tendrillar motion exhibited by these miniature artificial muscles may be harnessed to power and propel molecules and other beneficial substances through the blood stream. Akin to Dr. Cortez-Jugo's cargo-bearing proteins, these tiny nano-couriers may be used for the advanced and highly specific delivery of therapeutics; however, as the English proverb suggests, an ounce of prevention is worth a pound of cure.

Disease prevention with needle free vaccinations

Reducing the cost and improving the efficiency of vaccination programs is critical for the treatment of major diseases such as influenza. With this in mind, the ANFF-Queensland Node is supporting the fight against the prevention of communicable disease via its development and research into the "Nanopatch". The research effort, headed by Prof. Mark Kendall of the Institute of Bioengineering and Nanotechnology, intends to produce a viable alternative to the needle injections and eliminate the transport issues associated with liquid vaccines.

The nanopatch is an array of tiny needles, in the order of 50 to 100 μm in length (about the width of a human hair), pre-coated with vaccine. The patch is then pressed onto the skin, where it penetrates painlessly and delivers its payload to the body, evoking an immune response.

The innovative micro needle technology not only provides a painless medium for the therapeutic delivery of vaccines, it also uses significantly less vaccine that doesn't need to be refrigerated when it is distributed to the masses.

For projects like the Nanopatch and the other communicable disease projects conducted throughout the ANFF network, ANFF recognises that innovative advances in health research would not be possible without the support of its funding partners, dedicated instrument managers and expert staff within the ANFF nodes.

ANFF is dedicated to not only maintaining the health of all Australians through these, and other nation-wide collaborative projects, but committed to addressing all facets of the Australian Research Priorities.

Accessing ANFF

Full details of the quick and easy access process, including an initial contact form, are available from the ANFF website: **www.anff.org.au.**

