Abstracts

Gold 2015

David Thomson Lecture

David Thompson Lecture

The Pioneers of Gold Chemistry and Their Landmarks

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As reflected by ancient objects of cult, culture and coinage, the element gold has player a great role in the history of mankind. By contrast, its chemistry is a very young discipline which had a late start and a slow development as compared to the chemistry of most other elements. For millennia, the recovery of gold from natural resources relied mainly on its physical properties and some ill-defined chemical conversions. Even in the times of the alchemists, only a few centuries ago, very few chemical compounds of gold were actually known [1].

It was only in the late 20th century that several key discoveries in preparative chemistry, the growing arsenal of instrumentation for analytical and structural studies, and the enormous developments of quantum chemistry and physics, have finally led to an amazing upswing of gold chemistry research [2]. The element symbol **Au** now shines brightly from many pages of current chemistry and related interdisciplinary periodicals. Clearly, gold chemistry has evolved from a "sleeping beauty" to a "darling" field of chemistry, which is now of great relevance to many disciplines [3, 4].

Many of these achievements can be associated with the names of distinguished pioneers and members of their groups and schools, and in this lecture representative examples are presented which stand for some of the most fascinating contributions and had a major impact on the evolution of the field.

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Plenary Lectures

Simple Chemistry Catalyzed by Gold Nanoparticles

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Although gold in bulk is poorly active as a catalyst, it turns out to be uniquely active when deposited as nanoparticles (NPs) with diameters smaller than 5 nm on base metal oxides, carbon materials, and polymers [1, 2]. There are three important factors that define the catalysis by gold; selection of support materials, size and shape (contact structure) control. The characteristic features of gold catalysts are firstly ambient temperature activity, secondly promotion by water, and lastly unique selectivity which is usually different from that of Pd and Pt catalysts. Gold NPs deposited on semiconductor metal oxides such as TiO_2, Fe_2O_3 Co_3O_4, and NiO exhibit markedly high catalytic activity for CO oxidation even at a temperature as low as 200K. A perimeter hypothesis has been gaining increasing support not only by surface scientists [3] but also by theoreticians [4].

In particular, $Au/NiO/SiO_2$ modified with Mg and Al exhibits high catalytic activity and selectivity in the transformation of methacrolein to methyl methacrylate by the oxidation with molecular oxygen in methanol [5]. The catalyst is very stable and has been working in a commercial plant with a capacity of 100,000 ton/year since 2008.

Water is a good partner for gold to become practically useful. It enhances CO oxidation and propene epoxidation [6] in gas phase. For chemical transformation of biomass-derived compounds such as ethanol and glucose water is a good solvent, presenting a very high turnover frequency(45 s-1) and selectivities to carboxylic acids. Gold NPs also show good chemoselectivity in the hydrogenation of alkynes, di-enes, unsaturated aldehydes, and nitrobenzene when deposited on TiO_2, ZrO_2 or CeO_2.

It has recently been found that gold clusters smaller than 2 nm in diameter being composed of less than 200 atoms exhibit some fantastic catalytic properties which have not yet been obtained by gold NPs. Gold clusters can catalyze the gas phase epoxidation of propene with molecular oxygen alone in the copresence of water [4]. A challenge like this towards the simplest reactions will lead to innovation in chemical industry.

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Crystalline Facets in Gold Nanocrystals

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The growth of colloidal metal nanoparticles with controlled size and shape is one of the most promising ways toward the fabrication of nanomaterials and devices. It has been reported that the final nanocrystal shape is defined by the crystalline structure of the initial nuclei, as well as by the presence of ligands and capping agents that help stabilizing certain crystallographic facets. This talk will focus on recent progress on the understanding of the role of surfactants, counter-ions and other additives during the growth of gold nanocrustals [1-3], as well as the morphological changes derived from using such nanorods as seeds for overgrowth through additional gold reduction [4,5,6] (Figure 1). Under different growth conditions, the morphological changes and corresponding optical effects can be drastically different, which may provide important hints related to the growth mechanism of the nanoparticles.

