

# Highlights from recent literature

For further highlights and analysis of recent gold-based publications please see the *Gold Bulletin* blog [www.goldinnovationsblog.com](http://www.goldinnovationsblog.com)

## 1 Analytical

### 1.1 Gold-coated zinc oxide nanowire-based substrate for surface-enhanced raman spectroscopy

Zinc oxide nanowires with two distinct morphologies were synthesized on silicon substrates using a simple thermal evaporation and vapor transport method in an oxidizing environment. Muhammad A. Khan, Timothy P. Hogan, B. Shanker, *Journal of Raman Spectroscopy*, **40**, 1539. The as-synthesized nanowires were coated with gold to allow excitation of surface plasmons over a broad frequency range. SERS studies with near-IR excitation at 785 nm showed significant enhancement (average enhancement  $> 10^6$ ) with excellent reproducibility to detect monolayer concentrations of 4-methylbenzenethiol (4-MBT) and 1,2-benzendithiol (1,2-BDT) probe molecules. The Raman enhancement showed a strong dependence on the gold film thickness, and the peak enhancement was observed for a  $\sim 40$ -nm-thick film. The Raman enhancement was stronger for randomly oriented nanowires compared to aligned ones suggesting the importance of contributions from the junctions of nanowires.

## 2 Catalysis

### 2.1 Direct synthesis of $H_2O_2$ from $H_2$ and $O_2$ over gold, palladium, and gold-palladium catalysts supported on acid-pretreated $TiO_2$

Palladium-ringed gold: The acid-pretreated Au-Pd catalysts supported on  $TiO_2$  have a well-defined gold-rich core and palladium-rich shell. Jennifer K. Edwards, Edwin Ntainjua N, Albert F. Carley, Andrew A. Herzing, Christopher J. Kiely, Graham J. Hutchings, *Angewandte Chemie International Edition*, Vol 48, issue 45, 2009, 8512. This type of core and shell enhances the catalytic activity of the catalyst for the direct synthesis of  $H_2O_2$  from  $H_2$  and  $O_2$ .

### 2.2 Towards sustainable homogeneous gold catalysis: Cycloisomerization of functionalized allenes in water

In this study, chloroauric acid ( $HAuCl_4$ ) is used as a catalyst in water for the stereoselective cycloisomerization of various functionalized allenes to five- or six-membered oxygen- or nitrogen-containing heterocycles. Christian Winter and Norbert Krause, *Green Chem.*, 2009, **11**, 1309. Compared to traditional gold catalysts in organic solvents, this new catalytic system is more environmentally friendly, and the gold catalyst can be reused after complete conversion of the substrate.

### 2.3 Selective formation of lactate by oxidation of 1,2-propanediol using gold palladium alloy supported nanocrystals

The use of bio-renewable resources, such as glycerol, a by-product from bio-diesel manufacture, can provide a viable way to make valuable products using greener technology. In particular, glycerol can be reduced to give 1,2-propanediol that can then be selectively oxidised to lactate, which has immense potential as a monomer for the synthesis of biodegradable polymers. Nikolaos Dimitratos, Jose Antonio Lopez-Sanchez, Sankar Meenakshisundaram, Jinto Manjaly Anthonykutty, Gemma Brett, Albert F. Carley, Stuart H. Taylor, David W. Knight and Graham J. Hutchings, *Green Chem.*, 2009, **8**, 1209. The authors show that gold-palladium alloy catalysts can be very effective for the selective oxidation of 1,2-propanediol to lactate. Two supports,  $TiO_2$  and carbon, and two preparation methods, wet impregnation and sol-immobilisation, are contrasted. The addition of palladium to gold significantly enhances the activity and retains the high selectivity to lactate using  $O_2$  as oxidant (we observe 96% lactate selectivity at 94% conversion). Use of hydrogen peroxide is also possible but lower activities are observed as a result of the reaction conditions, but in this case no marked enhancement is observed on addition of palladium to gold. Comparison of the activity for  $C_3$  alcohols shows that the reactivity decreases in the order: glycerol  $>$  1,2-propanediol  $>$  1,3-propanediol  $\sim$  1-propanol  $>$  2-propanol. The use of a sol-immobilisation preparation method as compared to impregnation leads to alloy catalysts with the highest activity for lactate formation from the oxidation of 1,2-propanediol; the origins of these activity trends are discussed.

## 2.4 Application of copper-gold alloys in catalysis: Current status and future perspectives

The use of nanoalloys in catalysis is a rapidly expanding field. There has been immense interest in the use of supported gold nanoparticles as catalysts, and bimetallic catalysts containing gold in combination with other metals represents an emerging field of research. Bracey CL, Ellis PR, Hutchings GJ., *Chem Soc Rev.* 2009 **38**(8):2231. While bulk copper-gold alloys are well-known and, indeed, are much studied systems, bimetallic copper-gold nanoalloys have received relatively little attention. In this tutorial review we review the literature on bimetallic CuAu catalysts and present some options for their future development.

