

The University of Nottingham Nanotechnology and Nanoscience Centre (NNNC)

The Nottingham Nanoscience and Nanotechnology Centre is located in the heart of the University Park campus and boasts a wide range of microscopes and other analytical instruments. The Centre's Dr Chris Parmenter guides us through their catalogue and highlights some of their applications to date.

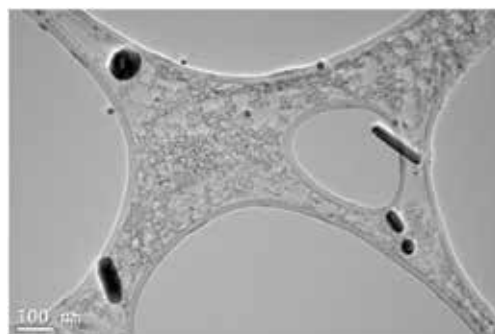


The Nottingham Nanotechnology and Nanoscience Centre, on the University Park campus.

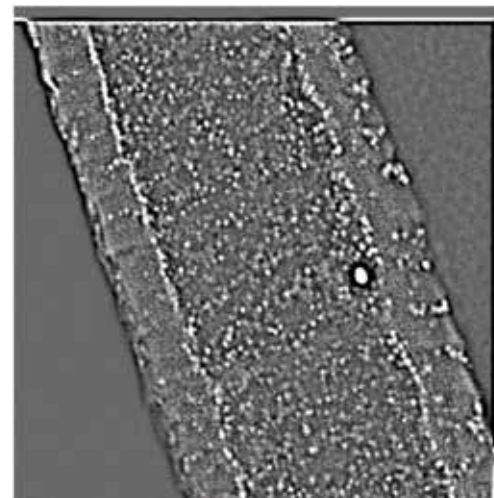
The NNNC, opened six years ago by Nobel Laureate Professor Sir Harry Kroto, was established by the Schools of Chemistry, Pharmacy, Physics & Astronomy and the Faculty of Engineering, with a £3.2m SRIF3 investment, to serve the University of Nottingham's diverse engineering, physical and life sciences research portfolio. The NNNC acts as a hub for nano and micro-scale research, is open to all, and works closely with both academic and industrial researchers in areas ranging from nanostructured carbons and catalysts to aerospace materials and drug delivery systems.

There are four members of staff, Emily Smith (XPS), Dr. Peter Milligan (Business Development), Dr. Mike Fay (TEM/FIBSEM, EM suite manager) and Dr. Chris Parmenter (FIBSEM/Cryo (SEM/TEM), with responsibility for the everyday running of the Centre. The NNNC is led by a director and a management board of academic advisors. In August 2013, Prof. Clive Roberts, the Centre's inaugural director, became Head of the School of Pharmacy and Prof. Andrei Khlobystov was appointed as the new NNNC director.

The Centre has two electron microscopes, a JEOL 2100F field emission gun TEM (FEGTEM) and an FEI Quanta 200i 3D FIBSEM with a range of holders and stages. The JEOL 2100F is equipped with single and double tilt holders, a rotational holder, and a high tilt tomography holder which has been configured for automated image acquisition in conventional diffraction contrast, high angle angular dark field (HAADF) and scanning transmission electron microscopy (STEM) modes. Additional holders include a Gatan cryo-holder for cryo-TEM or the investigation of temperature sensitive samples; a heating holder (up to 1000 °C) for studying high temperature processes *in situ*; a scanning transmission electron beam induced conductivity (STEBIC)



Snapshot from the observation of Fe_2O_3 nanorod growth [4].



Reconstruction of gold nanoparticles in a graphitic nanofibre, by dark field tomography [3].

holder for performing electrical measurements; and a gas-cell reaction holder. The FEGTEM also features a full complement of digital cameras and detectors, for bright and dark field STEM, electron energy loss spectroscopy (EELS), energy filter (GIF) and energy dispersive X-ray (EDX) analysis.

JEOL 2100F TEM is utilised for imaging molecules, nanoparticles and individual atoms entrapped inside carbon nanotubes which play a role of miniature test tubes with zeptoliter (10^{-21} litre) internal volume. TEM enables investigation of structures and dynamic behaviour of molecules confined in the nano test tubes, in real space and time, revealing some unique physical and chemical phenomena that can only emerge at the nanoscale. For example, chemical reactions can drastically change their mechanisms and pathways inside nanotubes leading to new unexpected products, such as graphene nanoribbons and unusual polymers, inaccessible by any other means. Carbon nanotubes hold the record for the World's tiniest test tube since 2005, and our latest work at the NNNC may prove them to be the World's tiniest chemical reactors [1,2].

To date the TEM has been used to gain tomographic data of nanoparticles on carbon nanotubes [3], observe the real-time growth of particles of iron oxide produced by hydrothermal synthesis

[4] and analyse the size and morphology of soot particles from diesel engines to mention but a few examples [5].