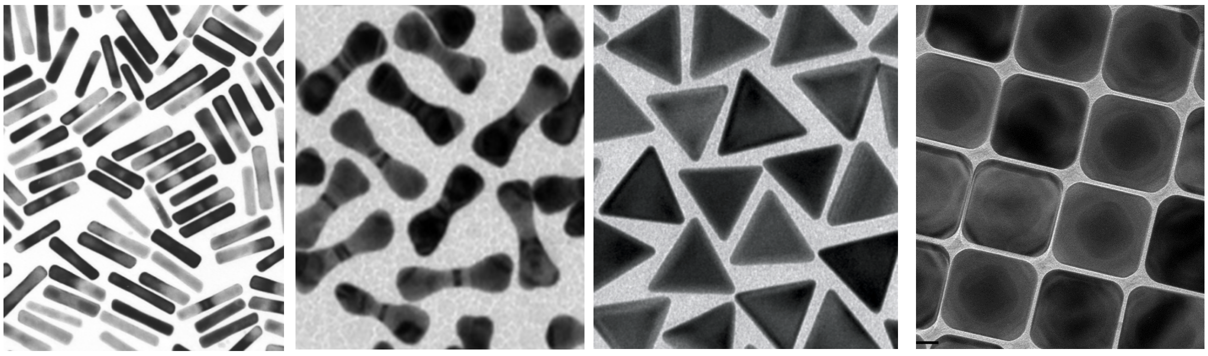

Figure 1. Examples of morphologies obtained by seeded growth on gold nanorods.

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A Golden Age for Colloidal Nanoparticles

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Gold colloids have been used for centuries in art, and for decades as contrast agents in electron microscopy. Only in the last 25 years or so has the community dived in to make, measure, and model colloidal gold nanoparticles with unprecedented control over size and shape. It is now routine for research groups to prepare gold nanoparticles that are the shape of spheres, rods, discs, stars, flowers, sea-urchins, etc. In the ~4-200 nm range, colloidal gold nanomaterials exhibit strong plasmon bands, resulting in high absorption and scattering (Figure 1) of visible and near-infrared light. Local electric fields and heat are generated upon illumination into the plasmon bands; measurements of these effects are of great interest to many scientists. These plasmon bands are the basis for many applications of these materials: optical sensing, biological imaging, and even photothermal therapy.[1-3]

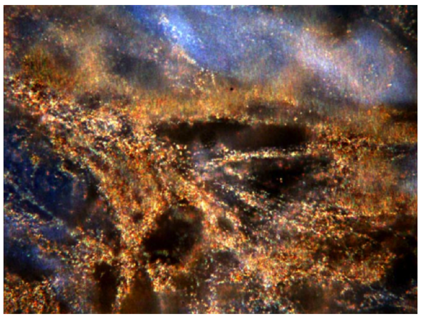

Figure 1. Darkfield microscopic image of gold nanorods immobilized in a collagen gel. Field of view = 3 mm. The "stars" are the gold nanorods, scattering white light; the misty colors are from the turbid gel.

As the field moves from fundamental chemistry to applications, new requirements are coming online. These nanomaterials require scalable synthesis; quality control; and well-defined surface chemistry. Advances are being made in all of these areas.

The biological applications of colloidal gold nanomaterials are among the most exciting. Yet unanticipated side effects of nanomaterials on living organisms is possible, and is becoming more of a concern. Depending on surface chemistry, the behavior of living cells can be affected by gold nanomaterials. If properly understood and controlled, these effects could become the basis for powerful new technologies in nanomedicine.

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Homogeneous Gold Catalysts for Selective Organic Synthesis

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This lecture will emphasis a reactivity driven approach to development of gold complexes as homogeneous catalysts for cycloisomerization, rearrangement, cycloaddition and addition reactions. Thus, particular attention will be devoted to the mechanistic hypotheses that form the basis for our discovery of gold-catalyzed transformations.

The development of these reactions stemmed from the hypothesis that the strong relativistic effects[1] governing the electronic structure of gold render it unique among the electrophilic late transition metals, and, specifically, that it may stabilize cationic intermediates in the course of Au(I)-catalyzed reactions.[2]

In addition, strategies towards developing gold(I) complexes for enantioselective catalysis will be presented. This will include the application of dinuclear chiral bisphosphine digold(I) complexes[3] and chiral counterions[4] to induce enantioselectivity.

