Chem Soc Rev

Chemical Society Reviews

www.rsc.org/chemsocrev

RSC Publishing is a not-for-profit publisher and a division of the Royal Society of Chemistry. Any surplus made is used to support charitable activities aimed at advancing the chemical sciences. Full details are available from www.rsc.org

IN THIS ISSUE

ISSN 0306–0012 CODEN CSRVBR 37(5) 873–1076 (2008)

Cover

See Roger M. Jarvis and Royston Goodacre, page 931. Abstract representation of bacterial SERS data collection from laser strike to spectrum. Cover image created by Richard O'Connor. Image reproduced by permission of Roger M. Jarvis and Royston Goodacre from *Chem. Soc. Rev.*, 2008, **37**, 931.

CHEMICAL SCIENCE

C33

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments in chemical science, showcasing newsworthy articles and significant scientific advances.

Chemical Science

May 2008/Volume 5/Issue 5

www.rsc.org/chemicalscience

EDITORIAL

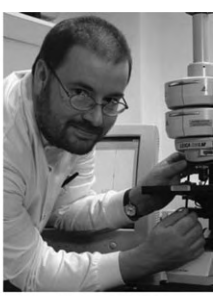
883

Chemical and bioanalytical applications of surface enhanced Raman scattering spectroscopy

Duncan Graham and Royston Goodacre

This special issue highlights the latest developments and applications of SERS giving an updated view on the status of SERS as a measurement technique.

Duncan Graham



Roy Goodacre

Chem Soc Rev

Chemical Society Reviews

www.rsc.org/chemsocrev

Chemical Society Reviews publishes accessible, succinct and reader-friendly articles on topics of current interest in the chemical sciences. The promotion of international and multidisciplinary awareness and cooperation is particularly encouraged. Chemical Society Reviews publishes two article types: tutorial reviews, which present an accessible introduction to the topic, and critical reviews, which provide a deeper evaluation of the current literature.

Chemical Society Reviews (print: ISSN 0306-0012; electronic: ISSN 1460-4744) is published 12 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF.

All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Distribution Services, c/o Portland Customer Services, Commerce Way, Colchester, Essex, UK CO2 8HP. Tel +44 (0) 1206 226050; Email sales@rscdistribution.org

2008 Annual (print + electronic) subscription price: £514; US$995. 2008 Annual (electronic) subscription price: £463; US$896. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT.

If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA.

US Postmaster: send address changes to: Chemical Society Reviews, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All dispatches outside the UK by Consolidated Airfreight.

PRINTED IN THE UK

INFORMATION FOR AUTHORS

The Editorial Board commissions articles that encourage international, interdisciplinary progress in chemical research. The Board welcomes proposals for new tutorial reviews or critical reviews and the appropriate synopsis pro forma should be requested from the Editorial Office (csr@rsc.org). Full details of how to submit material for publication in Chemical Society Reviews are given in the Instructions for Authors (available from http://www.rsc.org/authors). Submissions should be sent *via* ReSourCe: http//www.rsc.org/resource

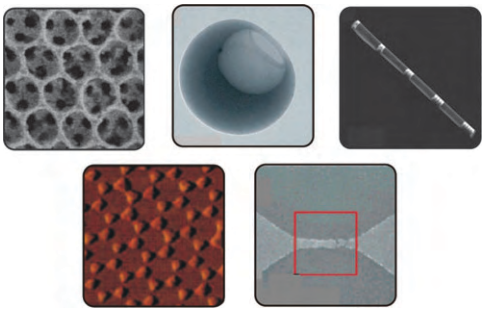
Authors may reproduce/republish portions of their published contribution without seeking permission from the RSC, provided that any such republication is accompanied by an acknowledgement in the form: (Original Citation) – Reproduced by permission of The Royal Society of Chemistry.

885

Rationally designed nanostructures for surface-enhanced Raman spectroscopy

Matthew J. Banholzer, Jill E. Millstone, Lidong Qin and Chad A. Mirkin*

New approaches from nanotechnology playbooks lead to new SERS substrates with improved sensitivity, tailorability, robustness, and reproducibility.

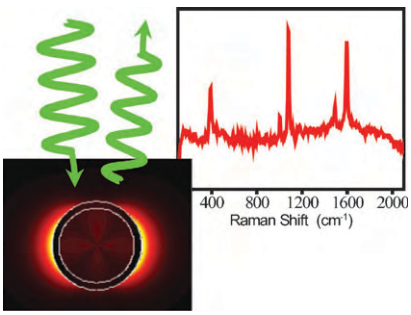


898

Tailoring plasmonic substrates for surface enhanced spectroscopies

Surbhi Lal, Nathaniel K. Grady, Janardan Kundu, Carly S. Levin, J. Britt Lassiter and Naomi J. Halas*

The design of metallic nanostructures tailored specifically for providing the electromagnetic enhancements needed for surface enhanced Raman and infrared spectroscopies.

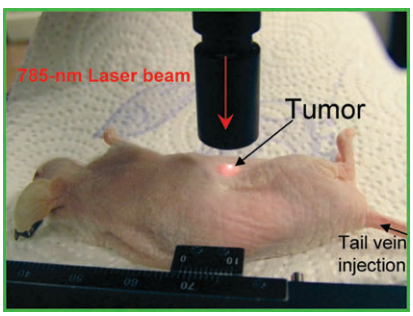


912

Single-molecule and single-nanoparticle SERS: from fundamental mechanisms to biomedical applications

X.-M. Qian and S. M. Nie*

Pegylated colloidal gold and surface-enhanced Raman scattering are used for *in vivo* tumor targeting and spectroscopic detection.

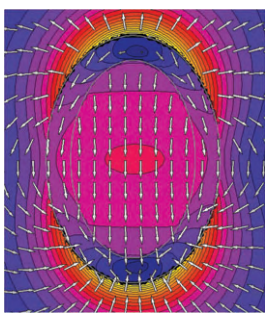


921

Tip-enhanced Raman scattering

Elena Bailo and Volker Deckert*

Molecular spectroscopy at the edge: tip-enhanced Raman scattering (TERS) provides structural information at the nanometre scale.

