



New Application Developments in PGMs – June 2010

Reactions in a crystal: Iridium

Chemistry World, 02 June 2010

<http://www.rsc.org/chemistryworld/News/2010/June/02061003.asp>

Image: Stacking diagram of crystals - channels in the structure allow gases to pass through, http://www.rsc.org/images/crystal-structure-410_tcm18-183449.jpg

Crystals that can alter their composition without changing the structure of their solid lattice have been developed by researchers from the Department of Chemistry, University of North Carolina at Chapel Hill. The crystals are made from an iridium complex bonded to dinitrogen (N₂), but other gases such as hydrogen (H₂) or ammonia (NH₃) can diffuse through the lattice and undergo reactions.

First images of 'heavy electrons': Ruthenium

Cornell Chronicle, 03 June 2010

<http://www.news.cornell.edu/stories/June10/HeavyFermions.html>

Image: In "heavy fermion" materials, free electrons that conduct electricity interact strongly with some atoms, pausing to dive to deep energy levels before emerging and moving on. Their slow travel time makes them appear "heavy.", <http://www.news.cornell.edu/stories/June10/fermions.jpg>

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Using an incredibly sensitive scanning tunneling microscope (STM) and a technique called "spectroscopic imaging" that measures the energy levels of electrons under the STM probe, a team led by J.C. Séamus Davis, the James Gilbert White Distinguished Professor in the Physical Sciences at Cornell and director of the Center for Emergent Superconductivity at Brookhaven National Laboratory, determined that electrons moving through a particular uranium compound appear "heavy" because their motion is constantly interrupted by interaction with the uranium atoms. Davis' team examined URu₂Si₂, composed of uranium, ruthenium and silicon, which has been a subject of much experimentation and debate since it was first synthesized 25 years ago. At about 55 kelvins (degrees above absolute zero), it begins to show heavy fermion behavior. At 17.5 kelvins it goes through a complex phase transition in which its conductivity, ability to absorb heat and other properties change.

Palladium/zinc oxide catalyst for methanol conversion

PNNL: Chemical & Materials Sciences Division: Research Highlights, June 2010

Imaging Atoms and Revolutionizing Laptop Computers

<http://www.pnl.gov/science/highlights/highlight.asp?id=777>

Professor Abhaya Datye, Director of the University of New Mexico's Center for Micro-Engineered Materials, is leading research into finding an affordable catalyst that can quickly and efficiently turn methanol into hydrogen. Part of the team's research involves imaging the interactions on the surface of the catalyst using high-powered microscopes and other instruments. To date, they've found that isolated palladium atoms migrate and end up isolated on top of columns of zinc within the zinc oxide structure. The team also found that these structures co-exist with others where zinc and palladium are together in bimetallic particles.

Catalyst goes viral: Rhodium

Latest News | Chemical & Engineering News, 11 June 2010

Nanotechnology: Material grown on a virus template performs better than catalysts grown conventionally

<http://pubs.acs.org/cen/news/88/i24/8824notw8.html>

Image: Building A Better Catalyst: The M13 bacteriophage (orange) nucleates ceria (yellow), nickel (green), and rhodium (purple) to create a nanocrystalline catalyst that can reform ethanol (shown as ball and stick) into hydrogen, http://pubs.acs.org/cen/_img/88/i24/8824NOTW_pg13.jpg

Angela Belcher and coworkers at MIT have used the M13 bacteriophage as a template for growing nanoparticles and nanowires of rhodium and nickel on ceria—a catalyst that can convert ethanol to hydrogen and is therefore promising for fuel cells. The virus-templated catalyst possesses significantly different physical properties from catalysts of identical composition grown without the M13 bacteriophage, the researchers report, including improved long-term stability and less vulnerability to surface deactivation.

Nanospheres stretch limits of hard disk storage: Platinum

ICT Results, 15 Jun 2010

<http://cordis.europa.eu/ictresults/index.cfm?section=news&tpl=article&id=91318>

A new magnetic recording medium made up of tiny nanospheres has been devised by European researchers. The technology may lead to hard disks able to store more than a thousand billion bits of information in a square inch.