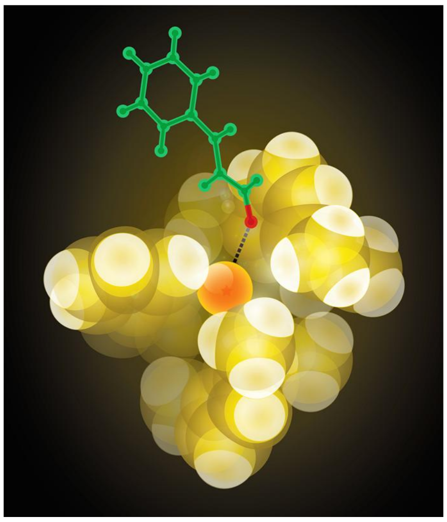

Figure 1. Cinnamaldehyde Bound to Gold(III) Catalyst

Finally, recent studies aimed at harnessing the reactivity of gold(III) will be introduced. This will include mechanistic studies on the reductive elimination for gold(III) and potential utility in cross-coupling chemistry.[5] Additionally, the oxidative addition to gold(I) to form well-defined and tunable gold(III) complexes (Figure 1) will be presented.[6]

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Keynote Lectures

The Development and Commercialisation of Gold Catalysts for VCM Production

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Abstract

Vinyl chloride monomer (VCM) is a major chemical intermediate for the manufacture of polyvinyl chloride (PVC) which is the third most important polymer today. Hydrochlorination of acetylene is currently the major route for the production of VCM in regions of the world where coal is abundant, mainly in China.

$HC\equiv CH + HCl$ ---- catalyst ---------> $H_2C{=}CHCl$

Currently, mercuric chloride supported on carbon is used as the catalyst in the commercial process. Apart from a short life time, these catalysts are associated with significant environmental and handling problems due to their toxicity. Although it has been known for over thirty years that gold supported on activated carbon is a superior catalyst for this reaction [1], preparation of these materials required high gold loadings and use of aqua regia as solvent [2].

It is only recently that we have developed economically viable gold catalysts for this reaction and these are now being commercialised. In this talk we describe our recent advances in the development of these highly active catalysts containing ultra-low levels of gold for this important reaction [3]. Furthermore, we discuss novel water based preparations for this new family of gold catalysis.

In the final part a view to the future of this new advent of gold catalysis will be discussed as well as the avenues for the commercial development of gold catalysis.

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Gold Nanotechnology Innovation at Mintek:

Creating and Capturing Value in the Biotechnology Sector

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Abstract

At this fast-paced global economy, gold nanotechnology innovation will bring enormous benefits for advanced and emerging economies. For emerging economies to realise these benefits, the community must adopt and apply systems of innovation and develop technologies that are unique in addressing rapid progress in their priority socio-economic needs.

For more than a decade, Mintek has been at the forefront in developing gold nanotechnology-based systems and devices for various applications through Project AuTEK Consortium and DST/Mintek Nanotechnology Innovation Centre (NIC). In an effort to address health challenges and other issues of national importance, the Mintek NIC has developed innovative gold nanotechnology-based systems and devices for life science applications. These include a plethora of innovative gold nanomaterial systems and nano-enabled diagnostic prototype devices for infectious and veterinary diseases. These innovative systems have reached the industrialisation and commercialisation stages and NIC has further established gold nanobiotechnology platforms which offer high quality services to Research Institutions and Industry.

This presentation will highlight the gold nanobiotechnology R&D and innovation activities at Mintek and the success stories in industrialisation and commercialisation.

Biosensing with a Twist: Detection and Characterization of Biomaterials with Sculpted EM Fields

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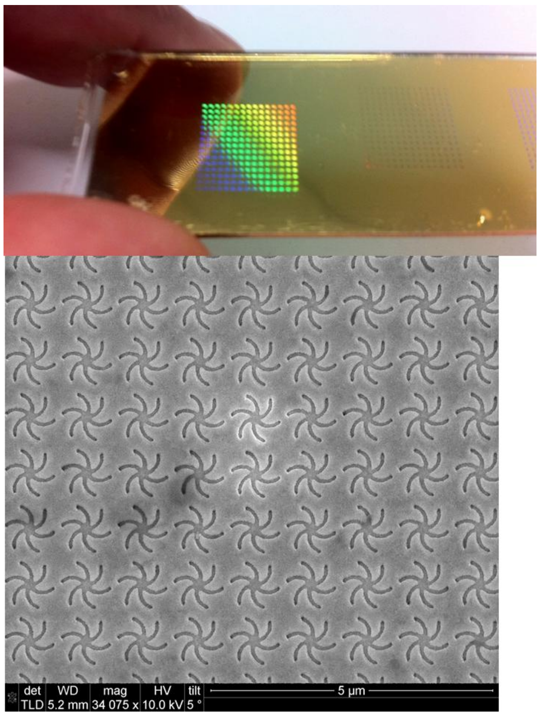
Sculpted electromagnetic (EM) fields created by artificially engineered metamaterials provide a route to new spectroscopic phenomena [1-3]. Thus enabling novel measurements, such as < picogram characterisation of the structure of biological materials [1], which would be impossible with conventional spectroscopic techniques. The scope for these new spectroscopic phenomena to make a significant impact as: generic research tools; medical diagnostics; or as biosensing platforms, is limited. Due to the fact that the metamaterials, which are formed from periodic arrays of individual (noble metal) nanostructures, are fabricated using electron beam lithography a costly time consuming production method. I present a new type of plasmonic nanomaterial, a continuous gold film that is moulded so it as nanoscale chiral indentations, which can be fabricated using a cheap high throughput method. We subsequently demonstrate the application of these nano templated chiral plasmonic films for (linear and non-linear) biospectroscopy.