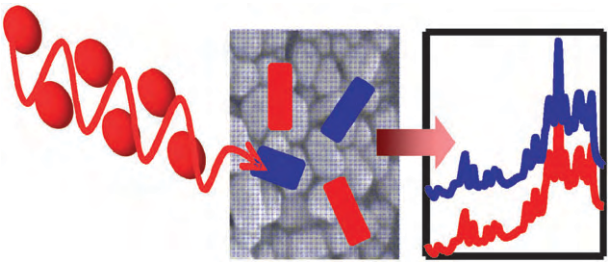


931

Characterisation and identification of bacteria using SERS

Roger M. Jarvis* and Royston Goodacre

This *tutorial review* reports developments in SERS for the characterisation and identification of bacteria.

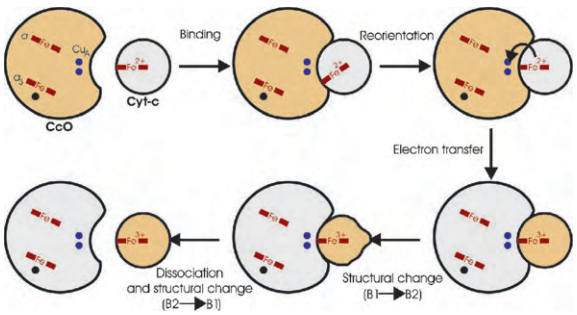


937

Disentangling interfacial redox processes of proteins by SERR spectroscopy

Daniel H. Murgida* and Peter Hildebrandt*

Time-resolved SERR spectroscopy is able to monitor electron transfer, orientation and structural dynamics of heme proteins at biomimetic electrodes.

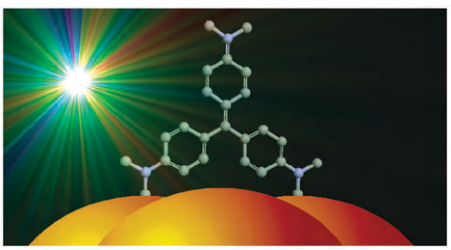


946

Single molecule analysis by surfaced-enhanced Raman scattering

Nicholas P. W. Pieczonka and Ricardo F. Aroca

The tutorial provides an analysis of the basic questions surrounding single molecule detection *via* surface-enhanced Raman scattering and surface-enhanced resonance Raman scattering for molecules coupled to Ag and Au nanostructures.

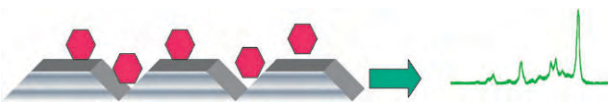


955

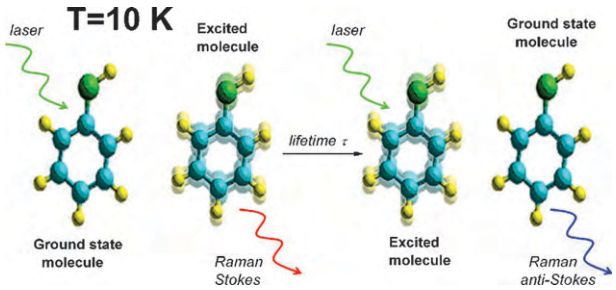
Practical understanding and use of surface enhanced Raman scattering/surface enhanced resonance Raman scattering in chemical and biological analysis

W. E. Smith

Review targeted at the development of practical applications.



965

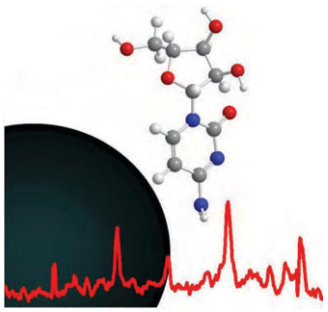


Vibrational pumping in surface enhanced Raman scattering (SERS)

R. C. Maher,* C. M. Galloway, E. C. Le Ru, L. F. Cohen and P. G. Etchegoin*

This *tutorial review* discusses the basics and surveys the current status of *SERS vibrational pumping*, which is coming of age and can shed light into fundamental aspects of the Raman signal enhancements.

980

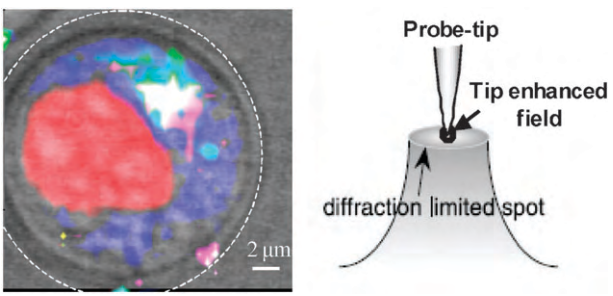


Surface enhanced Raman optical activity (SEROA)

Salim Abdali and Ewan William Blanch*

Theoretical and experimental work in developing SEROA and possible future directions of research for this novel chiroptical spectroscopy are presented.

993

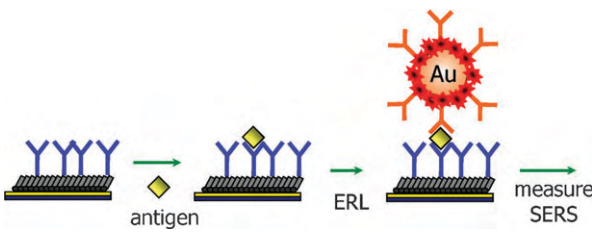


Intracellular applications of analytical SERS spectroscopy and multispectral imaging

Igor Chourpa, Franck H. Lei, Pierre Dubois, Michel Manfait and Ganesh D. Sockalingum*

Overview of live cells applications of nanoparticle-based analytical SERS spectroscopy and perspectives of the tip-enhanced Raman scattering (TERS) approach.

