Developing New Industrial Applications for Gold : Gold Nanotechnology

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Nanotechnology has transformed gold from a marginal into a very effective catalyst with unique properties. The astounding growth in gold nanoparticle research, as reflected in publications and patents, now promises new materials applications for gold nanotechnology and some possibilities are indicated in this article.*

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Introduction

Many of the applications of gold are based on its unique properties, and this uniqueness can be rationalized in terms of the large relativistic contraction of its *6s* orbitals resulting in a very small atomic radius compared with that which might be expected from the position of gold in the Periodic Table (1). Nanotechnology has already revolutionized our perception of gold catalysis and the current position is summarized here. Its potential for comparable impact in electronics and materials applications is illustrated by the examples from these areas cited in this paper. Colloidal gold is already well established as a means of colouring glass and tableware enamels.

Catalysis

Technical Position

One of the areas of gold science which has taken a giant leap forward in the past decade has been gold catalysis. The new gold catalyst systems, consisting of nanoparticulate gold on oxide supports, can be used for a wide variety of reactions (2, 3) and many of these have potential for applications in pollution control, chemical processing and fuel cells (4, 5).

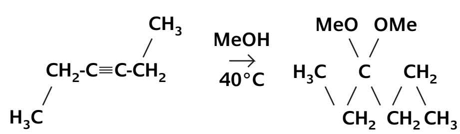
With respect to pollution control, the special low-temperature activity of gold catalysts has been employed by Mintek in South Africa to construct a prototype air purification unit which removes carbon monoxide from the air at room temperature (6). It is designed to be used in restaurants, hospitals, hotels and office blocks and is the result of collaborative work under Project AuTEK in which Mintek are collaborating with SASOL and the Universities of Cape Town, Witwatersrand and Pretoria in South Africa, Université Pierre et Marie Curie in France, and Leiden University in The Netherlands.

Another application where gold catalysts can be used to oxidize carbon monoxide at room temperature is the removal of carbon monoxide from the hydrogen feeds used in fuel cells in order to make the fuel cells more efficient (5). Using $Au/MgO/MnO_x$ at 20°C, B.E. Nieuwenhuys *et al* have shown that carbon monoxide is oxidized much more readily than hydrogen (7). In the Water Gas Shift (WGS), it has been demonstrated that gold catalysts are active at lower temperatures than the copper/zinc oxide catalysts used commercially, and this reaction is used for the production of hydrogen supplies for fuel cells and many other applications (3, 6, 8, 9).

Supported gold catalysts are active for the oxidation of methane and propane, and the removal of NO_x has also been demonstrated. In exploratory work, a gold on transition metal oxide catalyst system has shown potential as a low temperature three way catalyst for automobile emission control (4, 10) – with the light off temperatures lowered for both hydrocarbons and carbon monoxide when fresh catalyst is used. A further automotive use for gold catalysts could be the decomposition of ozone (11).

Both heterogeneous and homogeneous gold catalysts show promise for chemical processing for the synthesis of both heavy and speciality chemicals (2, 3). Work by Graham Hutchings *et al* in the 1980s clearly demonstrated that gold on carbon is the best catalyst for adding HCl to ethyne to produce vinyl chloride (2, 12). Masatake Haruta (13) has shown that propene can be converted into propene oxide in very high selectivities (>99%) but low yields, using gold on titania catalysts, and more recent work has improved the yields (14). Rossi *et al* have used gold on carbon in the liquid phase to selectively oxidize aminoalcohols to aminoacids: a reaction in which coordination of the amino group to the metal prevents the use of other precious metal catalysts (15).

The status for homogeneous catalysis by gold in solution was dramatically transformed by the results of Joaquim-Henrique Teles *et al* (16). This BASF group has described the use of cationic gold(I) complexes of the type [L-Au$^+$] (where L is a phosphine, phosphite or an arsine) for the addition of alcohols to alkynes:



The turnover numbers (number of moles of organic product formed per atom of gold) for this type of reaction are up to 2 x 10^5 moles of product per mole of catalyst, with turnover frequencies of up to 5400 h^{-1}. These gold catalyst systems are a significant improvement on the mercury catalysts used previously and the reactions are conducted under mild conditions (293 - 323 K) in the presence of acid co-catalysts.