## 2.5 Deposition of gold nanoparticles on carbons for aerobic glucose oxidation

Carbon materials such as activated carbon and carbon black have long been used as adsorbents, electrodes, and supports for metal catalysts. However, no attempt has yet been reported to deposit Au as small nanoparticles (NPs) on these carbon materials directly from Au precursor compounds. Until now, the most effective way to support Au NPs on activated carbon was to physically mix a carbon support with Au colloids prepared beforehand. Here the authors report that Au could be deposited as NPs on carbon materials directly from gold precursor compounds by deposition reduction method and by solid grinding method. Hiroko Okatsu, Naoto Kinoshita, Tomoki Akita, Tamao Ishida, Masatake Haruta, *Applied Catalysis A: 369*, 8. In particular, the solid grinding of carbons with dimethyl Au(III) acetylacetonate, which has a certain degree of vapor pressure at room temperature, is a simple technique but surprisingly effective to deposit Au NPs with a mean diameter as small as 1.9 nm. These highly dispersed Au NPs on carbon supports were tested for glucose oxidation in water with molecular oxygen. A Au/nanoporous carbon (NPC) catalyst which exhibited relatively high catalytic activity has been kinetically studied for comparison with Au/metal oxides catalysts.

## 2.6 Enantioselective one-pot organocatalytic Michael addition/gold-catalyzed tandem acetalization/cyclization

A one-pot process consisting of a Michael addition to a nitroenzyme and a subsequent acetalization/cyclization is reported, which results in the formation of nitro-substituted tetrahydrofuranyl ethers with high diastereo- and enantioselectivities. Organocatalysis and gold catalysis are compatible

and complementary in a one-pot process. Sébastien Belot, Kim A. Vogt, Céline Besnard, Norbert Krause and Alexandre Alexakis, *Angewandte Chemie International Edition*, **48**, 8923.

## 2.7 On the mechanism of hydrogen-promoted gold-catalyzed CO oxidation

The kinetics of CO oxidation, H<sub>2</sub> oxidation and preferential CO oxidation (PrOx) over Au/Al<sub>2</sub>O<sub>3</sub> catalysts have been investigated. Elodie Quinet, Laurent Piccolo, Franck Morfin, Priscilla Avenier, Fabrice Diehl, Valérie Caps and Jean-Luc Rousset, *Journal of Catalysis*, **268**, 2009, 384. The catalysts with the smallest particles (~2 nm) are the most active for all three reactions. As previously observed, the presence of H<sub>2</sub> greatly promotes CO oxidation, which becomes faster than CO-free H<sub>2</sub> oxidation at low temperature. From these results and on the basis of previous works, we propose a complete PrOx mechanism. The reaction involves Au–OOH, Au–OH and Au–H intermediates, also involved in H<sub>2</sub> oxidation, and benefits from the presence of low-coordination sites.

## 2.8 Gold-catalyzed [3+3]-annulation of azomethine imines with propargyl esters

The gold-catalyzed [3+3]-cycloaddition reaction of propargyl esters and azomethine imines has been developed. The reaction provides a rapid entry into a wide range of substituted tetrahydropyridazine derivatives from simple starting materials. Nathan D. Shapiro, Yun Shi and F. Dean Toste, *J. Am. Chem. Soc.*, 2009, **131** (33), 11654. A stepwise mechanism involving addition of the 1,3-dipole to a gold-carbenoid intermediate is proposed

## 2.9 Supported gold catalysts for the decomposition of VOC: Total oxidation of propene in low concentration as model reaction

Supported gold catalysts prepared by deposition-precipitation with urea were studied in the reaction of oxidation of propene in low concentration in a large excess of oxygen, so as to mimic the conditions of catalytic decomposition of a volatile organic compound of hydrocarbon-type (1200ppm C<sub>3</sub>H<sub>6</sub>, 9% O<sub>2</sub> in He). Laurent Delannoy, Katia Fajerweg, Pandian Lakshmanan, Claude Potvin, Christophe Méthivier and Catherine Louis, *Applied Catalysis B: Environmental*, **94**, 117. Several parameters were investigated: the nature of the oxide support (alumina, titania, ceria), the gold loading, the conditions of catalyst activation (oxygen or hydrogen). Titania and alumina alone did not show any conversion