1001



SERS as a bioassay platform: fundamentals, design, and applications

Marc D. Porter,* Robert J. Lipert,* Lorraine M. Siperko, Gufeng Wang and Radha Narayanan

Surface enhanced Raman scattering and nanoparticle labels are opening new avenues for ultrasensitive diagnostics for biomarkers and pathogens.

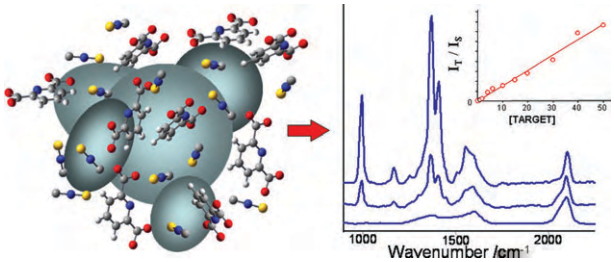
TUTORIAL REVIEWS

1012

Quantitative surface-enhanced Raman spectroscopy

Steven E. J. Bell* and Narayana M. S. Sirimuthu

Surface-enhanced Raman spectroscopy has now matured into a rapid and cost-effective quantitative analytical technique.

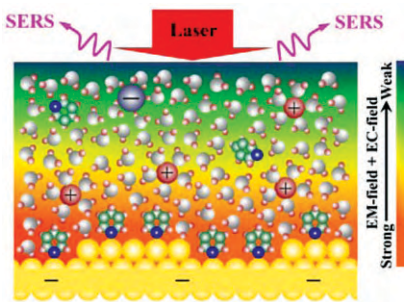


1025

Electrochemical surface-enhanced Raman spectroscopy of nanostructures

De-Yin Wu, Jian-Feng Li, Bin Ren* and Zhong-Qun Tian*

This *tutorial review* describes and discusses the history, features, methods, applications and prospective developments of electrochemical SERS (EC-SERS).

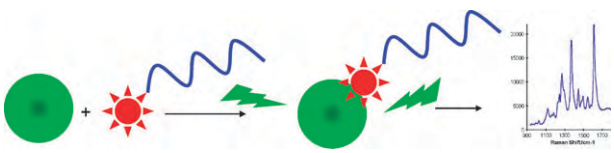


1042

Quantitative SERRS for DNA sequence analysis

Duncan Graham* and Karen Faulds

The conditions and procedures to enable the successful detection of DNA using SERRS are discussed.



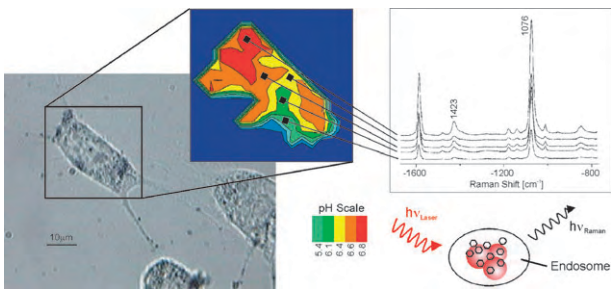
CRITICAL REVIEWS

1052

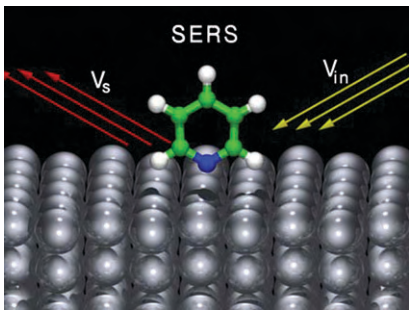
SERS—a single-molecule and nanoscale tool for bioanalytics

Janina Kneipp,* Harald Kneipp and Katrin Kneipp

SERS opens up exciting opportunities in bioanalytics such as probing chemical composition and pH in live cells at subendosomal resolution.



1061



Electronic structure methods for studying surface-enhanced Raman scattering

Lasse Jensen,* Christine M. Aikens and George C. Schatz

This *critical review* highlights recent advances in using electronic structure methods to study surface-enhanced Raman scattering. Examples showing how electronic structure methods, in particular time-dependent density functional theory, can be used to gain microscopic insights into the enhancement mechanism are presented.

FREE E-MAIL ALERTS AND RSS FEEDS

Contents lists in advance of publication are available on the web *via* www.rsc.org/csr – or take advantage of our free e-mail alerting service (www.rsc.org/ej_alert) to receive notification each time a new list becomes available.

Try our RSS feeds for up-to-the-minute news of the latest research. By setting up RSS feeds, preferably using feed reader software, you can be alerted to the latest Advance Articles published on the RSC web site. Visit www.rsc.org/publishing/technology/rss.asp for details.

ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

* Indicates the author for correspondence: see article for details.

Electronic supplementary information (ESI) is available *via* the online article (see http://www.rsc.org/esi for general information about ESI).

May 2008 / Volume 5 / Issue 5 / ISSN 1478-6524 / CSHCBM / www.rsc.org/chemicalscience

Chemical Science

High levels of inorganic arsenic found in milk made from rice

Arsenic exposure from rice milk

Researchers have found that levels of arsenic in rice milk exceed EU and US drinking water standards.

Andrew Meharg and colleagues at the University of Aberdeen, UK, have shown that people drinking rice milk are exposed to high levels of inorganic arsenic. It is well known that rice can contain high levels of, predominately inorganic, arsenic – a known human carcinogen. However the levels of inorganic arsenic in milk made from rice, a cow milk alternative for vegans and lactose intolerant sufferers, have not previously been of concern.

Meharg's team analysed samples of rice milk to see if inorganic arsenic transfers from the rice into the milk. They tested commercially available and home-made milks, made from globally sourced white and brown rice grains. And they also looked at arsenic levels in soy and oat milk.

EU regulations set limits on the amount of arsenic allowed in drinking water, and the US specifically limits inorganic arsenic levels. Neither closely regulates arsenic in foods, and it is not clear which category rice milk falls into.

