Finding the light perspective

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Chemists are quickly realising the value of the tools the Australian Synchrotron has placed at their disposal.

If you're reading this article, odds are that you have a keen interest in chemistry – and considerable expertise in your particular area. If someone asked what you do, you'd have a sensible explanation that you could tailor to suit your questioner.

A harder question is 'How would you define "chemistry" overall?' It's such a broad area that three chemists with a whiteboard would come up with at least four definitions – and that's just in the first few minutes! A quick net surf suggests it's 'the science of matter, the branch of the natural sciences dealing with the composition of substances and their properties and reactions' (<http://wordnetweb.princeton.edu/perl/webwn?s=chemistry>, viewed 3 June 2010). It's also 'the way two individuals relate to each other' (ibid.) and the title of several albums and singles from various performing artists.

Explaining what chemists do at the Australian Synchrotron is just as difficult, although the answer doesn't involve a rock band, at least not yet! The facility's beamlines provide unparalleled information on the detailed chemistry of diverse sample types for research and industrial purposes. More than 1800 researchers from around Australia have already used the synchrotron to help them achieve their research and development goals faster.

'You could probably argue that 100% of our users do chemistry. Proteins = biochemistry = chemistry!' says Rachel Williamson from the macromolecular crystallography (MX) beamline team. 'But I guess that around 10–15% would class themselves as chemists.

Micro-crystallography and beyond

'Chemists are an increasingly important user community on the MX beamlines,' Rachel says. 'The number of chemists coming here is increasing with each round.'

The micro-crystallography (MX2) beamline is especially popular with chemists.

'Some compounds never form crystals of decent size, but the intensity of MX2 means it's now possible to solve these structures,' says Rachel. 'We can obtain useful data from crystals that are only hundreds of nanometres across in the thinnest dimension. We've also collected data from 100 K to above room temperature so users can see how their structures change with temperature.'

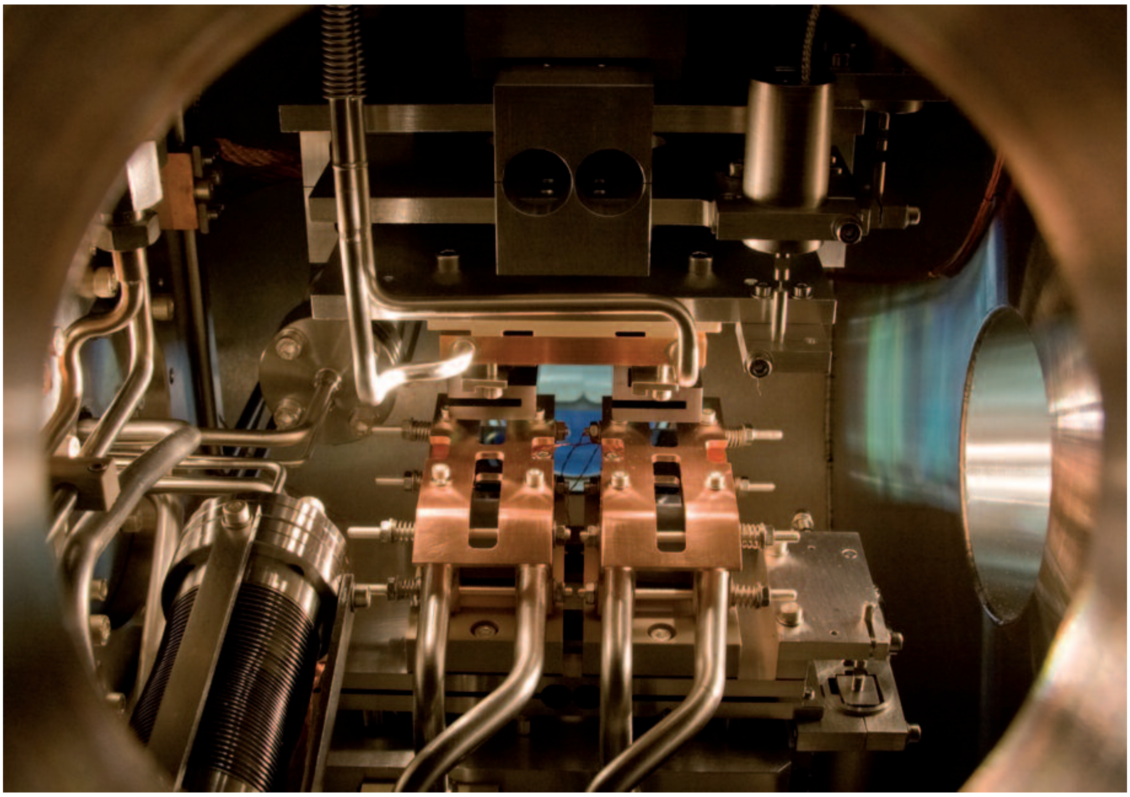
David Turner from Monash University collects MX data on supramolecular complexes and materials ranging from coordination polymers that display spin-crossover to discrete metal–organic complexes over 3 nanometres in diameter that can store significant amounts of gas. In collaboration with Stuart Batten and Keith Murray, David is exploring the formation, structure and properties of these materials. David is also studying hydrogen-bonded organic 'structural motifs' such as macrocyclic urea compounds.