With consumer PCs now being sold with hard disks of a terabyte or more – enough to record more than two years of music – storage capacity seems to be expanding without limit. But the limits are there and industry insiders know that they are approaching fast.

Present-day hard disks record information on a ferromagnetic layer. The layer is made up of grains about 7 nanometres across and each 'bit' of information is contained in a magnetised cell covering perhaps 60 to 80 grains. When the magnetic field is pointing one way a '1' is stored and when it points the opposite way a '0' is stored.

One way of packing information on to a disk would be to make the cells smaller. But with fewer grains per cell, the signal to noise ratio rises and with it the probability of a bit being misread.

The obvious answer is to use a recording medium with smaller grains, but then thermal stability problems arise. "Over time, if the thermal stability is not large enough, the magnetic orientation will flip to the opposite direction so it will lose its information," says Manfred Albrecht of the Chemnitz University of Technology.

Nanospheres

He favours a completely new approach using techniques from nanotechnology to construct a 'patterned' recording surface made up not of irregular grains but of purpose-made magnetic cells. "The problem now is how can you produce these nanostructures on a large scale at low cost?"

Albrecht coordinated the EU-funded MAFIN project which sought to build regular arrays of cells from tiny magnetised nanospheres. The spheres are made of silica and are commercially available in a range of sizes. After testing many different sizes the MAFIN team settled on spheres 25 nanometres in diameter, bigger than conventional grains but smaller than normal storage cells.

The attraction of using nanospheres is that they will assemble themselves into a regular array. The nanospheres are mixed with an alcohol-based solution that is dropped on to the substrate. As the alcohol evaporates the spheres are left in a regular pattern.

"We then deposited a magnetic film on top of the particles to form a magnetic 'cap'," Albrecht explains. "And if you do it right then this magnetic cap acts as a single magnet, with a north and a south pole, and the array can be used as a storage device."

Whether the cap is magnetised with a north or south pole upwards determines whether it is storing a '1' or a '0'.

Iron-platinum alloy

The magnetic film is an iron-platinum alloy that has already attracted interest within the magnetic storage industry. It is coated on to the nanospheres by magnetron-sputter deposition. As silica itself is non-magnetic, each cap is isolated from its neighbours and can hold its magnetisation well.

Self-assembly of the nanospheres is guided by pre-patterning of the silicate substrate by x-ray lithography to create tiny pits for the spheres to settle into.

"I believe that self-assembly-based approaches have the largest potential because they are not expensive," Albrecht says. "They are very low cost."

A spacing of 25 nanometres between spheres is equivalent to a storage density of one terabit (1000 gigabits) per square inch. Using the same approach with smaller spheres researchers should be able to attain densities up to six times higher.

As well as looking at the recording medium, MAFIN researchers have also investigated recording techniques. Iron-platinum is harder to magnetise than conventional media, so modifications will be needed to allow information to be easily recorded and read.

Opportunities for industry

The team investigated using a probe with a fine magnetic tip to magnetise and read each of spheres instead of a conventional recording head.

MAFIN finished in May 2009 but its work has carried over into a successor EU project, TERAMAGSTOR. While MAFIN was concerned with a proof of concept, the new project aims to demonstrate a hard disk with a storage density exceeding one terabit per square inch.

Albrecht sees opportunities for European industry to develop the manufacturing processes that new, nanostructured storage media will require. "In Europe we don't have a real industry that produces hard drives," he says. "It's all in Asia and the USA. But we have manufacturers of deposition tools and expertise in sputter technology."

The glass substrates of conventional hard disks will not be suitable for the high-temperature processes needed to deposit alloys, so European companies with know-how in ceramic materials may also have a role to play.

MAFIN received funding from FET – Open initiative of the EU's Sixth Framework Programme for research.