All the rice milks tested exceeded the EU drinking water standards

Meharg found that all the commercial rice milks exceeded the EU standard for water of 10 $\mu g\,l^{-1}$ and 80 per cent also failed the US standard of 10 $\mu g\,l^{-1}$ inorganic arsenic. The median total arsenic value was seven times greater those found in soy and oat milk samples.

David Polya at the University of Manchester, UK, is an expert on the risks of environmental chemicals to humans, and says that the research highlights 'an inconsistency in the regulatory treatment of carcinogens, such as arsenic, between food and drink. Groups particularly at risk, such as vegans, are not identified by average exposure estimates,' he adds.

Meharg says that his research group has recently received funding to begin breeding rice plants that take up less arsenic. He also intends to characterise the bio-availability of arsenic from rice in humans to add to the evidence that this exposure route is concerning.

Harriet Brewerton

Reference
A A Meharg *et al*, *J. Environ. Monit.*, 2008, **10**, 428 (DOI: 10.1039/b800981c)

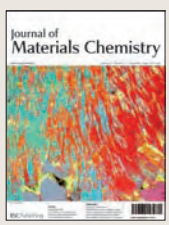
In this issue

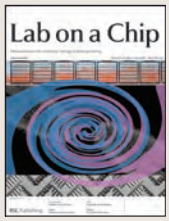
Cleaning up after nerve agents
Single-step destruction method for organophosphate chemical warfare unveiled

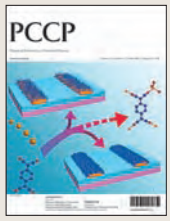
Zooming in on nanoparticles' defects
Bumpy surfaces are vital for nanoparticles catalytic activity

Interview: In the beginning....
Kenso Soai and Joanne Thomson discuss the origin of chirality in life

Instant insight: Nano-forms of carbon
Juan Luis Delgado, María Ángeles Herranz and Nazario Martín explore the cutting-edge in nanostructures made from carbon







A snapshot of the latest developments from across the chemical sciences

Research highlights

Puzzle of unexpectedly high levels of deuterated ammonia in space cracked

Solving a smelly space mystery

Researchers in Sweden have developed a new method to account for the vast abundance of deuterated compounds in space.

Terry Frankcombe and Gunnar Nyman at the University of Gothenburg in Sweden have focussed their interest on ammonia, a gas with a pungent odour. 'The fraction that is deuterated vastly exceeds what would be statistically expected,' says Frankcombe. 'We have developed a combined dynamics and statistically based model to investigate the formation of NH_2^+, one of the ammonia precursors. Our model leads us to suggest a new explanation for how the deuterium enrichment happens during the formation of the ion. In all isotopically substituted $NH^+ + H_2$ reactions in which both hydrogen and deuterium are present, the NHD^+ product is preferred.'

More earthly applications have partly motivated this work: 'In collaboration with the Copenhagen Centre for Atmospheric Research, Denmark, isotope effects have been used to understand better the composition of Earth's atmosphere and pin down sources and sinks for various species in the atmosphere,' says Frankcombe. But that isn't all. This is also an interesting system to study simply because developing a practical yet accurate treatment is challenging, he explains.

NASA

Researchers have developed a model to explain deuterium enrichment in space

Chris Williams, a theoretical chemist at Ohio State University, Columbus, US, explains that theoretical calculations are necessary because 'it is hard to reproduce the low temperatures and pressures of the interstellar environment in the laboratory. Conventional reactive scattering calculations can simulate this type of reaction but the computational cost is considerable.' This new route using the 'adiabatic capture centrifugal sudden approximation has proved to be invaluable for finding overall rate constants on this class of reactions'.

Frankcombe notes that even in the vacuum of interstellar space, treating the molecules in isolation isn't the whole story. 'The focus may shift to reactions occurring on and in grains of dust to complement the gas phase work, as it is has become clear that interstellar chemistry cannot be understood without understanding the condensed-phase chemistry occurring in and on grains.' They warn that in that case, 'performing accurate dynamics studies with presently available methods becomes essentially impossible'.

Colin Batchelor

Reference
T Frankcombe and G Nyman, *Phys. Chem. Chem. Phys.*, 2008, DOI: 10.1039/b801384e

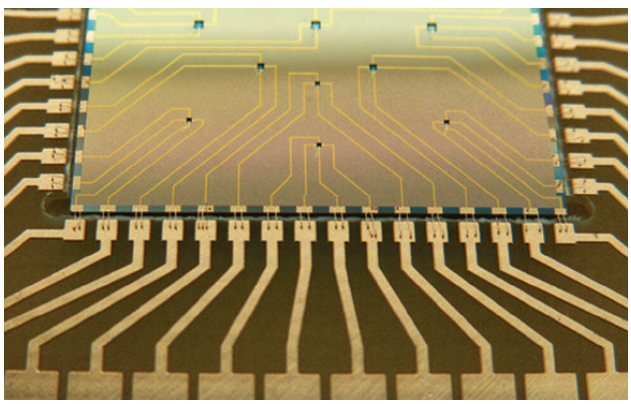
A new, innovative device for the ultrafast screening of anticancer drugs

3D chips assess drug viability

Scientists in Germany have developed a new 3D chip for the rapid and cheap assessment of potential anticancer drugs.

Andrea Robitzki and colleagues at the University of Leipzig have made a chip for the ultrafast characterisation of both 3D tissue samples, and for screening compounds to assess their anticancer activity.

3D multicellular cultures are commonly used to mimic in vivo conditions in tumours, as single cell assays do not give sufficiently realistic responses to anticancer drugs. However, to date screening devices for these 3D cultures are not advanced enough to become commercially available. 'The advantage of this novel chip is the microcavity structure keeps the tissue samples in culture and in a viable state for real time measurements of cellular changes,' explains Robitzki.