in  $C_3H_6$  oxidation up to 500°C, but when gold was added (1wt%), active catalysts were obtained with a higher activity for titania than for alumina. Ceria was the only support showing activity, and gold on ceria (1 wt%) led to the most active catalyst. For the Au/CeO<sub>2</sub> system, activation under H<sub>2</sub> at 300°C leads to more active catalysts than activation in O<sub>2</sub>/He at 500°C, especially for gold loadings lower than 1 wt%. XPS and CO oxidation performed at RT showed that gold on CeO<sub>2</sub> was fully reduced to Au<sub>0</sub> after activation under H<sub>2</sub> whatever the gold loading. In contrast, after calcination, most of the gold remained under the initial AuIII state for the low loaded samples ( $\leq 1$  wt%) whereas part of it was reduced for the 4 wt% Au/CeO<sub>2</sub>. Thus, ceria seems to be able to stabilise gold as AuIII up to a limited loading. Change in the gold oxidation state was detected for the calcined Au/CeO<sub>2</sub> (1wt%) during  $C_3H_6$  oxidation performed at increasing temperature, using CO oxidation and DRIFTS combined to CO adsorption. Indeed, gold, initially AuIII, starts reducing at 100°C to form metallic gold Au<sub>0</sub>, which was the active species for the reaction. Above 300°C, when 100% conversion was achieved, reoxidation of metallic gold species was observed.

### 3 Electrochemistry

#### 3.1 Performance of gold-coated titanium bipolar plates in unitized regenerative fuel cell operation

The corrosion of the carbon-based bipolar plate was studied under unitized regenerative fuel cell (URFC) operation conditions. At overpotentials higher than 2.0 V vs. normal hydrogen electrode (NHE), cell performance in the electrolyzer mode significantly decreases with time due to the increased ohmic resistance of the carbon-based bipolar plates. During fuel cell operation, the unit cell shows an ohmic resistance of approximately 0.15  $\Omega$ . Ho-Young Jung, Sheng-Yang Huang, Prabhu Ganesan, Branko N. Popov, *Journal of Power Sources*, **194**, 2009, 972. After the operation in the electrolyzer mode, the ohmic resistance of the cell increases up to 1.24  $\Omega$ . The surface image of the carbon-based bipolar plate after water electrolysis reaction at 2.0 V shows a drastic corrosion at the contact area of the bipolar plate with the electrode. The corrosion of the rib in the flow-field increases the contact resistance between the electrode and the bipolar plate, which leads to the observed decrease in cell performance. A gold coating of 1  $\mu$ m on the titanium bipolar plates is very effective in preventing titanium oxidation during the URFC operation. The

ohmic resistance of the cells that are prepared with bare titanium and gold-deposited titanium bipolar plates is 0.40  $\Omega$  and 0.18  $\Omega$ , respectively. In fact, the gold coating serves as a barrier layer, which inhibits the formation of the passive layer on the surface of titanium-based bipolar plates. The cycling experiments in the fuel cell and in the electrolyzer mode indicate that the gold-coated titanium bipolar plates exhibit a stable performance.

#### 3.2 Electrocatalytic oxidation of formic acid on functional MWCNTs supported nanostructured Pd–Au catalyst

In this work, PdAu nanocatalysts with different weight ratio of Pd and Au supported on functional multi-walled carbon nanotubes (f-MWCNTs) were prepared, and their electrocatalytic activity for the oxidation of formic acid was also studied. Shuxian Zhang, Ming Qing, Hui Zhang and Yanni Tian, *Electrochemistry Communications*, **11**, 2009, 2249. The electrocatalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrochemical results showed that the 4Pd1Au/f-MWCNTs (by weight) catalyst, exhibited distinctly higher activity and better stability in formic acid electrooxidation than the Pd/f-MWCNTs catalyst. The Nano-Au improves potentially the performance of Pd-based electrocatalysts for the direct formic acid fuel cells (DFAFCs).

### 4 Electronics and sensors

#### 4.1 Optical characterization for nearly spherical gold colloids via their polarization response

The authors optically characterized colloidal gold nanoparticles using polarized light scattering which is utilized to investigate both optical anisotropy and aspect ratio of the particle and to observe particle's rotational dynamics. Bassam M. Al-Qadi and Toshiharu Saiki, *J. Nanophoton.*, **3**, 039503(2009); doi:10.1117/1.3257622. By monitoring time-trace of the polarized scattering from a particle, they could observe rotational dynamics as fluctuations in the measured anisotropy. With typical particle dimension of 97 nm, the maximum anisotropy was measured experimentally to be 0.1 to 0.5, and with comparison to our analytical model, this range is equivalent to an aspect ratio range of 1 to 1.3, which reveals that the colloids are predominantly spherical as predicted by transmission electron microscope (TEM) images analysis. The method has the advantage to be simple, easy to implement, and can yield access to different projections of the particle due to its rotation.