Alternatively, contact one of our Node representatives via **info@anff.org.au.**

The Australian Microscopy & Microanalysis Research Facility

Infrastructure Enabling Outcomes

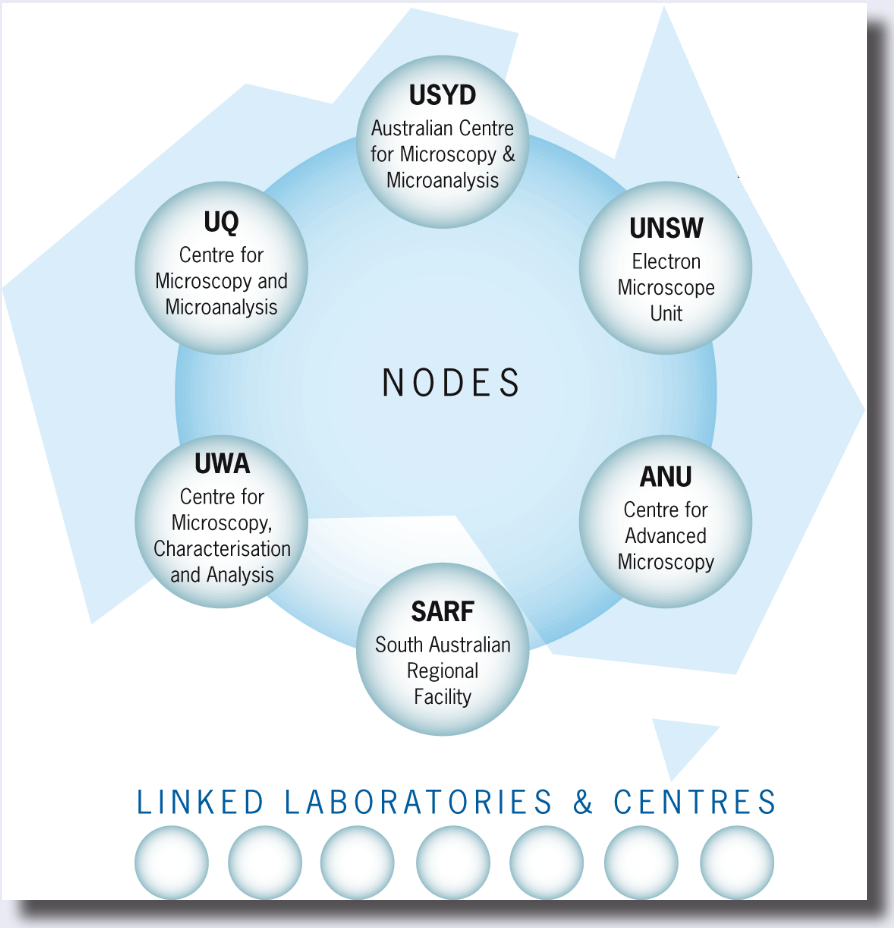
by Jenny Whiting

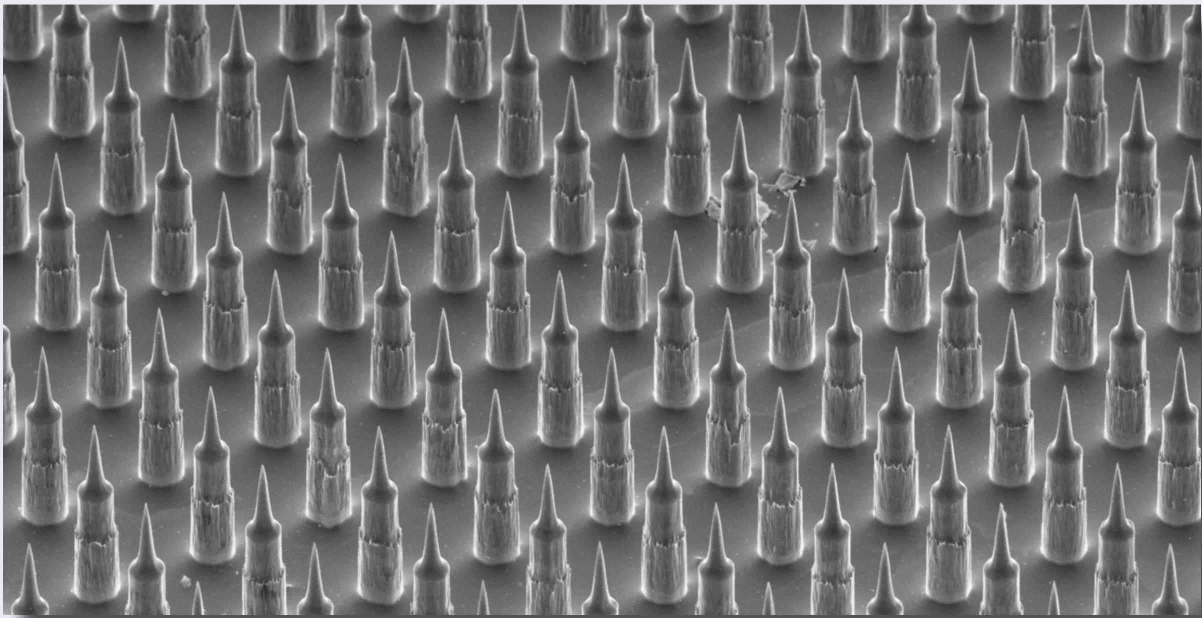
Australian Microscopy & Microanalysis Research Facility (AMMRF), Madsen Building F09, The University of Sydney, NSW, 2006, Australia.

Microscopy is a fundamental technology in research and the Australian Microscopy & Microanalysis Research Facility (AMMRF) provides all Australian researchers with access to a huge range of microscopy and microanalysis instruments, expertise and support in the area of nanostructural characterisation.

The AMMRF was established in 2007 under the Commonwealth Government's National Collaborative Research Infrastructure Strategy (NCRIS) and is a joint venture between Australian university-based microscopy and microanalysis centres.

With the ability to investigate everything from art history to medicine, and from engineering to agriculture the AMMRF offers optical, electron, X-ray and ion beam techniques and the high-end flagship





Nanopatch - SEM image of a Nanopatch. Created by Michael Crichton.

capabilities such as atom probes, secondary ion mass spectrometers and electron tomography and single particle analysis platforms. A few examples of techniques and realted outcomes are highlighted below.

Scanning electron microscopy (SEM) is a technique that reveals the topography of a sample or its surface structure according to differences in the atomic number of the elements at the sample surface. Additional detectors can also measure and map the precise elemental composition of the surface. It is very broadly applicable and available throughout the AMMRF. Prof. Mark Kendall and his team at the University of Queensland (UQ) use SEM in the development of their vaccine Nanopatch. Their patented Nanopatch technology directly targets specialised antigen-presenting cells (APCs) in the skin in a completely new approach to vaccination. The Nanopatch, covered with thousands of tiny projections is dry-coated with vaccine for application to the skin. The silicon projections are designed to pierce the tough outer layer of cells and project into the skin to the perfect depth to target the APCs. The dry vaccine coating makes the patch stable at room temperature overcoming the rather tenuous cold chain, a major point of failure in current vaccine programs in developing countries.

The use of SEM enables monitoring of the nanopatch structures and coatings, and helps the team visualise the skin after patch removal. The work has been published widely and Prof. Kendall has won many awards including The Australian Innovation Challenge.