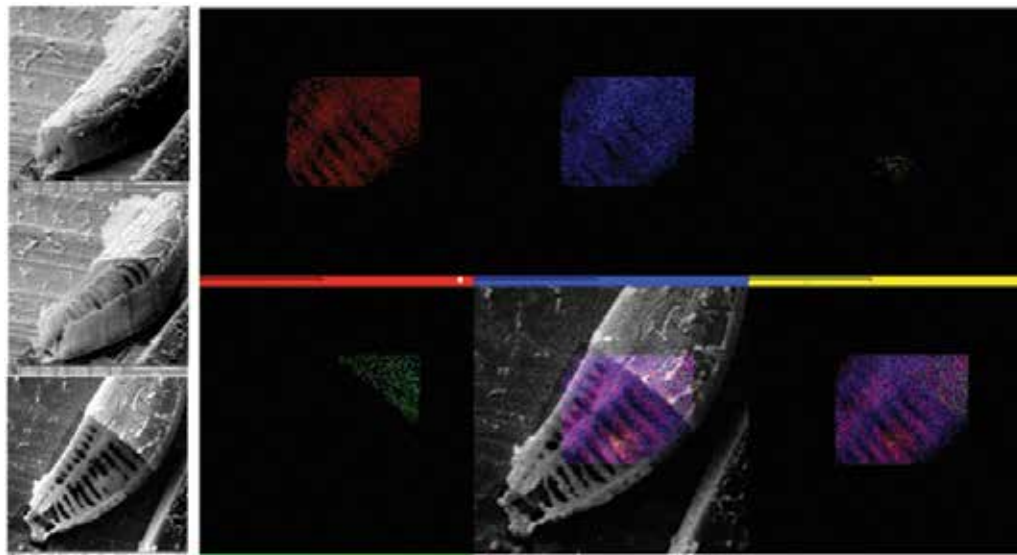
The FEGTEM is complemented by the FIBSEM, which is used for the preparation of electron transparent lamellae by site-specific thinning and lift-out using an Omniprobe. The FIBSEM is also used for the imaging and EDX analysis of a range of soft and hard materials. In particular, the FIBSEM is equipped with a Quorum 2000 PPT cryo-stage, which enables the preservation of delicate hydrated samples in a near-native state.

For example, the CryoFIBSEM has been used for the imaging of diatoms in their native states, being of interest to researchers in the Department of



HRTEM micrograph of soot extracted from a diesel engine [5].

Geography working on environmental science / ecology projects. Typically, diatoms are prepared from a body of water, from which they can be concentrated, dried and the organic remnants removed using acid to leave silicate shells. However, this approach effectively throws away the biological parts of the diatom, including the internal cellular material and the external biofilms. Use of the FIBSEM cryo-stage allows the stabilisation and preservation of organic components, whilst FIB has been used to reveal the internal diatom structures. EDX mapping allowed the silicon and oxygen of the silicate shell to be distinguished from carbon representing the diatom single-cell content and surface biofilm.



Micrographs of a diatom before and after outer layer removal by using a FIB, followed by EDX analysis, Oxygen (red), Silicon (blue), Carbon (yellow) maps shown.

Cryogenic preservation can be achieved in a number of different ways dependent on the nature of the sample. For CryoFEGTEM investigations, samples up to ~ 500 nm in thickness may be stabilised by rapid plunging into liquid ethane using the NNNC's Gatan CP3. This approach has facilitated the study of vesicles and polymer-DNA conjugates of interest to researchers from Engineering and Pharmacy.

Preparation of larger samples may be performed by vitreous sectioning, using an RMC Powertome and diamond knife, facilitating TEM analysis under cryogenic conditions. Samples may also be prepared by metal mirror freezing, using a Leica MM80, or by sucrose infiltration followed by plunging into liquid nitrogen. Metal mirror freezing has also been used to stabilise samples for Cryo-SEM or Cryo-FIBSEM investigations.

In addition to the EM instrumentation, the NNNC also hosts an Horiba confocal Raman microscope with four lasers covering the 400 cm^{-1} to 4000 cm^{-1} wavelength range, which makes it particularly useful for the investigation of drug molecule phases.

Recently, the NNNC added X-ray photoelectron spectroscopy (XPS) to its portfolio. A Kratos AXIS Ultra with a monochromated aluminium source (~1500 eV) and a delay line detector, previously

situated in the School of Chemistry, was moved to a newly refurbished laboratory in the NNNC in May 2013. This was joined in August 2013 by a new instrument, a Kratos Axis Ultra with a silver monochromated X-ray source (~3000 eV) and a bespoke sample stage for the *in situ* electrochemical investigation of ionic liquids.

The new silver source XPS provides information to greater sampling depths than the conventional aluminium source XPS (because the excited electrons are moving faster), whilst providing information content from electron orbitals which otherwise would be unexcitable. For example, the interpretation of complex peak structures to determine oxidation states is of great importance in the investigation of catalysts. The higher energy range now available sidesteps the problems associated with peak overlap in the transition metals, providing access to higher energy peaks, such as $\text{Mo } 2p_{3/2}$, which do not overlap, making interpretation significantly simpler.