Polarized light scattering can be an ultrasensitive measure for biosensing applications

## 5 Medical and dental

### 5.1 Cellular uptake and toxicity of gold nanoparticles in prostate cancer cells: A comparative study of rods and spheres

Using a series of gold nanoparticles with incremental increase in dimensions but varying geometries (spherical vs rods) we have evaluated the influence of shape, size, surface properties and concentration on cellular uptake, adsorption of proteins and toxicity in a human prostate cancer cell line (PC-3). Arnida, Alexander Malugin, Hamidreza Ghandehari, *Journal of Applied Toxicology, Early View* (Articles online in advance of print). In the range of 30-90 nm diameter studied, spherical particles of 50 nm in diameter without polyethylene glycol (PEG) had the highest uptake. Surface attachment of PEG reduced cellular uptake. PEGylated gold nanorods had a net positive charge compared with their spherical counterparts and particle geometry influenced cellular uptake. In the absence of serum proteins the uptake of plain spherical GNPs increased. These studies pave the way for the tailoring of gold nanoparticles for targeted tumor therapy applications.

### 5.2 Smart drug-loaded polymer gold nanoshells for systemic and localized therapy of human epithelial cancer

Near-infrared-light-sensitive multifunctional smart drug-loaded polymer gold nanoshells are fabricated as advanced prototypes, composed of chemotherapeutic agents (therapeutic antibody and anticancer drug-loaded polymeric nanoparticles) for systemic chemotherapy of human epithelial cancer and a polymer-based gold nanoshell for localized photothermal treatment by NIR light.

### 5.3 Challenging gold based filler metals for uses in medicine

Research has been carried out to investigate new soldering materials and technologies for the medical field. Bobzin, K., Lugscheider, E. Ernst, F., Rösing, J., Ferrara, S., *Materials Science and Technology*, **25**, 2009, 1422. The two soldering techniques, which have been considered, are diffusion and active soldering. In order to satisfy the most important medical requirement, the biocompatibility, gold based solders and soldering systems have been studied. According to the Directive 2002/95/EC of the European Parliament, lead as well as cadmium, hexavalent chromium and mercury have not been

alloyed in the developed solders. The examined soldering systems enable joining similar and dissimilar materials, which is essential in the field of hybrid microsystems engineering. Furthermore, the achieved low process temperatures reduce the incidence of damage and thermally induced stresses in the components being joined.

### 5.4 Intravenously administered gold nanoparticles pass through the blood-retinal barrier depending on the particle size, and induce no retinal toxicity

The retina maintains homeostasis through the blood-retinal barrier (BRB). Although it is ideal to deliver the drug to the retina via systemic administration, it is still challenging due to the BRB strictly regulating permeation from blood to the retina. Jeong Hun Kim, Jin Hyung Kim, Kyu-Won Kim, Myung Hun Kim and Young Suk Yu, *Nanotechnology*, 2009, **20**, 505101. Herein, the authors demonstrated that intravenously administered gold nanoparticles could pass through the BRB and are distributed in all retinal layers without cytotoxicity. After intravenous injection of gold nanoparticles into C57BL/6 mice, 100 nm nanoparticles were not detected in the retina whereas 20 nm nanoparticles passed through the BRB and were distributed in all retinal layers. 20 nm nanoparticles in the retina were observed in neurons ( $75 \pm 5\%$ ), endothelial cells ( $17 \pm 6\%$ ) and periendothelial glial cells ( $8 \pm 3\%$ ), where nanoparticles were bound on the membrane. In the retina, cells containing nanoparticles did not show any structural abnormality and increase of cell death compared to cells without nanoparticles. Gold nanoparticles never affected the viability of retinal endothelial cells, astrocytes and retinoblastoma cells. Furthermore, gold nanoparticles never led to any change in expression of representative biological molecules including zonula occludens-1 and glut-1 in retinal endothelial cells, neurofilaments in differentiated retinoblastoma cells and glial fibrillary acidic protein in astrocytes. Therefore, our data suggests that small gold nanoparticles (20nm) could be an alternative for drug delivery across the BRB, which could be safely applied *in vivo*.