'The synchrotron enables us to gather structural information from crystals too small for laboratory X-ray crystallography – and from porous materials in which the well-ordered material (the bit that diffracts) accounts for as little as 40% of the volume,' David says.

The main outcome of this work is fundamental knowledge. David says a deeper understanding of the structure–property relationship is needed before it will be possible to realise potential downstream applications such as magnetic data storage or gas storage for the new generation of hydrogen-powered vehicles.

Powerful diffraction

For users with polycrystalline samples rather than single crystals, the powder diffraction beamline provides high-resolution X-ray data that is ideal for determining struc-



Inside the MX2 beamline, which caters for difficult crystals. Image credit: Sandra Morrow.

tural information and studying rapidly changing processes such as chemical reactions.

Beamline head Kia Wallwork and her team recently expanded the beamline's capabilities by installing an integrated furnace capable of a temperature range of 25–2300°C. Early users of the new furnace include Mark Styles and his colleagues from the University of Melbourne and CSIRO, who conducted an in-situ experiment looking at how temperature and atmospheric oxygen affect phase composition for a commercial electrode material based on the Magnéli phases Ti_4O_7, Ti_5O_9 and Ti_6O_{11}.

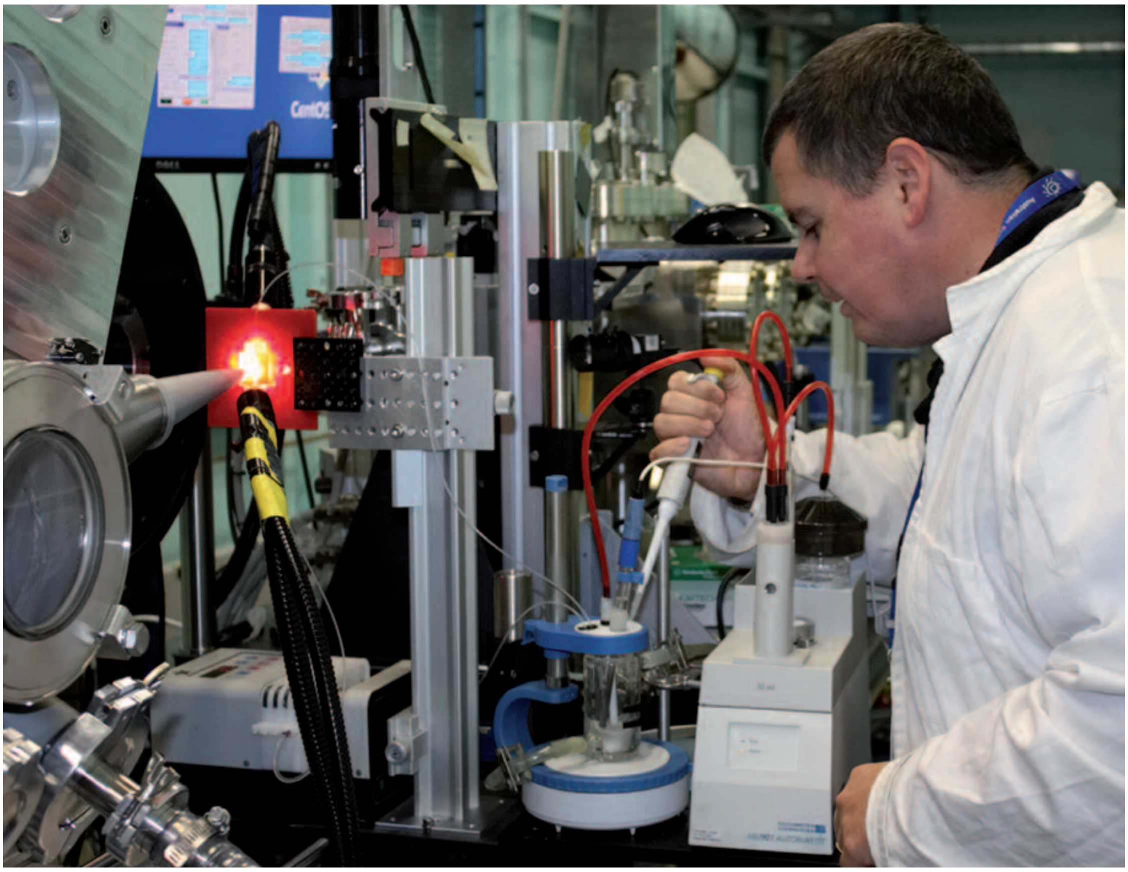
SAXS appeals to chemists

As well as being a handy acronym for suggestive headlines, SAXS stands for small-angle X-ray scattering. WAXS is the equivalent wide-angle technique. SAXS provides structural information in complex molecules and materials ranging in size from ~1 to 500 nanometres. WAXS provides information on the atomic scale down to ~0.1 nanometre, similar to standard X-ray diffraction techniques. Studies of processes such as nucleation and crystallisation use SAXS and WAXS together. SAXS/WAXS techniques complement NMR, electron microscopy, light scattering and small angle neutron scattering.