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Jahn-Teller Effects in Gold Nanoclusters

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The relationship between oxidation state, structure, and magnetism is well described for coordination compounds by the Jahn-Teller theorem.[1] This relationship is not well defined for ligated nanoclusters and nanoparticles, especially the nano-technologically relevant gold-thiolate protected metal clusters. Here we interrogate the relationships between structure, magnetism, and oxidation state for the three stable oxidation states of the thiolate protected nanocluster $Au_{25}(SR)_{18}$.[2] We present the single crystal X-ray structures of the previously undetermined charge state $Au_{25}(SR)_{18}^{+1}$, as well as a higher quality single crystal structure of the neutral compound $Au_{25}(SR)_{18}^{0}$. Structural data combined with SQUID magnetometry and DFT theory enable a complete description of the optical and magnetic properties of $Au_{25}(SR)_{18}$ in its 3 stable charge states -1, 0, and +1. In aggregate the data suggests a Jahn-Teller effect in this compound, which we believe is the first crystallographic observation of this effect in a metal cluster with at least one metal atom that is neighbored only by other metal atoms.

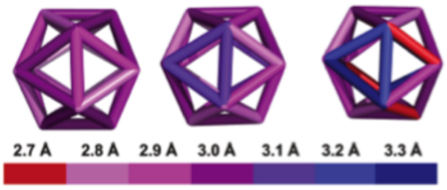

Figure 1. A 'heat map' showing evolution of bond lengths of the icosahedral core of $Au_{25}(SR)_{18}$ in three oxidation states, increasing from negative to positive from left to right.

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Visible light-induced photocatalysis through surface plasmon excitation of gold on titania surfaces

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Since Haruta's pioneering studies on catalytic properties of gold nanoparticles (NPs) [1], a lot of research has been carried out to explain nature of catalytic reaction and to find optimal conditions for efficient oxidation of organic compounds. Regarding catalytic and plasmonic properties of gold nanoparticles (NPs), the novel area of research on photocatalytic gold properties has been recently started. In contrast with catalytically active gold NPs, where nano-sized gold is recommended, our results showed that polydispersity of deposited gold NPs on semiconducting support was beneficial for photocatalytic activity under visible light irradiation [2]. It is thought that wide size/shape distribution of gold NPs, and thus the ability of absorption of light in a wide wavelengths range is responsible for the high level of photoactivity. The action spectrum analysis has proved that visible light-induced oxidation of organic compounds by gold-modified titania is initiated by excitation of gold surface plasmon [3].

Though desirable absorption properties of plasmonic photocatalysts can be easily obtained by preparation of NPs of different sizes and shapes, their photocatalytic activities under visible light irradiation are still low and should be enhanced. The improvement of photocatalytic activities under visible light irradiation could be achieved by: i) enlargement of interfacial contact between titania and NPs of noble metals by partial coverage of gold NPs (deposited on large titania) with fine titania NPs (Fig. 1a), ii) extension of photoabsorption ranges (by, e.g., preparation of NPs of various sizes and shapes, composed of two noble metals (e.g., Au-Ag, Fig 1b [4]), or combined with homogeneous photocatalysts (e.g., Ru complexes [5]), iii) and by deposition of noble metals NPs on faceted titania, i.e., octahedral (OAPs, Fig. 1c) and decahedral (DAPs) anatase particles [6].