This breakthrough has now been followed by the work of Stephen Hashmi *et al* (17) where it has been shown that soluble gold species can be used to catalyse the formation of new carbon-oxygen and carbon-carbon bonds, including the synthesis of highly substituted arenes from easily accessible furyl alkynyl compounds.

Commercial Position

Consistent with the above thoughts, the number of patents related to gold catalysis appears to be on a long term upward trend, with 27 patents granted during 2001 (Figure 1). In the last 10 years, around 50 industrial companies worldwide have successfully applied for patents in this area. Based on analysis by World Gold Council, the focus of the patents was approximately split by subject in the following way: Chemical Processing ~46%, Pollution Control ~29%, Catalyst Manufacture/Regeneration ~15%, and Fuel Cells ~10%.

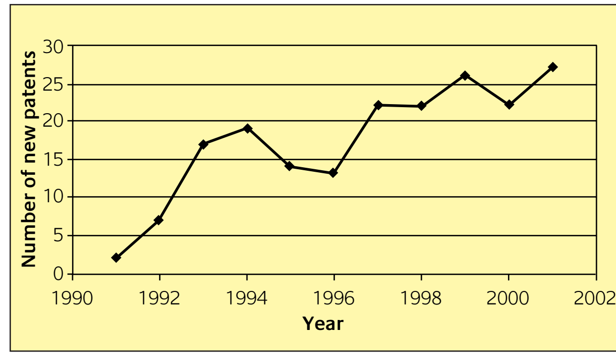


Figure 1
Number of patents based on catalysis by gold

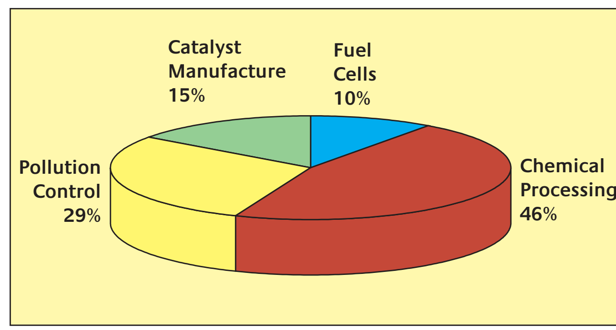


Figure 2
Gold catalysis patents (1991-2001) by subject area

Recent chemical processing patents include two where gold, combined with a redox active catalyst, is claimed for the WGS for the manufacture of hydrogen from carbon monoxide (18, 19). A recent announcement by BP plc indicates that a gold palladium catalyst is being used in the commercial manufacture of vinyl acetate monomer. (Further information in next issue). The selective oxidation of CO in the presence of hydrogen to purify the hydrogen streams has also been widely patented, for example by Haruta and Mitsubishi (20, 21). In the field of selective oxidation, Dow Chemical Company have patented the selective production of propene oxide by the epoxidation of propene in the presence of hydrogen and a gold on TiO_2/SiO_2 catalyst (22) and a more recent Bayer patent (14) has indicated improved yields of product. An Arco Chemical Technology, USA patent has been filed on the direct production of hydrogen peroxide using a gold catalyst supported on titania or zirconia (23). Another recent processing example is provided by Eastman Chemical Company on a vapour-phase carbonylation process using Au/Ir alloy catalysts for the production of carboxylic acids and esters from lower aliphatic alcohols and other organic feedstocks (24), and using gold alloy catalysts is becoming a promising development. The homogeneous gold-catalysed process developed by J.-H. Teles *et al* at BASF (see above) has been patented (16).

In the area of pollution control, some patents (25, 26) have been filed claiming use of gold catalysts in automotive emissions. The work carried out by John Marsh and his team at the Anglo American Research Laboratories in South Africa, see above (10), indicates some promise for applications in motor vehicle emission devices: these are most likely in the exhaust treatment for gasoline and diesel cars running over lower temperature ranges and for low light off applications, such as cold start conditions in gasoline engines. The use of gold on a clay mineral containing magnesium silicate hydrate has been patented by Toyota for use with ozone to destroy odours (27).