Cellular changes can be measured in real time

The technique used in the chip is impedance spectroscopy: a current is applied to the biological sample which then flows through to a counter electrode beneath. By measuring the electrical responses different cellular processes can be analysed under normal conditions or after applying drugs, toxins or other active compounds. 'This approach is a novel innovation for drug screening and for producing cost-effective pharmaceutical products and therapeutical concepts in a short time frame,' says Robitzki.

'The results show a relevant technology that will be appealing to industry and academics alike,' comments Jon Cooper, a bioengineer at the University of Glasgow, UK. 'One could easily imagine it being implemented in a high throughput format appropriate for the pharmaceutical industry,' he adds.

Sarah Dixon

Reference
D Kloß *et al*, *Lab Chip*, 2008, DOI:10.1039/b800394g

Single-step destruction method for organophosphate chemical warfare unveiled

Cleaning up after nerve agents

Destruction of nerve agents through a simple chemical reaction could help remove chemical weapon stockpiles and clean contaminated materials. US scientists have demonstrated that cheap, easily prepared chemicals can break down organophosphate nerve agents such as VX to a non-hazardous material.

Existing methods for destroying nerve agents such as oxidation with bleach are limited. Nerve agents in chemical weapons are often found as chemical mixtures, and bleach reacts indiscriminately - even explosively - with many chemicals such as propellants. It is also corrosive to materials and surfaces. Other approaches such as alkaline hydrolysis also have drawbacks, including low solubility and slow reaction rates. Furthermore some decontamination methods give by-products, such as thioic acids, which are almost as toxic as the original nerve agent.

Now David Atwood and Daniel Williams at University of Kentucky, Lexington, and Kennesaw State University and co-workers have devised a destruction method based on dealkylating agents. Organophosphate-based nerve agents and pesticides can now be cleaved in a single reaction. 'This research demonstrates the first technique whereby nerve agents or pesticides can be made inactive in a direct reaction. The resulting non-toxic byproducts would be solids that could be easily handled or disposed of,' explains Atwood. Looking to the future 'the technology could also be used to decontaminate vehicles or other objects that have been exposed to nerve agents', he adds.

User is wearing a suit with a breathing unit, and is pointing a detector at a simulated agent shell

Reference
A Mitra, *New J. Chem.*, 2008, DOI:10.1039/b717041f

The dealkylating agents are based on Schiff bases containing boron or aluminium and specifically cleave the phosphate ester bond in nerve agents or pesticides preventing unwanted side reactions or surface corrosion.

'The search for a non-corrosive decontamination of sensitive material and skin after exposure by toxic chemicals, for example pesticides and nerve agents, is an important but challenging task,' says Franz Worek an expert in organophosphate toxicology at the Bundeswehr Institute of Pharmacology and Toxicology, Munich, Germany. 'This new and promising approach may ultimately lead to a new type of mild and effective decontamination,' he adds.

Russell Johnson

New highly insulating aerogels inspired by bird nests

Strength in nanoworms

Scientists in the US have mimicked the structure of bird nests to overcome the extreme fragility of highly insulating aerogels.

Already used to protect NASA's Mars rovers' delicate electronics from the cold, aerogels are low-density materials prized for their insulating properties. However, the porous materials, made of interwoven nanoparticle strands, are also extremely fragile, limiting their use. Now Nicholas Leventis and colleagues at Missouri University of Science and Technology, Rolla, have made a stronger material by boosting the interlocking between strands.

Aerogels are typically made from pearl necklace-like strings of silica nanoparticles, and can be strengthened with a polymer coating, so that the strands form crosslinks wherever they meet. But inspired by the highly interlocked structures of bird nests, Leventis switched to vanadia-based structures, which form a more highly entangled worm-like nanostructure.

NASA

Aerogels help keep this Mars rover's electronics warm

Reference
N Leventis *et al.*, *J. Mater. Chem.*, 2008, DOI: 10.1039/b801770k

'Both crosslinked silica and vanadia are very strong materials. But crosslinked vanadia aerogels never fail under compression, and can absorb at least four times the kinetic energy of the silicon carbide ceramics used for armour,' said Leventis. 'Killer applications will be in areas where we can take advantage of the multifunctional character of these materials – strength in combination with acoustic and thermal insulation – such as lightweight structural materials for buildings, and the automotive and airplane industries.'

Bakul Dave who makes similar gel-based materials at Southern Illinois University, Carbondale, US, describes the work as a step forward. 'It seems the properties depend on the nanostructure morphology – so in principle, it should be possible to make these materials with components other than vanadium.'

Replacing vanadium with a cheaper alternative is Leventis' first goal. 'We are applying lessons learned from vanadia to silica, which under certain conditions can also produce worm-like structures,' Leventis adds.

James Mitchell Crow

News in brief

This month in *Chemical Technology*

Designer thermometers rise to new levels
Ionic liquids have been used in liquid-in-glass thermometers as alternatives to mercury and ethanol

A bright future for solar cells
A highly efficient light harvesting molecule could lead to cheaper solar cells, claim international scientists

Cellular power plants fuel molecular motors
Mitochondria have been used to power miniature motors for microfluidic devices

Nerve agent detector on a chip
A microfluidic device that can identify exposure to sarin could help identify individuals needing treatment at sites of terrorist attack

See **www.rsc.org/chemicaltechnology** *for full versions of these articles*

This month in *Chemical Biology*

The science of smell
Chip technology is helping French scientists to unravel the mysteries behind our sense of smell

Analysing aneurysms
In the future, doctors may be able to spot life-threatening blood vessel swelling more accurately, thanks to work by French scientists

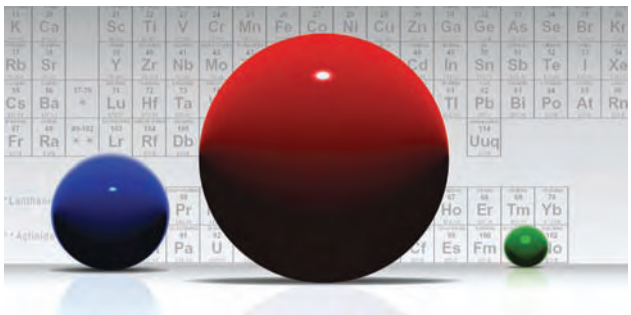
Spiky sponges share their secrets
Enzymes that make sponges spiky are promising leads for new silicon-based materials, say British scientists

Tumour treatments see the light
DNA-seeking probes could deliver anticancer agents right to the heart of tumour cells, say chemists in Italy

Computers get to the heart of gene expression
German scientists are unravelling the genetic basis of diseases by combining computational biology techniques

See **www.rsc.org/chembiology** *for full versions of these articles*

Refining atomic radii



The new list shows sensible trends along both the rows and groups of the periodic table

A new set of covalent atomic radii that is more comprehensive and precise than previous lists has been compiled by Spanish scientists from the University of Barcelona.