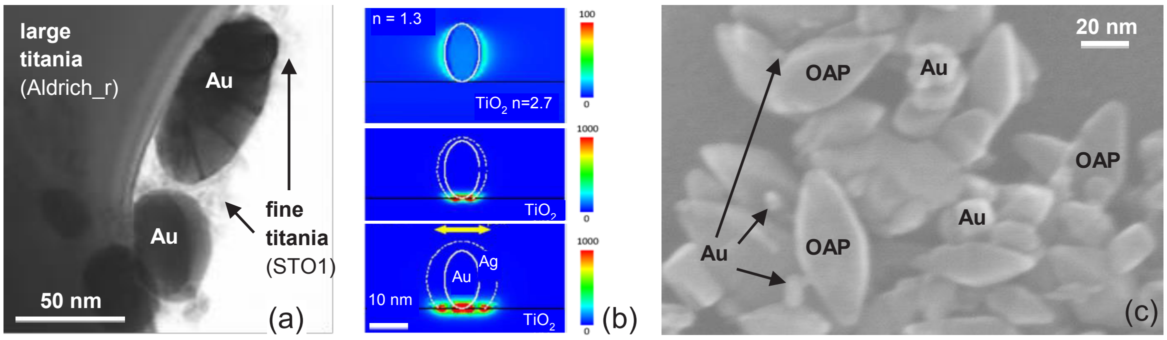

Figure 1. (a) STEM image of TiO_2/Au/TiO_2 obtained by subsequent photodeposition of gold on the mixture of bare TiO_2(Aldrich_r) and Au/TiO_2(ST01) (70:30); (b) the cross-sectional pattern of the near-field intensity enhancement factor for 10 nm x 10 nm x 30 nm spheroidal gold NP on the presence of coverage layer of silver of thickness t for: (top) t=0 at 510 nm wavelength, (middle) t=2 nm at 600 nm, bottom t=5 nm at 570 nm, n-refractive index [4]; c) STEM image of gold NPs deposited on OAPs [6].

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On Gold mechanistic studies and beyond

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Alkenes and alkynes constitute privileged building blocks for synthetic chemists. Their accessibility, robust nature, and broad functionalization potential made them attractive platforms used to assemble complex natural products, biologically active pharmaceuticals and molecular materials. As such, novel tools to incorporate functional groups across the π-C=C and C≡C systems have bloomed in recent years.

Taking advantage of Au(I)/Au(III) redox catalytic cycles and metal-mediated radical transformations we have developed attractive tools towards the efficient difunctionalization of alkenes and alkynes. This program has been successfully extended to the efficient introduction of C-F and C-CF_3 bonds into organic molecules in a regio- and stereocontrolled manner.[1]

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Synthetic Transformations via Gold-Carbenes

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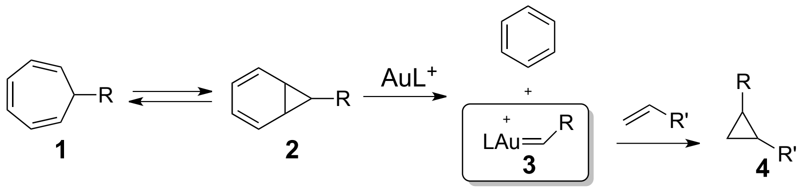
Following our discovery that cationic Au(I) complexes promote the retrocyclopropanation of 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes to form 1,3-disubstituted naphthalenes,[1] we also found that 7-substituted 1,3,5-cycloheptatrienes **1** react with cationic Au(I) complexes to form gold(I) carbenes **3** that can be trapped with alkenes in a new cyclopropanation reaction.[2] This unique transformation involves the cleavage of two C-C bonds of norcaradienes **2**, which are in equilibrium with cycloheptatrienes **1**. Indenes and fluorenes are also obtained by intramolecular reaction of these highly electrophilic gold(I) carbenes with alkenes and arenes. According to DFT calculations, the gold-catalyzed retro-Buchner process occurs stepwise, although the two carbon-carbon cleavages occur in a rather flat potential energy surface.[3] Gas-phase retrocyclopropanations of alkoxy substituted cyclopropanes with $[\text{AuIMes}]^+$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been reported.[4]



More recent work on the development of synthetic methods based on this and related processes will be presented.

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Efficient Homogeneous Gold Catalysis

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Starting from important publications in the year 2000,[1,2] homogeneous gold catalysis has become a highly active field.[3,4] Initially, the field was dominated by methodology development.[5] Subsequently, deeper mechanistic insights were obtained by isotope labeling,[6] in situ spectroscopy (including EXAFS)[7] and a computational explanation of the enhanced reactivity by fully relativistic calculations.[8] In the recent past the applications in synthesis, both for material science[9] and life science,[10] have become increasingly important and document the impact of homogeneous gold catalysis.