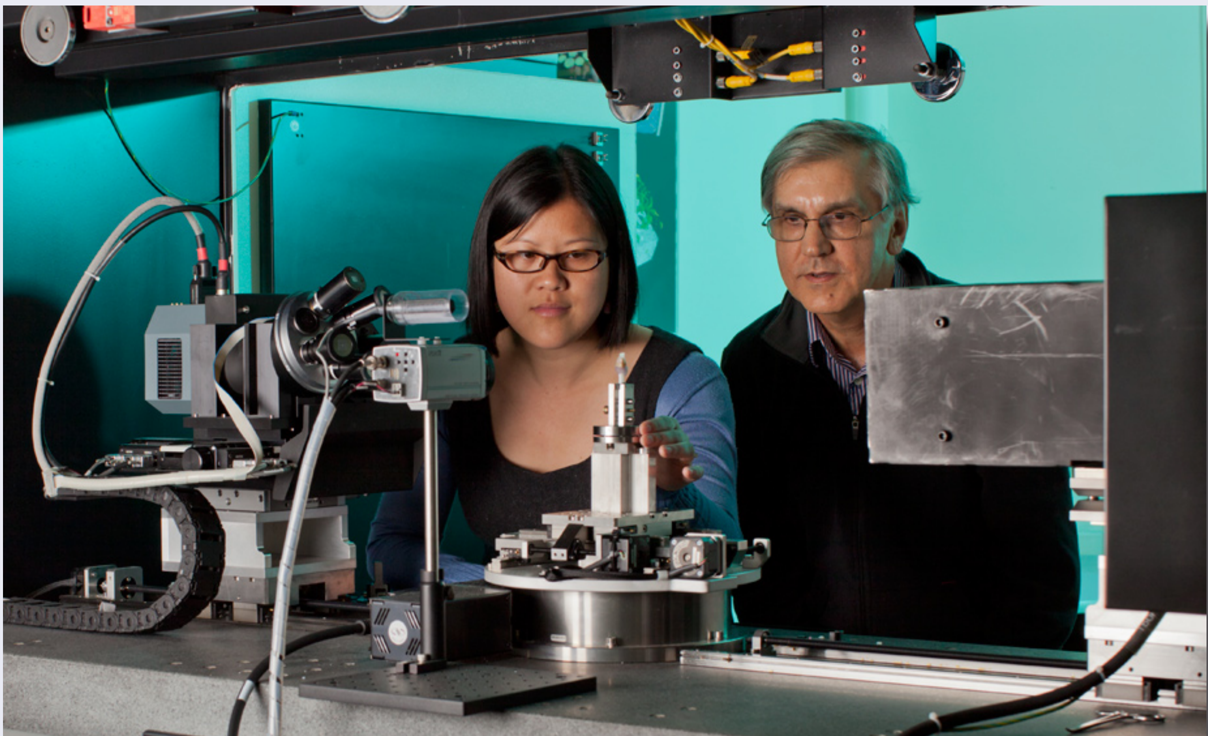
X-ray nano- and microtomography (also known as nano- and micro-CT) are also very popular techniques. They are non-destructive, allowing internal structural details to be revealed in just about anything where there is a large density difference between adjacent structural components. They are particularly well suited to the study of porous specimens. Some of the AMMRF systems are also set up to image small live animals.

Work done by Dr Jeremy Shaw on the iron-mineralised teeth of chitons has made use of many microscopy and microanalysis techniques available around the AMMRF including X-ray nano- and microtomography. Chitons are marine animals that scrape algae from rocks in tidal pools and other coastal habitats. They harden their teeth with a range of iron oxide and calcium-based minerals, including magnetite, one of the hardest and most magnetic iron oxides known. Dr Shaw's work has identified many of the cellular and crystalline processes along the path to mineralisation and is a showcase for the effectiveness of combining microscopy techniques to construct a complete picture of the workings of a complex system. X-ray tomography results have been invaluable to him in understanding the 3-D arrangement of the developing teeth and the orientation of the matrix of organic fibres on which mineralisation occurs. Understanding these biomineralised tissues will underpin the development of synthetic replicas for a range of applications in advanced technologies.

Transmission electron microscopy (TEM) has the resolving power to reveal the fine structure of a sample in an ultrathin section right down to sub-nanometre resolution and even to the atomic level for crystalline materials. The images generated are based on the electron density of regions within the sample. TEM can also map elements, and, on certain instruments, manipulate samples while imaging using cooling, heating, straining and indenting stages.