### 5.5 Inhibition of tumor proteasome activity by gold-dithiocarbamate complexes via both redox-dependent and -independent processes

We have previously reported on a gold(III) complex, namely  $[\text{AuBr}_2(\text{DMDT})]$  (*N,N*-dimethyldithiocarbamate) showing potent *in vitro* and *in vivo* growth inhibitory activities toward

human cancer cells and identifying the cellular proteasome as one of the major targets. However, the importance of the oxidation state of the gold center and the involved mechanism of action has yet to be established. Xia Zhang, Michael Frezza, Vesna Milacic, Luca Ronconi, Yuhua Fan, Caifeng Bi, Dolores Fregona, Q. Ping Dou, *Journal of Cellular Biochemistry*, **109**, 2009,162. Here we show that both gold(III)- and gold(I)-dithiocarbamate species, namely  $[\text{AuBr}_2(\text{ESDT})]$  (AUL12) and  $[\text{Au}(\text{ESDT})_2]$  (AUL15), could inhibit the chymotrypsin-like activity of purified 20S proteasome and 26S proteasome in human breast cancer MDA-MB-231 cells, resulting in accumulation of ubiquitinated proteins and proteasome target proteins, and induction of cell death, but at significantly different levels. Gold(I)- and gold(III)-compound-mediated proteasome inhibition and cell death induction were completely reversed by the addition of a reducing agent, dithiothreitol or *N*-acetyl-L-cysteine, suggesting the involvement of redox processes. Furthermore, treatment of MDA-MB-231 cells with gold(III) compound (AUL12), but not the gold(I) analog (AUL15), resulted in the production of significant levels of reactive oxygen species. Our study provides strong evidence that the cellular proteasome is an important target of both gold(I) and gold(III)-dithiocarbamates, but distinct cellular mechanisms of action are responsible for their different overall effect.

### 5.6 Anticancer therapeutics that target selenoenzymes: Synthesis, characterization, in vitro cytotoxicity, and thioredoxin reductase inhibition of a series of gold(I) complexes containing hydrophilic phosphine ligands

Gold(I) complexes bearing water-soluble phosphine ligands, including 1,3,5-triaza-7-phosphaadamantane (PTA), 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA), and sodium triphenylphosphine trisulfonate (TPPTS), in combination with thionate ligands, were screened for their antiproliferative activities against human ovarian cancer cell lines A2780 either sensitive or resistant to cisplatin. Elena Vergara, Angela Casini, Francesca Sorrentino, Olivier Zava, Elena Cerrada, Maria Pia Rigobello, Alberto Bindoli, Mariano Laguna and Paul J. Dyson, *ChemMedChem*, **5**, 96 In addition, the compounds were screened for their inhibition of mammalian thioredoxin reductases (TrxR), enzymes that are over expressed in many tumor cells and contribute to drug resistance. The gold(I)-phosphine complexes efficiently inhibited cytosolic and mitochondrial TrxRs at concentrations that did

not affect the related oxidoreductase glutathione reductase (GR). Additional complementary information on the enzyme metallation process and potential gold binding sites was obtained through the application of a specific biochemical assay using a thiol-tagging reagent, BIAM (biotin-conjugated iodoacetamide).

## 6 Metallurgy, materials and coatings

### 6.1 Noble metal nanoparticles for water purification: A critical review

Water is one of the essential enablers of life on earth. Beginning with the origin of the earliest form of life in seawater, it has been central to the evolution of human civilizations. T. Pradeep, Anshup, *Thin Solid Films*, **517**, 2009, 6441. Noble metals have been similarly associated with the prosperity of human civilizations through their prominent use in jewellery and medical applications. The most important reason for the use of noble metals is the minimal reactivity at the bulk scale, which can be explained by a number of concepts such as electrochemical potential, relativistic contraction, molecular orbital theory, etc. Recently, water quality has been associated with the development index of society. A number of chemical and biological contaminants have endangered the quality of drinking water. An overview of important events during last 200 years in the area of drinking water purification is presented. Realizing the molecular nature of contamination in drinking water, significant progress has been made to utilize the chemistry of nanomaterials for water purification. This article summarizes recent efforts in the area of noble metal nanoparticle synthesis and the origin of their reactivity at the nanoscale. The application of noble metal nanoparticle based chemistry for drinking water purification is summarized for three major types of contaminants: halogenated organics including pesticides, heavy metals and microorganisms. Recent efforts for the removal, as well as ultralow concentration detection of such species, using noble metal nanoparticles are summarized. Important challenges during the commercialization of nano-based products are highlighted through a case study of pesticide removal using noble metal nanoparticles. Recent efforts in drinking water purification using other forms of nanomaterials are also summarized. The article concludes with recent investigations on the issue of nanotoxicity and its implications for the future.