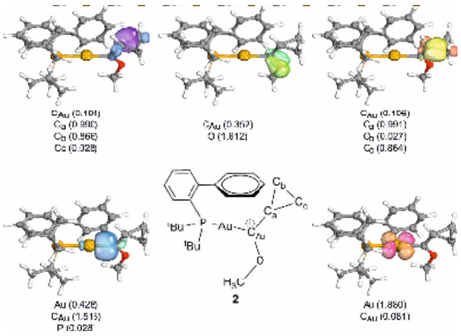

Figure 1. Computational studies.

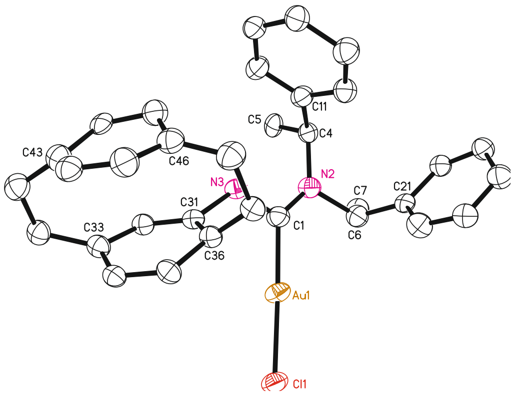

Figure 2. Chiral ligand on a gold(I) centre.

New classes of catalysts could be accessed by very efficient pathways, that are based on modular template syntheses.[11] Entirely new options now open up with these systems.

In the recent past we have investigated new reactivity patterns, some of these involving the combination of several components like oxidants, halogen donors.[12]

Other new reactions involve the involvement of two gold centers for the activation of the substrate, this can include a selective C,H insertion process or photocatalysis.[13]

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Solution Metallic Catalysis on the Nanoscale

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Three different types of solution catalysis by transition metal and plasmonic Nanoparticles are used in nanocatalysis and will be discussed: 1.Solid nanoparticles of different shapes, 2.Hollow nanoparticles of single and double shells, and 3.Hollow palladium nanoparticles containing spherical gold nanoparticles for photo-thermal heating:

1. In the first type, we show the importance of sharp corners and rough surfaces suggesting the importance of the chemically (valence) unsaturated atoms in solution nanocatalysis.

2.Evidence that the catalytic reaction occurring inside the Hollow space of the nano-catalyst will be given suggesting the importance of the cage effect and the increased reactivity due to the spacial confinements.

3.The photo-thermal property of plasmonic nanoparticles is used in determining the activation energy of a chemical reaction and in the photo-thermal enhancement of the catalytic activity of reactions occurring within transition metal hollow nanoparticle containing small solid gold nano-sphere imprisoned in its cavity.

Precise synthesis and non-scalable oxidation catalysis of gold clusters

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We have reported that Au clusters (< 2 nm) weakly stabilized by poly(*N*-vinyl-2-pyrrolidone) exhibit size-specific catalysis for various types of aerobic oxidation reactions [1]. These results have encouraged us to develop more robust and reusable Au cluster catalysts by immobilizing on solid supports. However, the structural parameters, such as size, composition, and surface state must be controlled at the atomic precision in order to optimize and understand the origin of catalysis of the supported Au clusters. We have exploited a synthetic method by using ligand-protected Au clusters [2] as precursors. This talk will introduce our efforts toward atomically precise synthesis of the supported Au clusters and impacts of the structural parameters on catalytic performance in aerobic oxidation.

Control of Size [3–5]: A series of Au_n (n = 10, 18, 25, and 39) on hydroxyapatite (HAP) (surface area ~100 m^2 g^{-1}) were synthesized by calcination of Au_n(glutathione)$_m$ at 300 ºC for 2 h under vacuum [4, 5]. Oxidation of cyclohexane over Au_n/HAP (n = 10, 18, 25, and 39) under an O_2 atmosphere (1 MPa) and solvent-free conditions at 150 ºC yielded cyclohexanol and cyclohexanone (KA oil) as the primary products with nearly equivalent yields; a small amount of TBHP was essential to initiate the reaction. The total selectivities for KA oil were ~99% for Au_n/HAP (n = 10–39), which are larger than that (~95%) for larger $Au_{\sim 85}$/HAP. The TOF values increase monotonically with increasing size in the range n = 10 to 39, but decrease in the range n = 39 to ~85. This result demonstrates that there is an optimal cluster size in the range n = 40 to ~80.