The ability to tilt samples in the microscope has lead to the possibility of doing electron tomography, building up a 3-D view of the sample from images collected at different angles. Single particle analysis is a variation on this theme where multiple images of single structures sitting at different orientations on a surface are collected and reconstructed to give a complete 3-D model. This is particularly suitable for determining the structure of non-crystalline materials such as macromolecules, molecular complexes and intracellular structures.

During her PhD research Ms Ya-Na Wu from the University of Sydney has found that gold-coated iron nanoparticles, around ten nanometres in diameter, can reduce cell division in oral cancer cells while having no obvious harmful effects on normal cells. She has used TEM imaging and spectroscopy to understand the structure of the particles and found that the state of the iron core is responsible for the slowdown in cell division. Although the precise mechanism by which the iron acts from within the gold coat is still unclear, the iron-in-gold nanoparticles



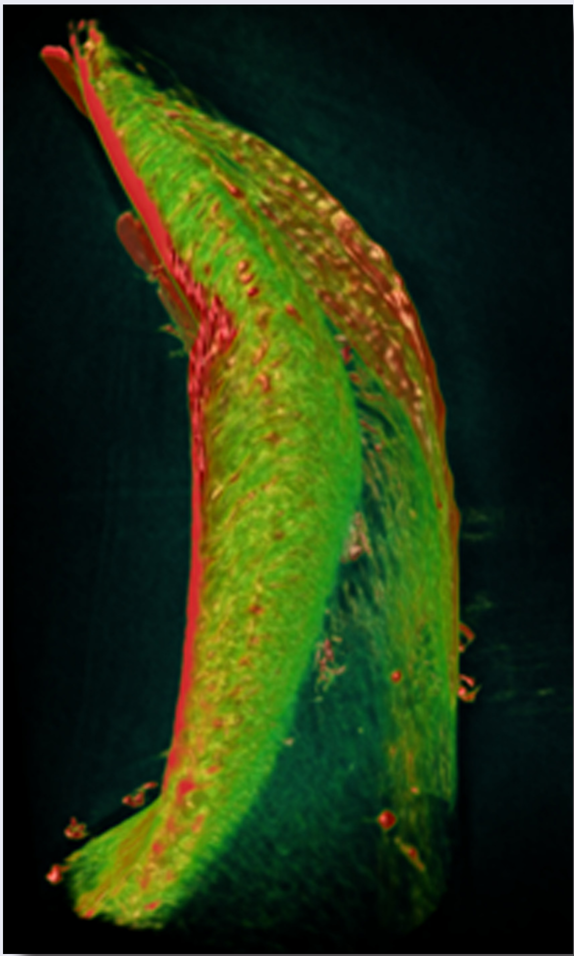
Using an X-ray microtomography instrument have been shown to cause an irreversible loss of mitochondrial membrane potential only in the cancer cells. They therefore have great potential as an anti-cancer agent.

Nanoparticles are studied for a completely different purpose in a project to make hydrogen and nano-onions from methane. Researchers led by Prof. Hui Tong Chua at the University of Western Australia (UWA) have come up with a clean method of producing hydrogen, where the only by-product is significant quantities of graphitic carbon nanomaterials, predominantly in the form of nano-onions. Consisting of layer upon layer of self-encapsulating carbon shells, the nano-onions have potential application and value as high-quality electrodes for use in electrochemical processes and batteries.

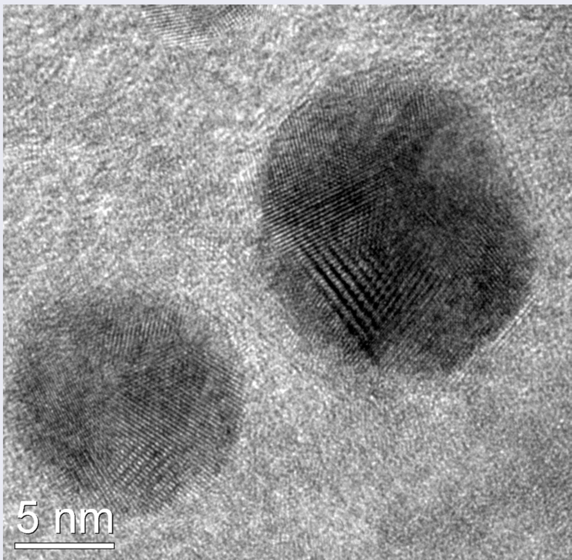
The researchers rely on the high-resolution scanning and transmission electron microscopy facilities in the AMMRF at UWA to investigate the structural and chemical properties of the carbon and the catalyst materials used in the cracking process.