## 6.2 Adsorption of gold on hydrogen terminated Si(001): Formation of chain structure

Possible formation of stable Au atomic wire on the hydrogen terminated Si(001):  $3\times 1$  surface is investigated under the density functional formalism. Bikash C. Gupta, Shyamal Konar and Rudra P. Bose, *Applied Surface Science*, **256**, 2009, 495. The hydrogen terminated Si(001):  $3\times 1$  surface is patterned in two different ways by removing selective hydrogen atoms from the surface. The adsorption of Au on such surfaces is studied at different sub-monolayer coverages. At  $4/9$  monolayer (ML) coverage, zigzag continuous Au chains are found to be stable on the patterned hydrogen terminated Si(001):  $3\times 1$  surface. The reason for the stability of the wire structures at  $4/9$  ML coverage is explained. It is to be noted that beyond  $4/9$  ML coverage, the additional Au atoms may introduce clusters on the surface. The continuous atomic gold chains on the substrate may be useful for the fabrication of atomic scale devices

## 6.3 A brief review of selected aspects of the materials science of ball bonding

Thermosonic ball bonding is a metallurgical process that until recently was rarely the subject of metallurgical analysis. C.D. Breach and F.W. Wulff, *Microelectronics Reliability*, **50**, 2010, 1. However, in recent years greater focus has been given to the materials science of thermosonic ball-wedge bonding in an attempt to better control and advance its application as an interconnect technology in advanced packaging. As with most materials processes, establishing a scientific understanding of the process requires knowledge from various sub-disciplines of physical science. This article briefly reviews selected aspects of the materials science of ball bonding, particularly using gold wire, focusing on 1st and 2nd bond formation and intermetallic growth.

## 6.4 Microstructure changes in nanoparticulate gold films under different thermal atmospheres and the effects on bondability

Sintering in a furnace under different thermal atmospheres of air, nitrogen (N<sub>2</sub>) or N<sub>2</sub> bubbled through formic acid (FA/N<sub>2</sub>) was carried out for a spin-coated gold nanoparticle (NP) ink. Seonhee Jang, Jaewoo Joung and Yongsoo Oh, *Acta Materialia*, **57**, 2009, 5613. Temperatures of 200, 250 and 290°C were applied for each atmosphere. The size of the NPs was measured by transmission electron microscopy and the decomposition temperatures of the solvent and the organic capping molecules of the

ink were determined by thermo-gravimetric analysis. The changes in the microstructure of Au NP films after sintering were studied using the field emission scanning electron microscopy, X-ray diffractometry, atomic force microscopy and focused ion beam analysis. Organic residues remaining on the film were detected by Fourier transform infrared spectroscopy and sheet resistance was measured using a four point probe for the calculation of resistivity. Wire bonding tests on the Au film were performed for bondability. The Au NP films sintered under air showed neck growth as temperature increased, while the films sintered under N<sub>2</sub> showed grain growth, except for the film sintered at 290°C. Coalescence and grain growth as well as porosity were observed in the film sintered under FA/N<sub>2</sub>. The infrared absorption peaks of stretch and deformation were found as organic residues, with C–O stretch peak only being detected in the film sintered under FA/N<sub>2</sub>. All of the samples represented a preferred Au (1 1 1) orientation. The film sintered under N<sub>2</sub> showed good quality compared with those sintered under air or FA/N<sub>2</sub> and the resistivity was about twice the bulk value. Wire bonding tests were successful in all the films sintered under air, N<sub>2</sub> or FA/N<sub>2</sub> atmospheres.

## 7 Nanotechnology

### 7.1 Facile synthesis of PtAu alloy nanoparticles with high activity for formic acid oxidation

The authors report the facile synthesis of carbon supported PtAu alloy nanoparticles with high electrocatalytic activity as anode catalysts for direct formic acid fuel cells (DFAFCs). PtAu alloy nanoparticles are prepared by co-reducing HAuCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> with NaBH<sub>4</sub> in the presence of sodium citrate and then deposited on Vulcan XC-72R carbon support (PtAu/C). Sheng Zhang, Yuyan Shao, Geping Yin and Yuehe Lin, *Journal of Power Sources*, 195, **4**, 2010, 1103. The obtained catalysts are characterized with X-ray diffraction (XRD) and transmission electron microscope (TEM), which reveal the formation of PtAu alloy nanoparticles with an average diameter of 4.6nm. Electrochemical measurements show that PtAu/C has seven times higher catalytic activity towards formic acid oxidation than Pt/C. This significantly enhanced activity of PtAu/C catalyst can be attributed to noncontinuous Pt sites formed in the presence of the neighbored Au sites, which promotes direct oxidation of formic acid.

## 7.2 The morphology of Au@MgO nanopeapods

The structure of metal nanoparticles embedded inside dielectric nanowires/nanotubes, namely nanopeapods, has been of increasing interest due to their unusual photoresponse and optical adsorption properties. This paper presents a type of new inorganic nanopeapod: faceted Au nanoparticles inside MgO nanowires. W.W. Zhou, L. Sun, T. Yu, J.X. Zhang, H. Gong and H.J. Fan, *Nanotechnology* **20**, 2009, 455603. The Au self-assembles into a nanoparticle chain during the vapor-liquid-solid growth of the MgO nanowires for which gold also serves as the catalyst. Surprisingly such a chain can follow the whole axis of the MgO nanowires even if the latter zigzag, provided that the amount of gold is sufficient. It is shown that such Au@Mg nanopeapods form not only under metallorganic chemical vapor deposition conditions (Lai et al 2009 *Appl. Phys. Lett.* **94** 022904), but also under their conventional vapor transport deposition condition. This new nanopeapod material might be a candidate for the study of electronic and/or plasmonic wave transport along nanowires.

