

Brighter than the Sun

Sometimes scientists can do things that are mind bogglingly stupendous. I was confronted with an example of this on the first day of my PhD, when I found myself in a donut-shaped building the size of five football pitches in the Oxfordshire countryside. Here, at the Diamond Light Source, the UK's national synchrotron, scientists generate light which is 10 billion times brighter than the Sun.

The intensity of the light generated at Diamond, and other synchrotrons across the globe, has allowed chemists to do things they would never have been able to do using conventional laboratory facilities, such as working out why some of the yellows in Van Gogh's paintings are fading and tracking the changes in microstructure during rapid thermal runaway in lithium ion batteries. Chemists all over the globe are now using synchrotron light to deliver ever deeper insights into the chemistry of the nanoscale and superfast worlds.

From cyclotron to synchrotron

The first synchrotrons were not developed to produce light; rather, they were designed as particle accelerators for high-energy particle physics experiments. The story of the synchrotron really begins in 1930, when a PhD student called Milton Stanley Livingston, working under the supervision of Ernest Lawrence at Berkeley University, built a device called a cyclotron. In the cyclotron, charged particles were accelerated around a circular track by a fixed magnetic field (the movement of the charged particles generated a magnetic field, leading them to interact with the fixed magnets). Later, it was found that particles could be accelerated to higher energies (while still remaining on a circular path) if they were collected into groups, and an increase in the magnetic field strength was synchronised with the rise in the particle energy; thus, the cyclotron became the synchrotron.

The synchrotron was very effective at accelerating particles, but for physicists there was an unwanted side-effect; once the particles hit relativistic speeds on their circular path, they generated very intense, narrow cones of light parallel to the direction of their motion. In 1947, the first observation of this light was made by a team of scientists at General Electric (GE) in the USA. The GE synchrotron emitted visible light, but later, higher energy machines emitted higher energy light: X-rays.

Synchrotron light sources

It didn't take long for chemists to see the potential of these bright X-rays, and in 1956 the first X-ray spectroscopy experiment was conducted at the Cornell University Synchrotron. For a couple of decades, chemists could only do experiments using synchrotron light by hijacking machines built for high energy particle physics. Happily, the situation improved in 1980, when the UK built the first synchrotron specifically for the production of high energy light for experiments at the Daresbury Laboratory in Cheshire.

There are now more than 50 synchrotron light sources worldwide, all configured in essentially the same way. The storage ring in which the light is generated has ports which open onto individual beamlines at which scientists set up their experiments. In modern synchrotrons, devices called insertion units (made up of arrays of magnets) are placed in long straight sections in the storage ring; these not only further enhance the beam's brightness, they also allow the wavelength of the X-rays to be tuned simply by adjusting the magnetic field strength.

It should be noted that synchrotrons don't just make X-rays; as mentioned above, the first synchrotron emitted visible light, and infrared, ultraviolet and terahertz waves can all also be generated (all forms of light being, of course, fundamentally the same thing [electromagnetic

radiation], varying only in their wavelengths and frequencies or energies). Synchrotron X-ray techniques, however, have been the most extensively exploited by chemists.

Synchrotrons and chemists

Synchrotron generated X-rays have several properties which make them attractive to chemists. For example, the high brightness of the beam (a trillion times brighter than an X-ray beam produced in a hospital) allows X-ray crystallographers to resolve diffraction spots which are very close together. The beam of X-rays is also incredibly thin, allowing exceptional spatial resolution when using methods such as X-ray computed tomography (CT) to image objects and X-ray fluorescence (XRF) and X-ray absorption near edge structure (XANES) to map elemental compositions and oxidation states, respectively. In addition, the X-ray beam can be pulsed, with pulse durations in the nanosecond regime achievable at certain synchrotrons, allowing scientists to investigate changes in rapid chemical processes.

Synchrotron X-ray techniques have been applied to both fundamental and applied chemistry; to illustrate their utility, let's consider two examples of the use of synchrotron X-ray techniques in applied chemistry.

Looking inside batteries

Li-ion batteries are now ubiquitous. They are not, however, without problems, the major one being that they very occasionally fail, leading to thermal runaway and fire. A better understanding of this process is necessary in order for manufacturers to be able to develop safer batteries. However, thermal runaway happens so quickly that it is very difficult to capture what is happening inside the battery using conventional methods.

A recent collaborative study involving researchers from University College London, the National Physical Laboratory and ESRF, the European Synchrotron made use of synchrotron X-ray CT and radiography, in conjunction with thermal imaging, to track the structural and thermal changes in a Li-ion battery undergoing thermal runaway.¹ The high speed of the synchrotron imaging techniques allowed the team to see changes in the battery as it was overheated in unprecedented detail, furnishing several new insights into the failure process which will be of great utility to battery manufacturers.

Fading colours

Synchrotron X-ray radiation has also been used to deduce chemical degradation mechanisms of pigments in various paintings, including those by Vincent Van Gogh and Henri Matisse. This is possible because the synchrotron X-ray beam is one hundred times thinner than a human hair, and thus techniques such as XRF, X-ray diffraction (XRD) and XANES can be used to track changes in chemical composition over tiny areas.

A team led by Koen Janssens of the University of Antwerp were able to use synchrotron X-ray radiation techniques to work out why it is that some paintings using chrome yellow (which gives the colour to Van Gogh's famous sunflower paintings) have faded, while some have not.² After artificially aging samples of lead chromate from three 100 year old samples of chrome yellow, they found that in one of them, a dark nanometre thick layer had formed. They made use of XRF, XRD, XANES and other techniques to establish that in this layer the lead chromate had been reduced from yellow hexavalent chromium to dark green trivalent chromium, and that this was the cause of the darkening of the painting.

Further synchrotron-based work from the same group has shown that orthorhombic sulfur-rich lead chromates show a greater tendency towards reduction than monoclinic sulfur-poor ones, and that

the degradation occurs on exposure to violet-blue light.³ This type of information, only available because of the synchrotron, is incredibly useful for museum curators as they work to display paintings in protective environments.

The future

Synchrotron light, especially X-ray light, has proven to be extremely useful to chemists who wish to study changes in chemical structures or processes on a very rapid or a very small scale. Fourth generation synchrotron light sources will aim to produce even brighter light; the current leading candidate is the hard X-ray free electron laser, which generates X-ray pulses of less than 100 fs in length which have a brightness millions of times greater than the X-rays beams produced by the most powerful third generation sources. These systems could be used to study processes that are too fast even for third generation sources to see, such as the very first steps of chemical reactions. The story of chemistry and synchrotron light is only just beginning.

References

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