Control of Composition [6, 7]: Au_{25} and Pd_1Au_{24} clusters were immobilized on multiwalled carbon nanotubes (CNTs) by calcination of $Au_{25}(SC_{12}H_{25})_{18}$ and $Pd_1Au_{24}(SC_{12}H_{25})_{18}$, respectively, at 450 ºC for 2 h under vacuum [6]. These clusters provide us an ideal opportunity to investigate the effect of single Pd atom doping on the catalysis. Doped clusters Pd_1Au_{24}/CNT exhibited much higher catalytic activity than Au_{25}/CNT for aerobic oxidation of benzyl alcohol. Theoretical study on Pd_1Au_{24} predicted that a doped Pd atom prefers to be located inside the Au cage and donates electronic charge to the surrounding Au atoms, which may cause enhancement of the catalytic activity [7].

Control of Surface Modification [8]: Au_{25} clusters partially passivated were prepared on hierarchically porous carbon nanosheets (surface area ~2300 m^2 g^{-1}) by calcination of $Au_{25}(SC_{12}H_{25})_{18}$ at 400–500 °C for 2–4 h under vacuum. The thiolate coverage on Au_{25} gradually decreased with increasing the calcination temperature and period and became negligibly small when the calcination temperature was 500 °C. The selectivity for benzaldehyde formation in the aerobic oxidation of benzyl alcohol was remarkably improved with the amount of residual thiolates on Au_{25}, while the activity was reduced. This observation is attributed to the dual roles of the thiolates: the reduction of the oxidation ability of Au_{25} by electron withdrawal and the inhibition of the esterification reaction on the cluster surface by site isolation.

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Population Distributions and Catalytic Hierarchy of Active Species in Gold on Iron Oxide Catalysts for Low Temperature CO Oxidation

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Gold on iron oxide catalysts have been investigated extensively by many groups over recent years for their activity in low temperature CO oxidation. Materials prepared by co-precipitation, deposition precipitation and sol-immobilization methods have all been studied and found to display varying levels of activity for this reaction. Furthermore, such materials when examined using high resolution TEM and aberration corrected scanning transmission electron microscopy show considerable variations in their nanostructures. So far, Au nano-particles, monolayer &bilayer sub-nm Au clusters, extended Au rafts, and even highly dispersed Au atoms have been identified in such catalysts and implicated as potential active species in the low temperature CO oxidation reaction (see Figure 1). The relative populations of the various supported Au species present in such Au/FeO$_x$ catalysts depends critically on the preparation method and precise synthesis conditions used. Naturally this structural complexity and catalytic variability has led to considerable debate over the nature of the active species/sites in such Au/FeO$_x$ catalysts.

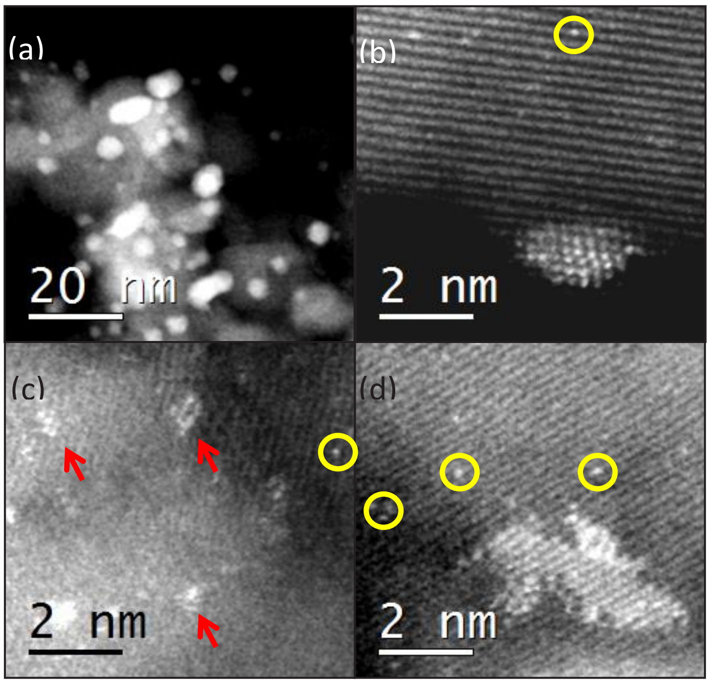

Figure 1. High angle annular dark field (HAADF) scanning transmission electron microscopy images showing the co-existence of supported Au nanoparticles (in (a) &(b)), sub-nm Au clusters (arrowed in (c)), extended Au rafts (in d) and isolated Au atoms (circled in ((b), (c) & (d)).