The concept of atomic radii is used in structural chemistry and X-ray crystallography to give a rough idea of the size of an atom in a molecule or crystal, and to establish bonding and non-bonding interactions between atoms. The new list of radii covers elements up to curium (atomic number 96) and shows sensible trends along both the rows and groups of the periodic table, explains team leader Santiago Alvarez.

The work began when Alvarez's team were trying to decide when to expect structures to have a through-ring metal–metal interaction, and discovered that existing lists of radii contained gaps and inconsistencies. They found periodic trends were erratic and that in the previously most complete set used by the Cambridge Structural Database (CSD) important metals such as nickel, palladium, platinum and gold were given default unrefined values of 1.50 Å.

The Spanish team derived their radii from a systematic search of 228 000 experimental bond distances in structures held in the CSD and the Inorganic Crystal Structure Database. They determined the radii from bond distances to nitrogen, carbon and oxygen atoms, as there many examples of covalent bonds from these to most other elements.
Michael Townsend

Reference
B. Cordero *et al, Dalton Trans.*, 2008, DOI: 10.1039/b801115j

Zooming in on nanoparticles' defects

US researchers have found a way to study defects on surfaces of nanoparticles, which are thought to be critical for catalytic activity.

Metal nanoparticles are the key to the activity of many catalysts, including those in car catalytic converters. To improve these catalysts it is important to know what is happening at the atomic level. Miguel Jose-Yacaman and colleagues at the University of Texas at Austin have found that, using microscopy and computer modelling, they can obtain much more detail than before about nanoparticle surface defects.

Jose-Yacaman's method uses abberation-corrected TEM (transmission electron microscopy), which uses software to correct distortions introduced by the microscope lenses. This enables imaging of atoms in non-regular environments (such as at surface defects), which is not possible with regular TEM. The team applied this technique to a gold–palladium nanoparticle, and not only found that it was a single crystal, but that it consisted of three distinct spherical layers, each with a different ratio of the two metals. They also obtained electron density profiles along different axes through the particle. By comparing these with computer models, they found that the nanoparticle contains steps, edges and kinks on its surface.

Nanoparticles bumpy surfaces are vital for their catalytic activity

Jose-Yacaman says their results show that 'the surface of the particle is rather rough at the atomic scale.'

David Cockayne, professor of materials chemistry at the University of Oxford, UK, is enthusiastic about the work, saying that it 'demonstrates the enormous potential for modern aberration-corrected TEM to explore the complex structures of nanoparticles'. Luis Liz-Marzàn, an expert in nanoparticles from the University of Vigo in Spain, echoed these thoughts, saying this 'represents a leap in electron microscopy capabilities for nanoparticle analysis'.
David Barden

Reference
D Ferrer *et al., J. Mater. Chem.*, 2008, DOI: 10.1039/b801320a

In the beginning....

Kenso Soai and Joanne Thomson discuss the origin of chirality in life

Kenso Soai

Kenso Soai is professor of applied chemistry at Tokyo University of Science, Japan. His research interests centre on chirality in organic synthesis, including asymmetric autocatalysis and spontaneous asymmetric synthesis.

What first inspired you to become a chemist?

I have been interested in the natural sciences since my childhood. My hope was to become a researcher in this area, although I hadn't decided on a specific subject. After entering university, I attended various lectures and seminars to help me decide. In the middle of my second year, I chose chemistry as the major subject because I thought that I would be able to contribute the most to this subject.

Much of your work focuses on asymmetric autocatalysis. Could you explain what this is and why it is important in understanding the origin of homochirality in life?

Asymmetric autocatalysis is a reaction in which the chiral product acts as a chiral catalyst for its own production. Because the structures of the catalyst and product are the same, consecutive asymmetric autocatalyses using the product of one round as the catalyst for the next significantly amplify the enantiomeric excess (ee) from extremely low to near enantiopurity. It also significantly increases the amount of product.

Living organisms use only L-amino acids and D-sugars. How this chirality originated and the method of enantioenrichment are questions of broad interest that are also related to the origin of life. Several theories have been proposed for the origin of chirality, but the ees induced by these mechanisms have been very low. Asymmetric autocatalysis could be the answer. An initial spontaneous fluctuation in the ratio of enantiomers could have led to asymmetric autocatalysis and the amplification of chirality in nature.

Asymmetric autocatalysis is not a mere purification or separation of enantiomers but an increase in the amount by self-replication, one of the essential features of life.

What else are you currently working on?

We are working on asymmetric induction in organic compounds by physical factors. We have found that quartz and circularly polarized light act as the origin of chirality to afford highly enantioenriched compounds. We have also demonstrated spontaneous absolute asymmetric synthesis, where enantioenrichment occurs without adding any chiral material. For example, the reaction between pyrimidine-5-carbaldehyde and diisopropylzinc affords enantioenriched pyrimidyl alkanol product because the initial tiny enantiometric imbalance is amplified by asymmetric catalysis. Our dream is to induce chirality in compounds by these chiral physical factors.

What do you enjoy most about your job?

The best part is that I am really interested in the research I do. The moment when a promising result is obtained, especially if it is unexpected, is very stimulating.