In many of the catalysed reactions in fuel cell technology, the current catalyst of choice is based on the use of platinum group metals (PGMs) (28). One of the current barriers to commercialization of fuel cells is the technology advance required to decrease precious metal contents in catalysts and yet still achieve the required power output (i.e. a reduction in the $/Kw price equation). Based on the achievement of acceptable technical performance, the use of gold in preference to platinum (or other PGMs) could help to reduce the cost of fuel cell technology.

It can be seen, Figure 3, that since 1997 - 98 the price of platinum and palladium has exceeded gold. In addition, the gold price has been characterised by a remarkably stable value compared to the widely fluctuating prices of the PGMs.

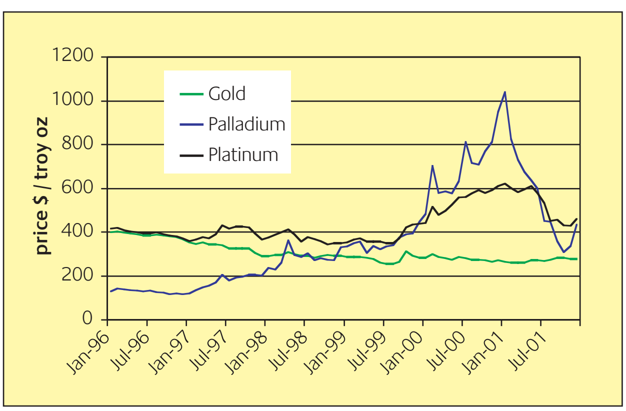


Figure 3
Variations in PGM and gold prices since 1996 (4)

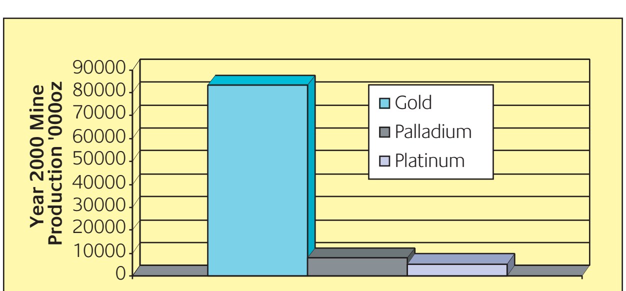


Figure 4
Gold and PGM mine production for the year 2000 (5)

A discussion centred on the exact reasons for metal price fluctuations and trends is outside the scope of this paper, but the relatively greater availability of gold compared to the PGMs is undoubtedly important in explaining the present comparative stability of the price of gold, Figure 4.

It is certainly true that concerns over platinum group metal supply in recent years have led to some issues arising with regard to the cost of these metals. Since the 1970's, national governments have gradually imposed increasingly stringent emissions regulations on the automotive industry, with the result that today's vehicles emit far lower levels of pollutants than previously. The success of the platinum group metals in helping manufacturers produce successive, improved generations of autocatalysts that have met these pollution targets is undeniable. The importance of these metals in such applications can be seen in the steady rise in their consumption over the last two decades. The total autocatalyst demand for platinum group metals (platinum, palladium and rhodium) rose from *ca* 5 hundred to 8 million troy ounces between 1983 and 2000 (I troy oz = 31.1g; 1 tonne = 32,151 troy oz) (28).

Should the commercialization of fuel cell-powered vehicles take place in the next decade as is predicted, the adequate cost-effective supply of PGM's may prove to be an issue in the long term. It is also probably reasonable to assume that large scale implementation of fuel cell technology will not be possible without PGM recovery. The comparatively large holdings of gold in the world would be a benefit, in that significant use as a catalyst in any one application will be unlikely to produce unpredictable fluctuations in supply and price, and this would favour its use compared to the platinum group metals.

Clearly then, with the ever present focus on long term cost-competitiveness, a comparatively more cost-effective precious metal such as gold is potentially very attractive for the fuel cell industry and similar considerations could be relevant to other applications for gold catalysis.