Tracking the "evolution" of nanoparticles as they decontaminate groundwater: Palladium
Lehigh University: News: News Article, 17 June 2010

<http://www4.lehigh.edu/news/newsarticle.aspx?Channel=%2fChannels%2fNews%3a+2010&WorkflowItemID=365e00ca-99a6-4165-b6e7-7569bc171531>

The aberration-corrected scanning transmission electron microscopy (STEM) used by Lehigh University researchers resolves images to 0.1 nm and allows measurement of chemical composition by X-ray energy dispersive spectroscopy (XEDS) down to the 1 nm scale. This instrument has allowed the researchers to map the surface and interior of the iron nanoparticle, locate the islands of palladium, and track the infiltration of the palladium to the particle interior.

The researchers also used X-ray photoelectron spectroscopy (XPS) to examine the changes in the chemical properties of the nanoparticles.

University of Twente develops catalysts for clean drinking water: Platinum, palladium
University of Twente, 18 June 2010.

<http://www.utwente.nl/news/ut-ontwikkelt-katalysatoren-voor-schoon-drinkwater>

Jitendra Kumar Chinthaginjala of the University of Twente has developed a catalyst that can efficiently remove nitrite and nitrate from drinking water. Chinthaginjala constructed the catalysts using extremely fine threads of carbon, a thousandth of the thickness of a human hair. Palladium or platinum nanoparticles are attached to these threads.

Mechanistic insights into the ruthenium-catalysed diene ring-closing metathesis reaction
Edwin F. van der Eide & Warren E. Piers, Nature Chemistry, 2010

<http://www.nature.com/nchem/journal/v2/n7/abs/nchem.653.html>

Ruthenium-catalysed ring-closing metathesis (RCM) is a powerful technique for the preparation of medium-to-large rings in organic synthesis, but the details of the intimate mechanism are obscure. The dynamic behaviour of an RCM-relevant ruthenacyclobutane complex and its reactivity with ethene were studied at the Department of Chemistry, University of Calgary, Canada, using low-temperature NMR spectroscopy to illuminate the mechanism of this widely used reaction.

Anomalous n-type transport observed in Pd-contacted CNTFET: Palladium
nanotechweb.org, 22 June 2010

<http://nanotechweb.org/cws/article/lab/42961>

Schematic: In the fabricated device, the presence of an individual CNT is confirmed using atomic force microscopy (AFM) operated in tapping mode, <http://images.iop.org/objects/ntw/journal/9/6/16/image1.jpg>
In a recent study, researchers from the University of Sheffield, UK, have observed for the first time an anomalous n-type (electron transport) behaviour in a palladium-contacted carbon nanotube field effect transistor (CNTFET).

Aryl rings get a fluorine fix: Palladium

Chemistry World, 24 June 2010

<http://www.rsc.org/chemistryworld/News/2010/June/24061003.asp>

A mild and effective method for coupling trifluoromethyl groups on to aryl rings has been developed by US chemists. Stephen Buchwald and his research team at the Massachusetts Institute of Technology have developed a catalytic system that can substitute aryl chlorides for CF₃ groups. The catalyst is based around palladium and one of the group's trademark biaryl phosphine ligands - BrettPhos - along with trifluoromethyl triethylsilane (Et₃Si-CF₃) and potassium fluoride.

Using nanotechnology to improve a cancer treatment: Platinum

HarvardScience, 25 June 2010

<http://harvardscience.harvard.edu/medicine-health/articles/using-nanotechnology-improve-cancer-treatment>

<http://dx.doi.org/10.1073/pnas.1007026107>

Harvard and Brigham and Women's Hospital researchers have devised a method that may allow clinicians to use higher doses of a powerful chemotherapy drug that has been limited because it is toxic not only to tumors but to patients' kidneys. The research, conducted in laboratory animals, marries chemistry and nanotechnology to deliver toxic platinum atoms to tumors while almost entirely blocking the platinum from accumulating in the kidney, according to Shiladitya Sengupta, a Harvard assistant professor of medicine and health sciences and technology whose Laboratory for Nanomedicine at Harvard-affiliated Brigham and Women's Hospital conducted the work. A novel polymer, glucosamine-functionalized polyisobutylene-maleic acid, where platinum can be complexed to the monomeric units using a monocarboxylate and an O → Pt coordinate bond was engineered. At a unique platinum to polymer ratio, this complex self-assembles into a nanoparticle, which releases cisplatin in a pH-dependent manner.