Chemistry is a bridge combining people with the same interests and passions. Listening to the excellent lectures, discussions and collaborations about chirality with chemists all over the world makes my life really exciting.

You have received numerous awards and honours during your career, including the Chirality Medal in 2005. What do you think is the secret to successful research?

I have been working on the enantioselective addition reaction of alkylmetal reagents to aldehydes for nearly 30 years. We reported the first asymmetric autocatalysis in 1990, but it took us another 5 years to finally find asymmetric autocatalysis with amplification of enantiopurity. We kept at it because I thought it was a really fascinating project. Persistence, therefore, may be one of the conditions necessary to obtain success.

What do you do in your spare time?

I usually go for a walk along the banks of my local river and read a book. I like to read books about history. Although at school we learned the history of heroes and politicians, we didn't learn much about the lives of normal people in ancient and medieval centuries.

If you weren't a chemist, what you be?

When I was a student, I was attracted to scientific subjects such as biology, chemistry, mathematics and geology. If I weren't a chemist, I would most likely be a biologist.

Bruker BioSpin

Just one NMR sample per hour?
Or sixteen?

CryoProbe™

The Bruker CryoProbe™ cools the NMR coils and preamplifiers to improve sensitivity by a factor of 4, and throughput by a factor of 16!

Only From Bruker...

- Over 600 cryoprobes installed in laboratories worldwide, including over 400 inverse triple resonance ^{1}H (^{13}C, ^{15}N) z-gradient Cryoprobes, used extensively for protein studies
- Sensitivity-optimised Cryoprobes for a range of nuclei (^{1}H, ^{19}F, ^{3}H, ^{13}C, ^{2}H, ^{15}N, ^{31}P, etc.)
- Available for a range of tube diameter sizes and types including 1.7mm (for small quantities), 5mm (for standard-sized samples), 10mm (for polymer applications), and shaped tubes (for high dielectric samples)
- Convertible to flow cell applications such as LC-NMR, and use with liquid handling robots
- Winner of four R&D Awards

Contact us for more details: 024 7685 5200 sales@bruker.co.uk www.bruker-biospin.com

think forward

NMR Solutions

Instant insight

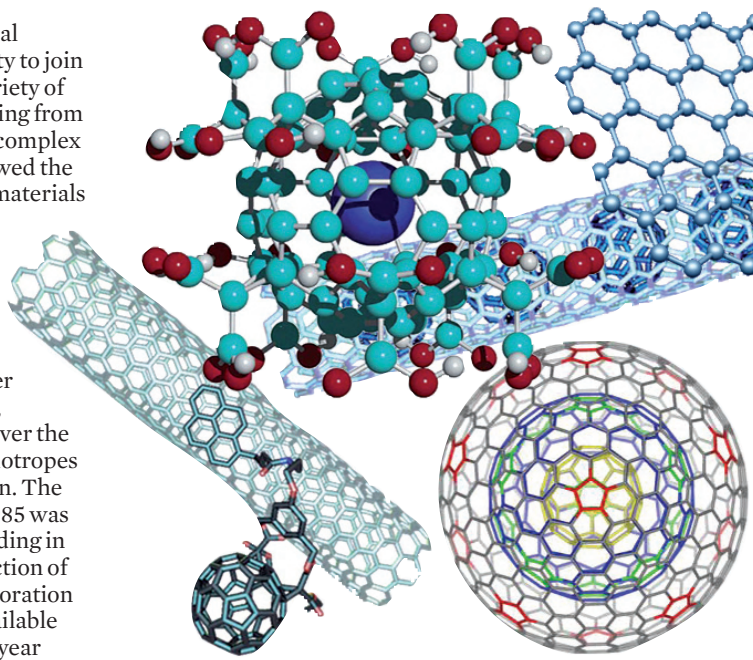
Nano-forms of carbon

Juan Luis Delgado, María Ángeles Herranz and Nazario Martín at Complutense University of Madrid, Spain, explore the cutting-edge in nanostructures made from carbon

Carbon is a singular chemical element with a unique ability to join together forming a wide variety of fascinating molecules, ranging from a few carbon atoms to long complex chains. This ability has allowed the creation of numerous new materials and molecules of interest for a very diverse range of applications.

The discovery over two decades ago that carbon can form stable and ordered structures other than graphite and diamond, stimulated researchers all over the world to search for other allotropes - structural forms - of carbon. The discovery of fullerenes in 1985 was followed by another key finding in 1990: the multigram production of C_{60} using a simple arc-evaporation apparatus that is readily available in most labs. The following year using a similar evaporator, Sumio Iijima discovered fullerene-related multiwalled carbon nanotubes (MWNTs). This was followed two years later by tubes containing only one graphitic sheet, known as single-walled carbon nanotubes. These are made by doping one of the electrodes used to produce MWNTs with metals such as Fe or Co.

Also in the early 1990s, new types of structures started to be made that consist of carbon spheres of increasing diameters layered on top of each other, akin to the wooden Russian dolls. Due to their layered design these were coined nano-onions. The nano-onions were only the tip of the iceberg, with a wide variety of new carbon nanostructures such as endohedral cup-stacked nanotubes, nanohorns, nanotori, nanobuds and graphenes now emerging as new and fascinating forms of carbon whose chemical and physical properties are currently being unravelled.



Different nanoforms of carbon

Of particular interest are endohedral fullerenes - carbon cages that encapsulate atoms or molecules in their inner space. Made using the so called 'molecular surgery' approach - the fullerene cage opens in a controlled way, allowing atoms or small molecules to enter, and then closes to reform the pristine fullerene structure. Alternatively, the interesting family of trimetallic nitride templated endohedrals are obtained directly with relatively high yields, by varying the composition of the cooling gas atmosphere in the arc-burning process used in the production of fullerenes. They have an inner metal cluster that can stabilise a large variety of carbon cages that can not exist otherwise.

Graphenes - materials that are single atomic flat layers of carbon atoms - were considered one of the biggest breakthroughs in 2007. This carbon form was found to be a useful sensor able to detect a single molecule of gas.