'The beamline is easy for users to run and it allows many types of chemistry, biology and materials experiments,' says Nigel Kirby, who heads the SAXS/WAXS beamline team. 'Bench chemistry experiments can be done on the sample stage in real time, with temperature control, simultaneous X-ray diffraction and SAXS, on more or less any form of solid or liquid sample – and surfaces too. Around 30% of users are chemists.'

Ben Boyd, Dallas Warren and Mette Anby from the Monash Institute of Pharmaceutical Sciences recently put their in-vitro digestion model (aka artificial tummy) on the SAXS beamline to examine how different conditions (lipid structure, lipid composition, level of bile) encountered in the human digestive system affect the geometry of self-assembled lipid structures. The group's studies of lipid-based drug products are assisting the development of more effective drug products.

An estimated 25–40% of drug candidates fail to lead



Ben Boyd (Monash Institute of Pharmaceutical Sciences) feeds his 'artificial tummy' on the SAXS beamline. Image credit: Nancy Mills.

to successful drug products because of their limited solubility in aqueous environments. Drugs work best when our digestive system can absorb them completely so they pass into the bloodstream and become available where they are most useful.

'Only a small number of molecules are currently known to self-assemble in the right way,' says Ben. 'We're looking for ways to control the geometry of the self-assembled structures. The structural information from SAXS will be complemented by in-vivo functional studies of drug release from self-assembly structures.

'Without access to the high-intensity synchrotron source for our SAXS studies, we would not be in a position to relate structure to function.'

Soft X-rays help answer hard questions

Soft X-rays (100–3000 eV) are useful for characterising surfaces, thin films and near-surface interfacial layers, particularly when carbon is an important constituent.

The soft X-ray beamline can examine the local electronic and geometric structure around any particular element, potentially providing information on bond lengths, coordination numbers, local coordination geometry and oxidation states of atoms in solids and some liquid systems.

The beamline end-chamber offers a full range of standard surface science preparation techniques. Argon ions or nitrogen ions can be used to bombard the surface of materials to create atomic holes (vacancies), which can have a very significant effect on electronic properties. This capability was used recently by Mladen Petravic and colleagues from the University of Rijeka, Croatia, and the Institute for Technology Research and Innovation, Deakin University, who are investigating the potential to create molecular magnets from boron nitride (BN) nanostructures.

The group used the soft X-ray beamline to create and directly identify nitrogen vacancies in BN nanotubes

Curtin University researchers are using synchrotron IR to study fingermarks collected on gold and stainless steel plates. Image credit: Simon Lewis, Curtin University of Technology.

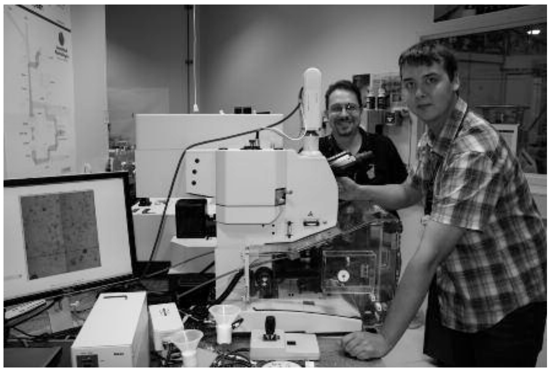
and sheets. Nitrogen vacancies can lead to magnetism in BN nanotubes, which involves bonding electrons from s- and p-orbitals rather than the d- and f-orbitals of traditional magnetic materials.

Magnetic nanotubes can be used as nano-carriers for targeted drug delivery, externally driven through blood vessels by a magnetic field to specific locations in the body, or incorporated into thin films for magnetic recording.

Seeing infrared

Like its conventional laboratory counterparts, synchrotron infrared (IR) spectroscopy has many applications. However, a synchrotron IR source provides several distinct advantages. The beam's high collimation and brightness enable researchers to examine chemical compositions and interactions with high sensitivity and at high spatial or spectral resolutions. On the IR microspectroscopy beamline, spatial resolutions of 3–5 micrometres can be achieved. This enables close examination of complex heterogeneous samples.