## 7.3 Polyvalent oligonucleotide gold nanoparticle conjugates as delivery vehicles for platinum(IV) warheads

Amine-functionalized polyvalent oligonucleotide gold nanoparticles (DNA-Au NPs) were derivatized with a cisplatin prodrug, and the resulting DNA-Au NP conjugates were used to internalize multiple platinum centers. Shanta Dhar, Weston L. Daniel, David A. Giljohann, Chad A. Mirkin and Stephen J. Lippard, *J. Am. Chem. Soc.*, 2009, **131** 41, 14652. A platinum(IV) complex, c,c,t-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(OH)(O<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)], was tethered to the surface of DNA-Au NPs through amide linkages. The platinum-tethered gold nanoparticles were taken into several cancer cells. The drop in intracellular pH facilitated reductive release of cisplatin from the prodrug, which then formed 1,2-d(GpG) intrastrand cross-links in the cell nuclei, as confirmed by an antibody specific for this adduct. The cytotoxicity of the platinum(IV) complex increases significantly in several cancer cell lines when the complex is attached to the surface of the DNA-Au NPs and in some instances exceeds that of cisplatin.

## 7.4 Facile strategy for stability control of gold nanoparticles synthesized by aqueous reduction method

A facile strategy for controlling sizes and stabilities of gold nanoparticles synthesized by aqueous reduction method was experimentally examined and

reported. Tanyakorn Muangnapoh, Noriaki Sano, Shin-Ichi Yusa, Nawin Viriya-empikul and Tawatchai Charinpanitkul, *Current Applied Physics*, **10**, 2010, 708. When pH of the solution of HAuCl<sub>4</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> was controlled by introducing either NaOH or HCl with different concentration, the zeta potential of suspension of gold nanoparticles changed accordingly. With the strategy using a control of pH in a range of 5–9, the zeta potential of synthesized gold nanoparticles was regulated in a range of –60 to –40 mV, resulting in a stable red suspension of gold nanoparticles. Under a condition with pH < 5.0, gold nanoparticles could agglomerate after being kept quiescently for a day due to an adsorption of H<sup>+</sup> on their surface, which in turn enhanced the attractive van der Waals interaction. On the other hand, synthesis of gold nanoparticles with pH > 9.1 would provide a lower amount of gold nanoparticles due to the formation of NaAuO<sub>2</sub>. Based on these results, a potential mechanism of gold nanoparticle synthesis was also discussed.

## 7.5 Multimodal gadolinium-enriched DNA-gold nanoparticle conjugates for cellular imaging

A Gd<sup>III</sup> enriched DNA-AuNP conjugate for intracellular magnetic resonance and fluorescence imaging is reported. The agent exhibits high relaxivity per particle and high cell uptake properties that provide a means to image and map small cell populations. Ying Song, Xiaoyang Xu, Keith W. MacRenaris, Xue-Qing Zhang, Chad A. Mirkin, Thomas J. Meade, *Angewandte Chemie International Edition*, **48**, 9143.

## 7.6 Modulation of DNA polymerases with gold nanoparticles and their applications in hot-start PCR

A new gold-nanoparticle (AuNP)-based strategy to dynamically modulate the activity of DNA polymerases and realize a hot-start (HS)-like effect in the polymerase chain reaction (PCR) is reported, which effectively prevents unwanted nonspecific amplification and improves the performance of PCRs. Lijuan Mi, Yanqin Wen, Dun Pan, Yanhong Wang, Chunhai Fan, Jun Hu, *Small*, **5** 22, 2597. A high-fidelity Pfu DNA polymerase is employed as the model system. Interestingly, AuNPs inactivate the polymerase activity of Pfu at low temperature, thus resembling an antibody-based HS PCR. This inhibition effect of AuNPs is demonstrated for the preamplification polymerization activity of the PCR, which largely suppresses nonspecific amplification at temperatures between 30 and 60°C and leads to highly specific and sensitive PCR amplification with Pfu. Significantly, the fidelity of Pfu is not sacrificed

in the presence of AuNPs. Therefore, this AuNP-based HS strategy provides a straightforward and potentially versatile approach to realize high-performance PCR amplification.