NASA researchers have resparked interest in the original carbon nano-onions, considering them as potential additives for aerospace applications. The nano-onions have demonstrated superior lubrication properties to other conventional lubricants, and we foresee a very promising future for these and other new and still unexplored forms of carbon.

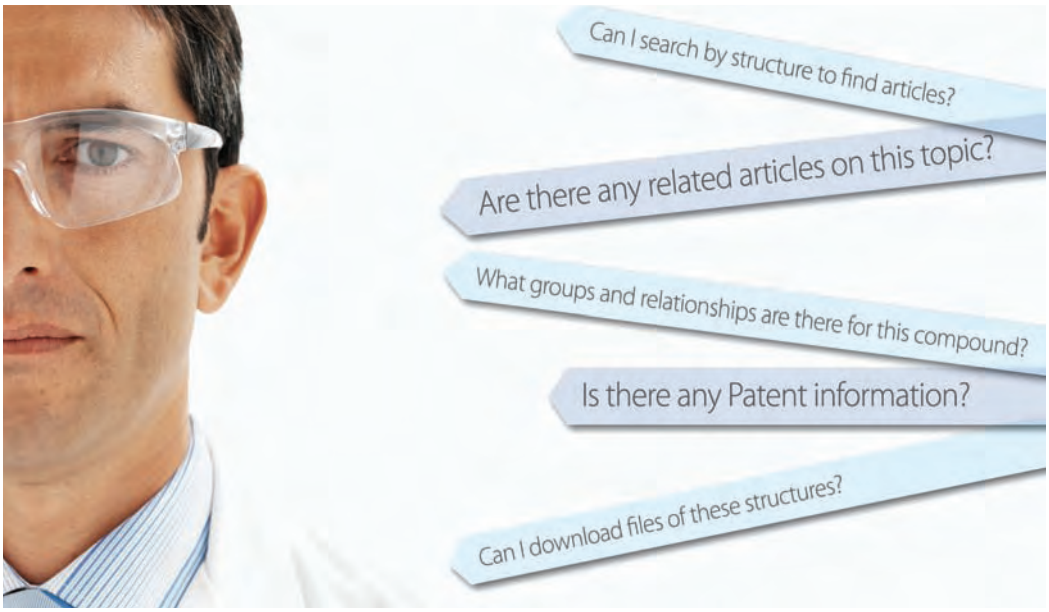
Although the scientific community are not yet entirely satisfied with all the expectations and excitement that emerged from the initial discovery of fullerenes and carbon nanotubes, the spectacular properties that these species reveal day by day will make them play an essential role in the future.

Reference
J L Delgado, M A Herranz and N Martín, *J. Mater. Chem.*, 2008, **18**, 1417 (DOI: 10.1039/b717218d)

Read Nazario Martín et al's feature article 'The nano-forms of carbon' in issue 13, 2008 of Journal of Materials Chemistry

Essential elements

Faced with questions?



Finding the answers to questions like these has just become a lot easier, thanks to the latest features introduced for *RSC Prospect* enhanced HTML articles.

Linking together related articles by subject ontologies and identified compounds, *RSC Prospect* enhanced HTML articles already provide you with definitions, synonyms, structures and RSS feeds.

One new feature that we've just introduced is a structure and sub-structure searching function to help you find relevant articles by drawing your own molecule using ChemAxon's MarvinSketch or pasting in a ChemDraw or ISIS/Draw file.

We've also widened the compound identifiers to include groups and relationships via the ChEBI (Chemical Entities of Biological Interest) ontology. Links to patent information in SureChem and to compounds in PubChem have also been added.

Winner of the 2007 ALPSP/ Charlesworth Award for Publishing Innovation, *RSC Prospect* was first released in February 2007. There are now more than 1600 articles that have been enhanced with these features.

As Richard Kidd, informatics manager at RSC Publishing says: 'We believe that the application of open and standard identifiers for both compound and subject matter will transform the future of publishing. We are proud to be leading the way amongst scientific publishers with *RSC Prospect*.'

You can read more about the new features, and view examples of articles, on the website: www.projectprospect.org

Did you know...

RSC Publishing book series provide authoritative insights into critical research, appealing to a broad cross-section of scientists in multiple disciplines. The book series cover new and emerging areas of scientific interest such as Green Chemistry, Energy, Nanoscience & Nanotechnology and Biomolecular Sciences.

Our prestigious Biomolecular Sciences series is devoted to the coverage of the interface between the chemical and biological sciences and has contributions from leading experts in the fields of structural biology, chemical biology, bio-and chemo-informatics, drug discovery and development, chemical enzymology and biophysical chemistry. This month sees the publication of two new titles to join the series.

Written by a team of experts, *Protein–Nucleic Acid Interactions: Structural Biology* bridges the gap between the DNA- and RNA-views of protein–nucleic acid recognition which are often treated as separate fields. *Therapeutic Oligonucleotides* takes a unique look at all the modern approaches and the many advances experienced in the field of protein folding and aggregation during the past 10 years. Both titles are not to be missed, and will serve as ideal reference and state-of-the-art guides at the graduate and postgraduate levels. Look out for more exciting new titles to join the Biomolecular Sciences series later this year.

For more information visit: www.rsc.org/biomolecularsciences

Chemical Science (ISSN: 1478-6524) is published monthly by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge UK CB4 0WF. It is distributed free with *Chemical Communications*, *Dalton Transactions*, *Organic & Biomolecular Chemistry*, *Journal of Materials Chemistry*, *Physical Chemistry Chemical Physics*, *Chemical Society Reviews*, *New Journal of Chemistry*, and *Journal of Environmental Monitoring*. *Chemical Science* can also be purchased separately. 2008 annual subscription rate: £199; US $396. All orders accompanied by payment should be sent to Sales and Customer Services, RSC (address above). Tel +44 (0) 1223 432360, Fax +44 (0) 1223 426017. Email: sales@rsc.org

RSC Publishing