The Wider Potential for Nanotechnology

Gold catalysis depends on activation of small nanoparticles of gold on transition metal and other oxide supports and, as such, it is part of the wider field of nanotechnology. This aspect was highlighted by Professor Michael Cortie at the LBMA Precious Metals Conference in Istanbul in May 2001 (29). As readers of the Nanotechnology abstracts in the *Gold Bulletin* 'Highlights from the Literature' section will know, gold is very amenable to preparation in nanosized particles and these have many potential uses in electronics materials and biomedical applications. Amongst the metals only silver and platinum compete: but silver can be too reactive with

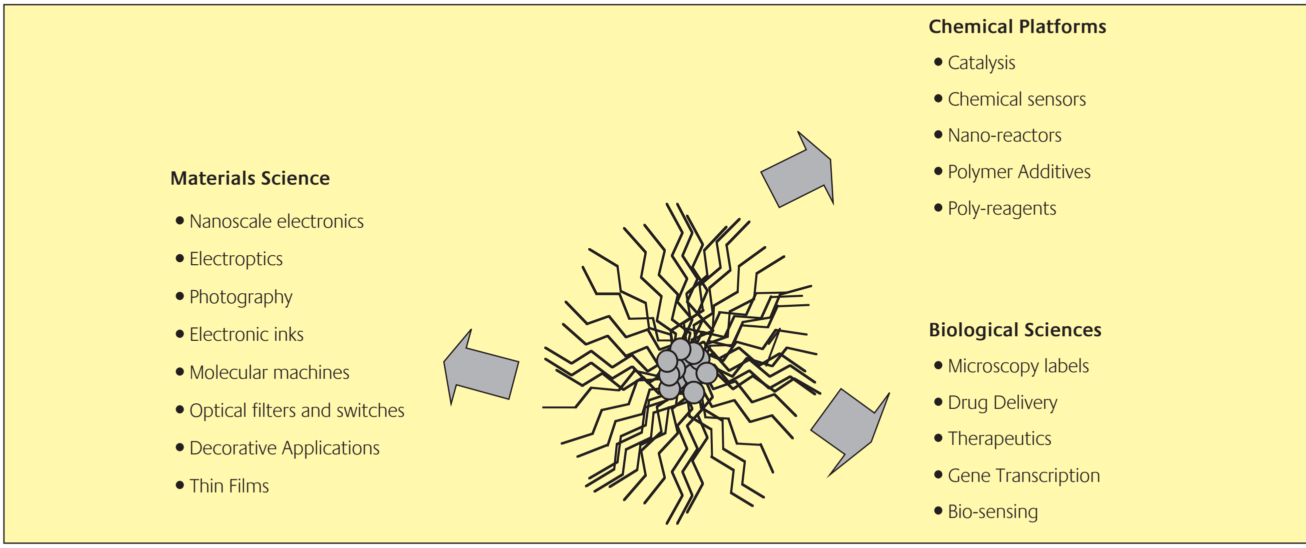


Figure 5
Possible application areas for monolayer-protected clusters (based on reference 32)

the environment and platinum is significantly more expensive than gold (see above). Studies in academia include both methods for controlling the growth of gold nanoparticles and for studying their properties and interactions with molecules of all shapes and sizes. Appropriate characterization methods have also been devised.

When nanotechnology became a 'buzzword' about a decade ago, its meaning was not quite clear and just how the field will develop is still unclear, but its ability to attract public investment has recently been noteworthy. The US Federal Government doubled its expenditure between 2000 and 2001 to $400 million and Japan increased its spending on nanotechnology by 40% between these two years. Several European countries have made nanotechnology a priority (30).

Nanotechnology sits somewhere between chemistry, which is based on interactions between single atoms and molecules, and large scale traditional engineering which lies behind so many of the manufactured products used in today's society, but it is much closer to the atomic and molecular dimension (29). In a review of the basic science of nanotechnology and the resulting emerging applications (31) the five Australian authors forecast that nanotechnology will soon be as significant as genetic engineering. Certainly, the number of publications and patents is expanding very rapidly, and the research represented by these is likely to lead to innovative applications.

Monolayer Protected Cluster Molecules

Schiffrin *et al* were responsible for opening up research in the area of monolayer-protected clusters (MPCs) (32, 33). They showed that the classical two-phase colloid preparation of Faraday could be combined with current knowledge of phase transfer and alkane thiolate/Au chemistry to prepare in a simple procedure, very small clusters of gold atoms (of up to 5 nm core diameter) coated with alkane thiolate monolayers. Understanding the reactivities of MPC monolayers and developing strategies to functionalize them is key to their application in areas such as chemical sensing. MPCs have been prepared which have multiple functionalities, spherically organized around a central metal core. The spatial arrangement is somewhat similar to dendrimers, but whereas dendrimers are typically more dense at their perimeter than their core, MPCs are 'soft objects with hard cores'. Current research is helping to define synthetic routes to core-monodisperse MPCs and to those with rationally designed ligand shells and core compositions. A better understanding and control of these and other factors may lead to applications of the type illustrated in Figure 5.