Summary

The AMMRF provides up to the minute microscopy and microanalysis research infrastructure to the entire research community in Australia. Projects across the spectrum of academic disciplines and industrial research and testing can benefit from the instruments and expertise. Visit ammrf.org.au for lots more information on techniques and outcomes and make sure you check out the Technique Finder and MyScope while you are there.



NanoCT-tooth
X-ray nanotomography reconstruction of a chiton tooth showing the organic fibres in green and the mineralised areas in red. image: Jeremy Shaw

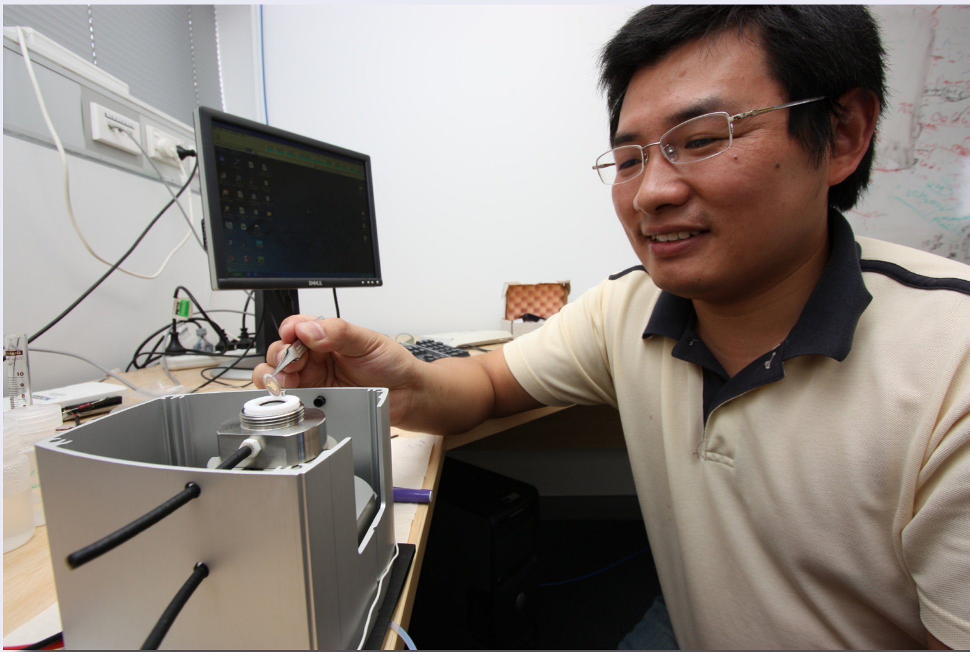


Ya Na's nanoparticles
TEM image showing the crystalline nature of the iron in gold nanoparticles.
Created by Ya-Na Wu

NanoBubbles

An Idea That Won't Stick

Dr Tim Wetherell



Dr Guangming Liu demonstrates the nanobubble cell in his lab

When we wash our dishes, we're removing protein, fats and all manner of other contaminants from a ceramic surface. If you were to simply run cold water over the plates it's unlikely that the results would be very satisfactory. However a combination of what's known as a surfactant (soap), warm water and a bit of scrubbing with a sponge achieves what most householders would call a nice clean plate. But just how clean is such a surface at the molecular level? Probably not very! There are many protiens that bond extremely well to surfaces leaving a layer perhaps only a molecule or two thick. Fine for hygienic dining, but not good enough for some scientific and industrial applications.

Many industrial processes require components to be so clean that their surfaces have no trace of contaminants. To make matters worse some components such as the metallic parts of silicon chips or detectors can't be scrubbed or abraded in any way. This can necessitate the use of multistage cleaning processes that can be messy and expensive. However a group of scientists at the Australian National University have recently discovered a simple technique that may have widespread potential to revolutionise a whole range of industrial and domestic cleaning applications. The secret is nanobubbles.

When an electric current is passed through water, electrolytic decomposition of the water molecules results in the production of oxygen and hydrogen gas. The process occurs rapidly in salt water but very much more slowly in pure water because of its vastly lower conductivity. This in turn is due to the fact that water has a very limited ability to self ionise, in other words for two H2O molecules become hydronium H3O+ and hydroxide OH-.

The upshot of all of this is that when a small voltage is applied between a conductive component and a second electrode in a water bath, bubbles of gas begin to form. If the component is used as the cathode (negative electrode) hydrogen gas forms on its surface. But if the water is pure, the conductivity is very low and the quantity of gas is miniscule. This means the bubbles that form are only a few nanometres across – way too small to see even with a microscope.