It is likely that most of these supported Au species exhibit some catalytic activity for CO oxidation activity, albeit to varying degrees. In order to understand the overall activity exhibited by a particular catalyst sample containing a mixture of these supported Au species, one therefore has to gain some quantitative measure of their relative population distributions and an understanding of their ranking in terms of catalytic activity. The overall activity can then be represented as a sum of the activity of each species present weighted by its relative abundance in the catalyst sample. In this presentation, we outline some practical strategies for attempting to determine the catalytic hierarchy of this family of supported Au species and propose a new experimental protocol for measuring their size distributions and relative populations. This knowledge of species populations is then used to rationalize the activity variations displayed by some systematic sets of Au/FeO$_x$ catalysts prepared by co-precipitation and deposition precipitation as a function of the calcination treatment they receive.

Luminescent Gold-Containing Molecular Photofunctional Materials

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Recent works in our laboratory have demonstrated that novel luminescent metal-based molecular materials could be assembled from various metal-ligand building blocks. In particular, the rich luminescence properties displayed by a number of gold complexes, with some of them associated with their strong tendency to form aggregates owing to the aurophilic nature of gold, have aroused our interests in the exploration of supramolecular photofunctional materials based on gold complexes. In this presentation, various design and synthetic strategies together with the successful isolation of new classes of mono-, di- and polynuclear gold complexes and their supramolecular assemblies will be described. A number of these complexes have been structurally characterized and shown to display rich luminescence properties. Correlations of the luminescence behavior with the electronic and structural effects of the metal complexes have also been made. With a thorough understanding of the spectroscopic origin and the structure-property relationships of the gold-containing metal complexes, the characteristics of these complexes could be fine-tuned for specific applications and functions through rational design and synthetic strategies, and may find potential applications and functions as supramolecular assemblies, triplet light-emitting materials, and luminescence signalling probes.

Gold nanoparticles of unusual morphologies

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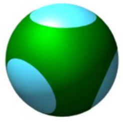
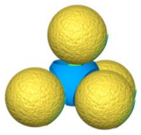
A fundamental goal of material science is the design and synthesis of materials with tailored shape and size. There has been tremendous progress over the past decade in the synthesis of gold nanoparticles of various sizes and shapes and with good yield and monodispersity. In this talk we will summarize some of the emerging protocols for shape control of gold nanocrystals and we examine some of the mechanism currently proposed. Similarly we will provide overview on gold nanostructures that can be elaborated by using the concept of patchy nanoparticles, i.e. spherical nanoparticles with a controlled number of patches. The selective functionalization of the patch areas or the inter-patch areas offers the possibility to create complex supracolloids with unusual optical signatures suitable for applications such as (bio-) sensing, metamaterials or catalysis.


Patchy NP


Au$_n$ nanocages


Au$_n$nanoclusters


Filled nanocages

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Invited Lectures

An Unexpected Discovery Revisited: Gold as an Hydrogenation Catalyst

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Despite early work at high temperatures and an extensive patent literature, it was widely believed in 1970 (and theoretically proved) that gold could have no useful catalytic properties. It was therefore surprising to find[1] that Au/SiO_2 catalysts prepared by gentle thermal treatment of impregnated $HAuCl_4$ possessed measurable activity for 1-pentene hydrogenation at 373K, and that TOF based on gold content increased by a factor of about 7000 as it was decreased from1% to 0.01%. The mauve colour of such catalysts suggested the formation of highly dispersed gold particles; Au/Al_2O_3 catalysts did not show this behaviour. Subsequent work[2,3] with contributions from Hull, Glasgow and Orleans demonstrated highly selective hydrogenation of butadiene (gold in this respect resembling palladium), reaction of C_2H_4 with D_2 giving products typical of platinum, and esr signals indicative of "spin-orbit coupling of small particles (<4 nm) having localised atomic orbitals".

These observations, which pointed implicitly to the over-riding importance of small particle size, did not result in an immediate surge of interest in catalysis by gold; this had to await the somewhat more dramatic work of Haruta a decade later. It has been disappointing and a little surprising that some of the methods used in this early phase of the work have not been further extended or exploited. In particular, the use of isotopic tracer methods to estimate chemisorbed H atoms and to investigate mechanisms in hydrogenations has not been extensive, and work on esr has not been developed. However our work in the 1970s gave clear signals of the potential for catalysis of small gold particles for any who cared to read them.

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