The electrochemistry stage modification to the instrument is intended to provide researchers with more accurate temperature and voltage/current measurements, appropriate of the *in situ*

investigation of ionic liquids. This opens up a wide range of new experimental options for investigation. The original Al-source XPS has always been heavily used by researchers across campus. Siting both instruments within the same laboratory in the NNNC provides a useful focal point for all XPS users in the future.

In 2012, the NNNC invested in an Avizo Fire 3D imaging and analysis package from VSG. This software supports the interpretation of data from the TEM and FIBSEM, whilst also being useful for X-ray tomography, positron emission tomography (PET) and magnetic resonance imaging (MRI) investigations, all of which are available at the University.

Outreach

The NNNC has been involved in a number of outreach projects including 'NanoWhat?' and 'Let Nano Fly' (a Nano-aerospace programme). The NNNC has taken part in the creation of a number of educational videos for both the Periodic Tables Videos and the Sixty Symbols series, including the imaging flakes of snow and the writing of 'Merry Christmas' on a snowflake (http://www.youtube.com/watch?v=_hpc5NT0Ayl). The NNNC now hold two Guinness World records, for the smallest Periodic Table (<http://www.youtube.com/watch?v=cQU2IAsQak8>), and the smallest advertisement (http://www.youtube.com/watch?feature=player_embedded&v=SfAoIsaSLJ0), both of which were written onto human hair. Following these records, the NNNC was contacted by a local school who wanted use the Centre's SEM to investigate the effect of hair care products on hair of differing ethnicity. As part of this project, the NNNC milled their school emblem onto the teacher's hair. This became the focus of a local news story and led to staff from the NNNC appearing on local radio.

For the Queen's Diamond Jubilee celebrations in 2012 the NNNC teamed up with Prof. Martyn

Poliakoff and filmmaker Brady Haran (Periodic videos) to engrave the image of the queen onto a layer of diamond.

The NNNC regularly hosts visits from students on the 'seeing the un-seeable' programme, in conjunction by the School of Physics & Astronomy. Dr Mike Fay regularly provides outreach sessions for schools, science fairs and education centres.

Future Collaborations

The staff at the NNNC are always open to collaboration with researchers in both academia and industry and regularly collaborate on one-off, short and longer term research projects with those who want to make use of the facility.

If you would like more information on the centre, are interested in using the facilities or would like to propose some exploratory work with them, please go to <http://www.nottingham.ac.uk/NNNC> or contact Dr Peter Milligan, peter.milligan@nottingham.ac.uk or 0115 84 67729.

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Chris Parmenter has a PhD in Chemistry with a specialism in polymer science and electron Microscopy. After a post-doc at the University of Warwick from 2005 – 2008, he moved to a post as a Research Officer at the NNNC at the University of Nottingham. His current interests are in Cryo-electron microscopy (Cryo-TEM and Cryo-FIB-SEM), self-assembly systems and polymeric vesicles. Chris has been an RMS fellow since 2006 and sits on two committees (Materials and Electron Microscopy).

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Raymond Coleman, author of *Virtual Microscopy* (December 2012 issue)

KEYENCE

VHX-2000 – Super Resolution Digital Microscope with Automated Measurements

Pioneering the field of digital microscopy, KEYENCE has released its latest microscope system, the VHX-2000. The VHX Series Digital Microscope was designed to alleviate the shortcomings of traditional, optical light microscopes - shallow depth-of-field, short working distance, lack of portability and versatility, sample limitations, etc. By integrating advanced zoom optics with a CCD camera, 17" LCD monitor, light source, controller and analysis/reporting software, the VHX streamlines testing and improves the speed and efficiency of the inspection process.



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Building on top of the VHX platform, the VHX-2000 incorporates several new features. A colour filter wheel has been added to allow users the option of choosing a specific wavelength (red, green or blue) of light for their samples. A Super Resolution mode combines the blue filter with KEYENCE's pixel shift technology, capturing images with 25% better resolution.

To improve the operation and ease-of-use, the VHX-2000 can be equipped with a motorised XY stage along with motorised Z-axis lens control. Users can adjust movement in all three axes by using an included control pad. When combined with our Double'R lens/magnification recognition function, the VHX-2000 can automatically provide the ideal movement speed for the XY stage and enables one-push automatic focus and calibration. The Image Stitching function can now be completed with just the push of a button, and at much higher speeds, to produce up to a 20,000 x 20,000 pixel image that expands the viewing area by up to 200 times.

Automated measurement functions simplify the most difficult of measurement tasks and help to remove variation between different users. The system also has the ability to save a portion of the image/measurements as a template to be used to measure future samples with a click of the mouse.

For VHX-2000 Digital Microscope specifications and applications, please go to: www.keyence.co.uk/prvhx2

Keyence UK

Avebury House, 219-225 Avebury Boulevard, Milton Keynes MK9 1AU, U.K.
 Masahide OKANO
 Phone: +44 (0)1908 696900 ext.819
 Fax: +44-(0)1908-696777
KeyencePR@keyence.co.uk