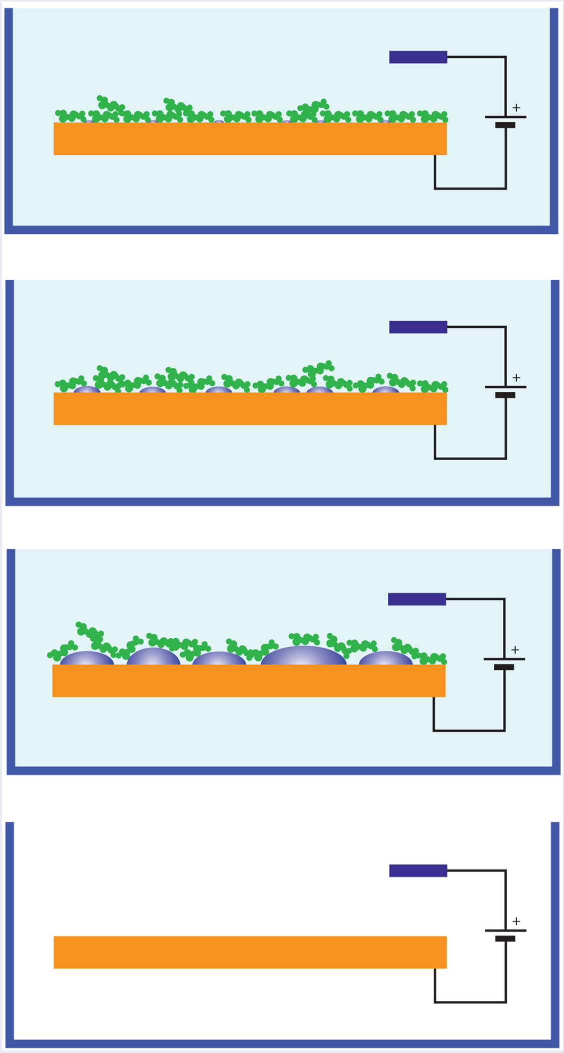
However, although the bubbles may be invisible, their effects are not. The gas forms directly on the surface, beneath the contaminants. As the bubble grow it lifts the surface film off and carries it off into the water. If the process is repeated a few times it is possible to clean a component in a matter of seconds without the use of chemicals or abrasion.

Nanobubbles are a relatively recent discovery; scientists hadn't looked for them because in theory, they shouldn't exist. When a bubble of gas in a liquid is very tiny, the quantity of gas it contains is miniscule and it's surface area is large. Its Laplace pressure (the pressure difference between inside and outside the bubble) is also very high. All this should lead to such tiny bubbles simply dissolving into the surrounding liquid. The researchers believe that reason this doesn't happen when the bubble is on a surface is that the curvature of the bubble where it contacts the surface is very much lower than would be expected.

Although nanobubbles may have many future applications in cleaning, the potential of this technology isn't limited to just removing contaminants. It may have a role in preventing the adsorption of materials onto conductive surfaces in the first place. One potentially exciting use of such a system is marine anti-fouling.

When ships are new their hulls are clean and smooth and they slide through the water easily and quickly. However as they age, marine organisms such as barnacles begin to grow below the water line creating a rough surface that induces turbulent flow and friction. To counter this, shipbuilders have used a number of techniques. One of the earliest was to attachcopper sheets to the bottom of ships, leading to the common phrase "copper bottomed" – meaning solid and trustworthy. The use of copper bottomed ships with their higher speed was one of the deciding factors in the supremacy of the British navy in the eighteenth century.

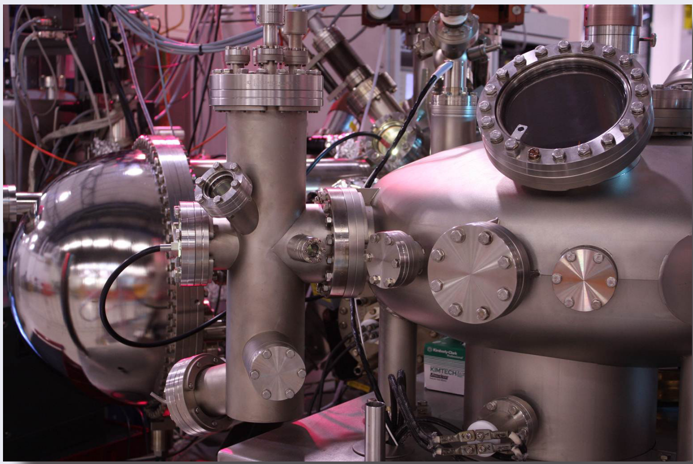
Modern ships are coated with toxic anti fouling paint rather than copper sheets, but this is expensive and can lead to environmental problems when the paint needs to be removed and replaced. If one day it were possible to incorporate nanobubble technology into the design of ships, they may be able to clean themselves in the water without the need for toxic coatings.