Researchers at many of the world's top technological companies are becoming interested in the nano domain. In the section below, a few of the many possible examples are given to illustrate the potential of the recent research. We think that gold will have a special role to play in this field due to its especially suitable properties that include its high conductivity and readiness to form nanoparticles with controlled particle sizes.

Applications for Nanotechnology

Sensors

In an article by A.N. Shipway and I. Willner (34), metal particle arrays crosslinked by molecular receptor units on electrodes are described which act as selective sensing interfaces with controlled porosity and tunable sensitivity. Photosensitizer/electron-acceptor bridged arrays of gold nanoparticles on conductive supports act as photoelectrochemically active electrodes. Nanoparticles incorporated into hydrogel matrices yield new composite materials with novel magnetic, optical and electronic properties.

New approaches to methods for biomedical diagnosis are being based on nanotechnology. An electrochemical nanoswitch operating on fewer than thirty electrons has been described by David Schiffrin's group in Liverpool (35) and molecular switches which could form a basis for a memory chip involving ultrathin wires and tiny particles of gold have recently been announced. Sensors based on nanotechnology, including catalysis, are already being developed.

A nanocluster consisting of eleven gold atoms joined together, undecagold, is being manufactured by Nanoprobes Inc in the US for use in some very selective biomedical diagnoses (36). The AMBRI biosensor is being developed for both medical applications such as the critical care pathology market where valuable rapid results are produced, and non-medical applications such as rapid analysis for food contamination and for individual components of wines and other drinks (36).

Optically Active Materials

The red colour of gold-ruby glass is caused by small particles of metallic gold that form when gold-containing colourless glass is annealed (37). The ruby colour is produced by metallic gold particles with an optimum size of 5 - 60 nm. Turkevich (38) has reviewed the literature on the colloidal golds, known as 'Purple of Cassius', used for obtaining the ruby red colours and produced by the reduction of soluble gold salts by tin chloride, a process known since the 17th century to produce the colour also observed in glasses from ancient times. Investigations using Mössbauer spectroscopy have shown that quenched samples of the glasses obtained from both $HAuCl_4.xH_2O$ and $KAu(CN)_2$ as the source of gold have the gold in its monovalent state. Remelting of a coloured annealed specimen at 1,400°C and subsequent quenching again produced a colourless glass with gold again present as Au(I). This shows that the transformation of Au(I) to metallic gold is reversible and that monovalent gold is stabilized by the glass matrix.

Work at Johnson Matthey (39) has shown that precious metal gold inks used for decorative applications, containing nanoparticle precursors, thermally decompose to produce bright gold films. Use of thiol-stabilized nanoparticles in decal applications has removed interactions with the gold ink and the methacrylate resin covercoat that leads to a purple colouration at the edge of the gold decoration. Reproducible batches of gold nanoparticles may be prepared in 0.5 kg quantities using a modified synthetic procedure previously described in the open literature. Structural studies of gold thiolate species reveal novel structural arrangements where