### 7.7 Defect-free nanostructured alumina coating doped with noble metal nanoparticles

Nanostructured alumina coatings loaded with platinum or gold nanoparticles were prepared by two different methods. In the first method the alumina coatings were prepared in the presence of metal ions, which were reduced using UV irradiation once the film was deposited. In the second method, polyvinylpyrrolidone-stabilized nanoparticles were first synthesized and then incorporated in the coating. Miroslava Malenovska, Marie-Alexandra Neouze, Ulrich Schubert, Veronique Monnier, Emmanuel Scolan and Raphael Pugin, *Applied Surface Science*, **256**, Supplement 1, 2009, Pages S9. The texturation of the coating occurred in a last step by hot water treatment.

### 7.8 Quantitative investigation of compartmentalized dynamics of ErbB2 targeting gold nanorods in live cells by single molecule spectroscopy

Understanding the diffusion dynamics and receptor uptake mechanism of nanoparticles in cancer cells is crucial to the rational design of multifunctional nanoprobe for targeting and delivery. Jiji Chen and Joseph Irudayaraj. *ACS Nano* (2009), **3(12)**, 4071. In this report, for the first time, we quantify the localization and evaluate the diffusion times of Herceptin-conjugated gold nanorods (H-GNRs) in different cell organelles by fluorescence correlation spectroscopy (FCS) and examine the endocytic diffusion of H-GNRs in live ErbB2 overexpressing SK-BR-3 cells. First, by colocalizing H-GNRs in different cellular organelles depicted by the respective markers, we demonstrate that H-GNRs colocalize with the endosome and lysosome but not with the Golgi apparatus. Our study shows that Herceptin-conjugated GNRs have similar intracellular localization characteristics as Herceptin–ErbB2 complex, with a higher concentration found in the endosome ( $72 \pm 20.6$  nM) than lysosome ( $9.4 \pm 4.2$  nM) after internalization. The demonstrated approach and findings not only lay the foundations for a quantitative understanding of the fate of nanoparticle-based targeting but also provide new insights into the rational design of nanoparticle delivery systems for effective treatment.

### 7.9 Branched nanotrees with immobilized acetylcholine esterase for nanobiosensor applications

A novel lab-on-a-chip nanotree enzyme reactor is demonstrated for the detection of acetylcholine. Klas Risveden, Kimberly A. Dick, Sunil Bhand, Patrik Rydberg, Lars Samuelson and Bengt Danielsson. *2010 Nanotechnology* **21** 055102 (8pp). The reactors are intended for use in the RISFET (regional ion sensitive field effect transistor) nanosensor, and are constructed from gold-tipped branched nanorod structures grown on SiN<sub>x</sub>-covered wafers. Two different reactors are shown: one with simple, one-dimensional nanorods and one with branched nanorod structures (nanotrees). Significantly higher enzymatic activity is found for the nanotree reactors than for the nanorod reactors, most likely due to the increased gold surface area and thereby higher enzyme binding capacity. A theoretical calculation is included to show how the enzyme kinetics and hence the sensitivity can be influenced and increased by the control of electrical fields in relation to the active sites of enzymes in an electronic biosensor. The possible effects of electrical fields employed in the RISFET on the function of acetylcholine esterase is investigated using quantum chemical methods, which show that the small electric field strengths used are unlikely to affect enzyme kinetics. Acetylcholine esterase activity is determined using choline oxidase and peroxidase by measuring the amount of choline formed using the chemiluminescent luminol reaction.

### 7.10 Gold nanoparticles: Past, present, and future

This perspective reviews recent developments in the synthesis, electrochemistry, and optical properties of gold nanoparticles, with emphasis on papers initiating the developments and with an eye to their consequences. Rajesh Sardar, Alison M. Funston, Paul Mulvaney and Royce W. Murray, *Langmuir*, 2009, **25** (24), 13840. Key aspects of Au nanoparticle synthesis have included the two-phase synthesis of thiolated nanoparticles, the sequestration and reduction of Au salts within dendrimers, the controlled growth of larger particles of well-defined shapes via the seeded approach, and the assembling of a variety of nanoparticle networks and nanostructures. The electrochemistry of thiolated Au nanoparticles is systemized as regions of bulk-continuum voltammetry, voltammetry reflective of quantized double-layer charging, and molecule-like voltammetry reflective of molecular energy gaps. These features are principally determined by the nanoparticle core. Interesting multielectron Au nanoparticle



voltammetry is observed when the thiolate ligand shell has been decorated with redox groupings. Another development is that Au nanoparticles were discovered to exhibit unanticipated properties as heterogeneous catalysts, starting with the low-temperature oxidation of CO. Substantial progress has also been made in understanding the surface plasmon spectroscopy of Au nanoparticles and nanorods. The need to investigate the optical properties of metal particles of a single, well-defined shape and size has motivated the development of a number of new techniques, leading to the study of electron transfer and redox catalysis on single nanoparticles