Science News: For platinum catalysts, smaller may be better

Berkeley Lab News Center, 28 June 2010

<http://newscenter.lbl.gov/feature-stories/2010/06/28/for-platinum-catalysts-smaller-may-be-better/>

Image: In these STM images of a platinum catalyst, (A) shows the terraced the surface under ultrahigh vacuum, (B) as the surface is covered with carbon monoxide and pressure increases, the terraces widen (C) when coverage is complete and press reaches one torr, the terraces fracture into nanoclusters (D) enlarged view shows triangular shape of the nanoclusters, two of which are marked by red lines, <http://newscenter.lbl.gov/wp-content/uploads/Pt-nanocluster-catalystts.jpg>

A study led by Gabor Somorjai and Miquel Salmeron of Berkeley Lab E28099s Materials Sciences Division showed that under high pressure, comparable to the pressures at which many industrial technologies operate, nanoparticle clusters of platinum potentially can out-perform the single crystals of platinum.

Functionalize silica surfaces via a robust coupling method: Rhodium, Iridium
Noteworthy Chemistry, 28 June 2010

http://portal.acs.org/portal/PublicWebSite/noteworthy/archive/CNBP_025116

Image:

http://portal.acs.org/portal/binfetch/consumption?fileUrl=/stellent/groups/web/documents/article/%7Eexpo%7Ert/CNBP_025116%7E3%7EHTML_DC_TEMPLATE%7ESNIPPET_LAYOUT/23884-4.jpg

J.-W. Park and C.-H. Jun of Yonsei University (Seoul, Korea) developed a functionalization and coupling route for inorganic substrates that uses a catalyzed, transition-metal-mediated pathway. Specifically, the authors used vinylsilanes to react with hydroxyl groups in the presence of transition metals (e.g., iridium and rhodium) and HCl on a silica surface. They chose vinylsilanes because of their hydrolytic stability and functional group versatility.

Tackling the plastic menace: Palladium(0)-triggered depolymerisation

Green machine - tech - New Scientist, 28 June 2010

<http://www.newscientist.com/article/dn19097-green-machine-tackling-the-plastic-menace.html>

Self-destruct

Scott Phillips and Wanji Seo at Pennsylvania State University in University Park have developed self-destructing plastics that could lead to packaging that is more easily recycled and friendlier to wildlife. Working with the polymer poly(phthalaldehyde), the team attached one of two chemical end groups, or "triggers" – either a silyl ether or an allyl ether – to each phthalaldehyde building block.

When a square of the polymer was exposed at room temperature to fluoride ions, the central section, where molecules were capped with the silyl ether, underwent rapid depolymerisation and broke down. Those sections capped with the allyl ether remained unchanged (Journal of the American Chemical Society, DOI: <http://dx.doi.org/10.1021/ja104420k>).

The technique could be modified to develop plastic products that quickly degrade when exposed to triggers in the environment, he says. If a bag made of the right plastic reaches the ocean, for example, microbial enzymes in the water would make the material depolymerise and "the bag just disappears", Phillips says.

By capping all the polymer sections with an end group that responds to a certain chemical, the technique could also be used as a low-energy method for recycling plastic waste, says Phillips. The resulting monomers would have to be re-polymerised to create a new plastic, but this may prove cheaper than separating different polymers before recycling can begin, he says.

Smart materials

So far the team has developed polymers with end groups that react with fluoride ions, palladium (tetrakis(triphenylphosphine)palladium(0)) and hydrogen peroxide, and they are also hoping to develop polymers that respond to enzymes, he says.

The team cautions that the research is still at the proof-of-concept stage. Work remains to be done to find polymers that break down into substances that are more environmentally friendly than phthalaldehyde. Another problem is that the polymers they have so far made are sensitive to acidity and need to be more stable to be usable.

For more scientific research papers on platinum group metals go to: www.platinummetalsreview.com