Honours student Patrick Fritz and his supervisors



Patrick Fritz (right) and Simon Lewis from Curtin University check their fingerprint samples on the IR microspectroscopy beamline. Image credit: Nancy Mills.

Simon Lewis and Bill van Bronswijk from Curtin University of Technology are part of an Australia-wide team investigating the chemistry of latent (invisible) fingermark deposits, with the aim of improving current detection techniques. Preliminary results show that synchrotron IR microspectroscopy is particularly good for studying oils and fats in fingermark deposits, which typically consist of an emulsion of natural skin secretions (waxes, oils and aqueous components) and contaminants present on the skin.

The far IR and high-resolution IR branch of the beamline allows gaseous samples to be examined to extremely high resolutions: 0.000 96 cm^{-1}. Typical applications involve atmospheric and space chemistry. This beamline also extends into the terahertz region, which is particularly useful for examining weak intermolecular bonds such as hydrogen bonds in condensed-phase samples. Greg Metha from the University of Adelaide recently used this capability to examine the chemical structure of metal-carbide nanoparticles that could potentially provide viable alternatives to platinum-group industrial catalysts.

Extraordinary X-rays

Techniques unique to synchrotrons include X-ray absorption spectroscopy. XAS provides information on bond lengths, coordination numbers, local coordination geometry and oxidation states of atoms (Ca to U at the Australian Synchrotron) in a wide range of solids and liquids. The new detector uses the beamline's high-flux X-rays to detect much lower concentrations and enable much faster data collection.

Hugh Harris and colleagues from the University of

Adelaide became the first users of the new detector in May 2010 when they analysed a range of cultured human tissue samples for selenium. The work is part of a larger investigation of the chemical forms that selenium takes in different organs.

In small amounts, dietary selenium can help prevent cancers such as colon cancer. However, slightly larger amounts can lead to health issues such as cardiovascular problems. Selenium's impact on the body is strongly influenced by its chemical form, but both organic and inorganic selenium can cause health problems if they are ingested in high enough concentrations.

XAS is the only technique that can determine selenium's chemical form in biological samples without sample preparation methods that could affect the chemical form. Hugh says preliminary findings show 'that different chemical forms have distinct fates in the cells, a finding that is at odds with established literature'.

The group is also using the Australian Synchrotron's X-ray fluorescence microprobe (XFM) beamline to look at selenium distribution in kidney sections from rats fed small quantities of selenite.

X-ray fluorescence mapping techniques on the XFM beamline can potentially map all elements present across a sample in one go. The beamline can then focus on a single area between 100 nanometres and 2 micrometres in size to determine oxidation state and chemical environment (bonding etc.) for particular elements of interest. Applications include studies of metal-based drugs in biological systems and the geochemistry of mineral ore samples.

Synchrotron business

The Australian Synchrotron's business development activities are attracting a steady stream of enquiries from large and small businesses keen to find out how the synchrotron's customised experimental facilities can help them develop new products and improved manufacturing processes.

In June 2010, the PACIA (Plastics and Chemicals Industry Association) national conference featured a presentation from David Cookson, the synchrotron's head of beamline science and operations. David asked delegates to think of the synchrotron as a state-of-the-art tool set that offers better ways to characterise materials and processes.

Synchrotron techniques can help speed up product and process development cycles by providing exquisitely detailed knowledge of structure and function at the molecular level. Businesses can gain access to these tools by applying to use the synchrotron beamlines themselves, collaborating with synchrotron staff, or working with researchers in tertiary institutions with appropriate expertise.

The next generation

The synchrotron's education activities include tours for secondary and tertiary students, and laboratory sessions for secondary students, which mainly address the VCE (Victorian Certificate of Education) physics curriculum. Education and outreach officer Jonathan de Booy is working to extend coverage of the laboratory sessions to the chemistry curriculum as well.

'The synchrotron is included under analytical techniques in VCE Chemistry, along with TLC, GC and HPLC, and AAS, IR, NMR, visible-UV and mass spectroscopy,' Jonathan says.

'Our current laboratory sessions show students how visible light and microwaves can measure some of the physical properties of materials,' Jonathan says. 'The reason why researchers do similar measurements with X-rays and infrared is usually to obtain information about the chemical structure and behaviour of materials. Most synchrotron applications involve some level of chemistry.

'We're developing a "synchrotrons and nanotechnology" session that will introduce students to diffraction and X-ray photoemission spectroscopy (XPS) as ways of seeing what tiny structures such as carbon nanotubes actually look like.'

Something for everyone

On Sunday 15 August 2010, Victoria's National Science Week activities will be launched at the Australian Synchrotron's annual open day. The facility will also offer online synchrotron 'tours' on its website <www.synchrotron.org.au>.

Nancy Mills <nancy.mills@synchrotron.org.au> is grateful to synchrotron users and staff for their mostly polite responses to her persistent questions.