Electrolytically formed nanobubbles on a conductive surface lift contaminants such as adhered proteins.

Thin layers have big potential

Molecular 'sandwiches' made from thin layers of different molecules could help solve technological challenges associated with today's electronic devices.



La Trobe University researchers are using soft x-rays at the Australian Synchrotron to investigate new materials for use in electronic devices. Photo: Nancy Mills, Australian Synchrotron

Molecular 'sandwiches' made by combining thin layers of different molecules could provide answers to some of the technological challenges associated with the current generation of electronic devices. For example, molecular electronic devices may provide cost-effective architectures for optoelectronics devices that have both electrical and optical functions, and photovoltaics such as solar cells that convert light into electric power.

The properties of these hetero-structured materials are governed to a large extent by the electronic properties of the interfaces between the molecular layers. Because their interfacial properties can be tuned and optimised by systematically varying the electronic structure of the molecules that make up the different layers, molecular materials are valuable for fundamental studies as well as the potential development of new electronic devices.

For example, scientists can tune interfacial properties to devise functional devices such as organic photovoltaic devices. The molecular layers in these devices are selected so that exposing the device to light causes a current to be generated across the interface.

Dr Chris Pakes from La Trobe University is particularly interested in understanding interfacial charge transfer in hetero-materials formed by overlaying technologically important materials such as silicon, diamond and organic semiconductors with organic molecular layers. Pakes leads the university's Atom-scale Research Laboratory.

Carbon for the future

Carbon is essential for life as we know it. Its diverse forms – including three-dimensional diamond and graphite, two-dimensional graphene, nanotubes and fullerenes – are also leading to an increasing number of potential industrial applications.

"Materials science is undergoing a carbon renaissance, with carbon's many forms proving to be an interesting arena for the study of science in the solid state," says Pakes.

"Diamond may well be the material of choice in emerging quantum industries, driven by its outstanding properties and recent rapid improvements in the quality of synthetic single-crystal diamond materials. Being made of carbon, it's also bio-compatible."

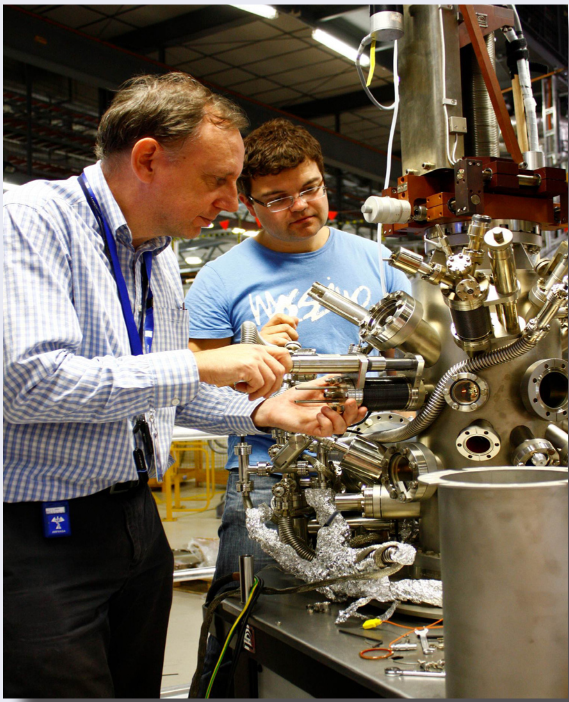
Over the past decade, there has been significant growth in Australian interest in diamond-based materials for nanoelectronics, quantum computation, magnetic sensing and quantum optical technology.

With diamond, molecular overlayers can be chosen to enable the transfer of charge to or from the underlying material – a process known as "surface transfer doping". This creates an electrically conducting layer in the diamond surface that can form the basis of a device useful in chemical and biological sensor technology or a field effect transistor capable of amplifying high-frequency, high-power signals appropriate for communication technology.

Despite considerable worldwide effort, the mechanisms that govern the charge transfer process are not well understood, either for systems based on conventional semiconductors such as diamond or for organic semiconductors such as those used in photovoltaic devices. Knowing how the charge transfer process works is important for optimising device design. For example, this enables scientists to maximise the number of charge carriers (mobile electrons or 'holes' that can transmit electric charges) in the device. Scientists can also use this information to help them select or design a molecular dopant (a molecule added in small quantities to the original material) to introduce new functional properties such as optical control.