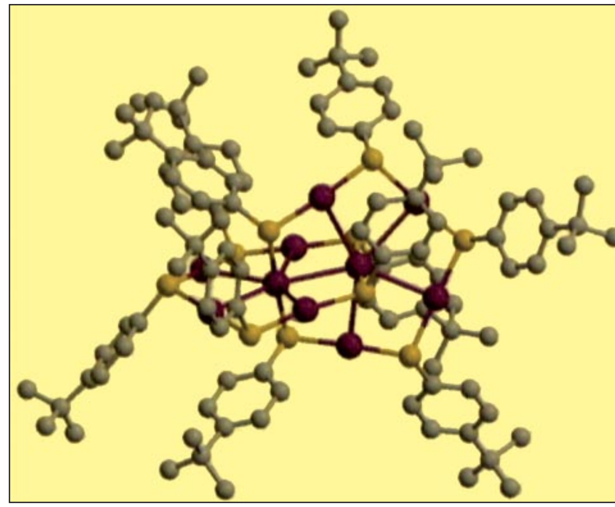


Figure 6

$[Au_{10}(SR)_{10}]$ where SR = p-tert-butylphenyl mercaptide, purple spheres = Au; yellow spheres = sulphur; grey spheres = p-tert-butylphenyl moiety. Au-S range = 228.8-234.3pm, S-Au-S range = 172.52-178.01°, Au...Au interactions average = 305pm (39)

Au-Au interactions dominate a ten-membered interlinking ring consisting of gold ions and thiol groups (Figure 6).

Hyper-Rayleigh scattering spectroscopy has been used to measure non-linear optical properties in gold nanoparticle arrays (40). The results showed that both symmetry and distance are important in determining the non-linear optical behaviour of nanoscale objects (free-electron metal particles) connected by molecular bridges *eg* thiol-functionalized phenylacetylene 'templates' of various lengths whose symmetries dictate the symmetry of the resulting aggregate.

Gold Colloid Paint for Road Vehicles

Following the use of gold to colour glass and glass enamels, Nippon Paint has recently developed the technology for use in paints for cars, based on a polymer-stabilized gold colloid (41). This paint appears black in shaded areas and red in illuminated areas, giving a dynamic effect as the vehicle is in motion due to varying light conditions, Figure 7. Use of this type of dynamic colour effect could be envisaged for use in security devices, such as 'watermarking' of valuable or confidential documents, and biomedical testing kits.

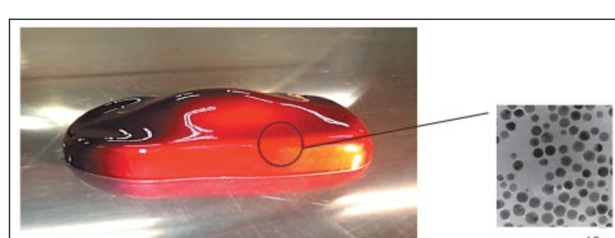


Figure 7

Polymer-stabilized colloidal gold (shown as TEM image) produces a 'dynamic' paint effect (Picture courtesy of Nippon Paint) (41)

Electronics Applications

The applications for gold in electrical and electronic components are many and varied, and the quantity used is growing steadily, especially with the growth in consumer electrical and electronic goods. Applications are derived from the physical and chemical properties of gold relative to other candidate materials. The question of reliability versus cost inevitably enters into the decision to use gold in a particular application, but the use of gold is widespread nevertheless, since it is often cost effective (42).

K.D. Hermanson *et al* (43) have shown that a new class of microwires can be assembled by dielectrophoresis from suspensions of gold nanoparticles. These researchers at the University of Delaware have developed new, self-assembling and repairing gold microwires, which could find application in the development of nanoelectronics. These scientists used tiny particles of gold, suspended in an aqueous solution. When electrodes were inserted into the suspension, gold wires more than 5 mm in length could be formed. The wire structures (see Figure 8) grew *via* the application of alternating electric fields across the nanoparticle suspension. They were generally of the order of 1 micron in diameter. It has been shown that these wires can be used as microscopic sensors for certain chemicals, such as thiols and cyanides. The principle of making electrical connections, by assembling rudimentary circuits using this technique has been established.

The silicon chip microprocessor and the computers they operate are becoming smaller and smaller. Now they have met fundamental physical barriers that will impede further miniaturization, at least using current technology. These problems could be overcome by designing a completely new type of computer using nanotechnology.

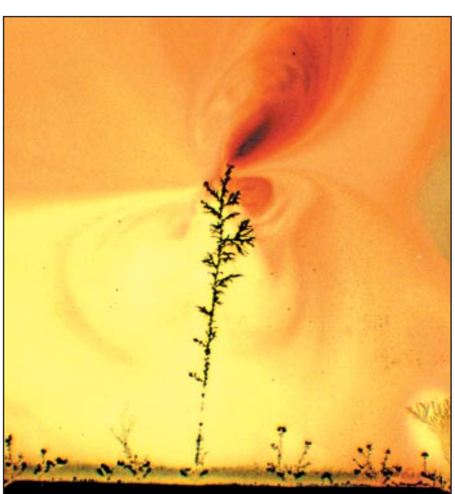


Figure 8
Growth of wires from a nanoparticle suspension (Picture courtesy of University of Delaware (43))

World Gold Council Projects

When compared with the other precious metals, the use of gold in industrial applications is a relatively low proportion of total demand, suggesting that there is significant potential as yet undeveloped (1, 2). Some aspects of gold science, its chemistry in particular, have been somewhat under-explored and this has hindered development of new industrial uses and increased gold demand. World Gold Council, supported by the gold mining industry, is now implementing a strategy recognising the importance of actively promoting and developing the industrial uses of gold. The potential for new applications for gold was recently summarized at the Annual Meeting of the WGC (44). One key element is the encouragement of commercial exploitation of applied gold-based research by dissemination of the latest science in *Gold Bulletin*. Another key element is the encouragement of innovative research studies into the basic science of gold and in applying this to new potential applications. With this objective in mind, selective funding is now available using the WGC GROW programme (Grow Research Opportunities Worldwide) to support some key short term R & D projects on basic gold science and technology and its applications, especially those feasibility studies focused on new or expanded uses of gold in industrial applications (see *Gold Bull*., 2002, **35**, 27). Some GROW projects focused on nanotechnology are already underway, and the WGC is also supporting a European Commission Network project entitled AURICAT which includes eight university and four industrial partners, and aims to understand the mechanisms of gold catalysis and define its full scope (6).

Two international conferences have recently highlighted the growing interest in the use of gold as a catalyst, and reports on both of these, which took place in April and September in Cape Town and Limerick respectively, have been published in *Gold Bulletin* (45). The overall impression gained from these meetings was that in-depth gold catalysis research relevant to practical applications has started very late compared with investigations of other catalytic materials but the recent advances have demonstrated exciting potential for new uses for gold in pollution control, fuel cells and chemical processing.

Following the success of these two meetings, highlighting the potential for catalysis by gold nanoparticles, a conference with four gold themes is now being planned, i.e. catalysis, chemistry, nanotechnology, and materials. The programme is being arranged by WGC in collaboration with the Canadian Institute of Mining Metallurgy and Petroleum and will take place in Vancouver from 28 September - 1 October 2003. The conference, **Gold 2003** (www.gold2003.org), will be organized along similar lines to the Cape Town meeting so that there will be plenty of opportunity for open discussion between academics and industrialists, and assessment of the potential for applications of the exciting new developments in many aspects of gold science and technology (see *Gold Bull*, 2002, **35**, 108). More information on new and existing applications for gold can be found on the World Gold Council website, www.gold.org

Conclusions

It is clear that catalysis by gold has the potential of becoming a substantial new commercial use for this metal. Further research into gold chemistry and technology will lead to other new uses for gold. The fact that gold has unique properties means that it is probable that gold will turn out to have a special catalytic chemistry of its own, comprising both heterogeneous and homogeneous aspects, and leading to appropriate applications.

New commercial uses for gold catalysts in pollution control, gas detection, fuel cells and chemical processing are envisaged. Experience from the platinum group metals markets teaches us that if a successful application can be found for a precious metal catalyst, a significant demand can be generated.

Gold nanotechnology is still in its infancy but has tremendous potential for applications, not only in catalysis but also in the electronics, materials, decorative and biomedical fields. The WGC's GROW programme will support feasibility projects designed to develop these new applications for gold.

About the Authors

Dr Christopher Corti is Director, International Technology, World Gold Council, responsible for industrial applications and jewellery technology support programmes. He has 39 years experience in metals and materials research and applications, 24 years in the precious metals industry and was formerly research manager for materials and then technical director, Colour & Print division of Johnson Matthey plc. He is editor of *Gold Bulletin* and *Gold Technology* journals.

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Dr David Thompson has over 40 years experience in precious metals catalysis research with ICI, Johnson Matthey and World Gold Council, and was Manager of the multidisciplinary New Technology Department at JM. He is currently consultant to World Gold Council, having been Technical Editor of *Gold Bulletin* for more than six years, until mid-2002.

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