Enter the synchrotron

In 2009, the La Trobe team began using the Australian Synchrotron to investigate how to control the electronic properties of diamond surfaces, by adding one or more layers of carbon in the form of fullerenes. Fullerenes (short for buckminsterfullerenes – named in honour of R.



Bruce Cowie and Anton Tadich prepare to upgrade experimental equipment on the soft x-ray beamline at the Australian Synchrotron.
Photo: Nancy Mills, Australian Synchrotron

Buckminster Fuller's geodesic domes) are hollow spheres of 60 carbon atoms (C60 'buckyballs') arranged in five- and six-membered rings. The fullerene family also includes larger spheres and carbon nanotubes, which are sometimes called 'buckytubes'.

The carbon atoms at a cut diamond surface are reactive. Diamond surfaces can be passivated by hydrogen, which terminates the reactive surface carbon atoms, producing 'hydrogen-terminated diamond'. Hydrogen atoms on the diamond surface modify its electronic properties to more easily permit transfer of electrons from the diamond into a molecular overlayer. Fullerenes are efficient electron acceptors – when they are deposited on the hydrogen-terminated surface, transfer doping causes a deficiency of electrons in the surface region, making it electrically conductive.

The La Trobe researchers led a series of measurements using the soft x-ray spectroscopy beamline at the Australian Synchrotron to study surface transfer doping of hydrogen-terminated diamond and porphyrin-based organic semiconductors. Porphyrins are a family of organic compounds characterised by four heterocyclic rings linked in a larger ring or macrocycle; they include pigments such as chlorophyll and heme, the iron-containing core of hemoglobin.

For this work, Pakes and his colleagues used overlayers made from fluorinated fullerenes, which are efficient electron acceptors because they have a high affinity for electrons. Every carbon atom in a C60 fullerene is bonded to three others. Because a carbon atom has the capacity to bond to four other atoms, each C60 carbon atom therefore has the potential to bind to one other atom. In practice, not all the carbon atoms will bond to fluorine atoms, because this would cause too much strain in the molecule. A typical example of a fluorinated fullerene is C60F48, with the fluorine atoms sitting on the outside of the sphere.

The researchers combined a well-known technique called core-level photoelectron spectroscopy with the energy tunability and high energy resolution of synchrotron-generated soft x-rays to obtain new information about how the molecules interact with the diamond surface. Photoelectron spectroscopy with soft x-rays enables researchers to determine the binding energy of the electrons that are ejected from a material when it is exposed to synchrotron light. This yields information about the chemical state of the atoms and molecules from which the electrons were ejected.

The team's synchrotron experiments on hydrogen-terminated diamond surfaces revealed for the first time the presence of C60F48 molecules with two charge states at low levels of molecular coverage: negatively charged molecules that were involved in charge transfer and neutral molecules that were not. Resolving these two species was only possible because of the high energy resolution of the incident x-rays, and the ability to tune the x-ray energy to maximise the sensitivity of the measurements to carbon species at the surface.

By examining how the photoemission spectra changed as the number of surface fluorofullerenes increased, the researchers were able to experimentally evaluate the surface transfer doping efficiency. This allowed them to determine the relative position of the fluorofullerene molecular energy levels compared with those of the underlying surface, assisting the development of a theoretical model to explain the charge transfer process [1].

The La Trobe group has observed similar behaviour at the interface of fluorofullerene with a porphyrin-based semiconductor, showing that the results of their study are valid for very different hetero-structure materials. Their results can therefore serve as a platform for the design of future devices using hetero-junctions – regardless of whether these are conventional or organic. This work was conducted by two postgraduate members of the La Trobe laboratory, Mark Edmonds and Yaou Smets, in collaboration with Dr Anton Tadich from the Australian Synchrotron and Professor Lothar Ley from the University of Erlangen (Friedrich-Alexander-Universität Erlangen-Nürnberg) in Germany.

In parallel with their synchrotron photoemission studies, the La Trobe group is exploring molecular surface doping of semiconductors on the atomic-scale using ultra-high vacuum scanning tunnelling microscopy. This work aims to investigate how surface charge transfer influences the assembly of acceptor molecules on the semiconductor surface and to develop methods for using La Trobe's low-temperature scanned-probe instrumentation to manipulate individual acceptor molecules. The program's long-term goal is find ways to directly pattern individual acceptor molecules on the surface.

Reference [1]: M.T. Edmonds, et al., "Surface transfer doping of hydrogen-terminated diamond by C60F48: level scheme and doping efficiency", J. Chem. Phys., 136, 124701 (2012).

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