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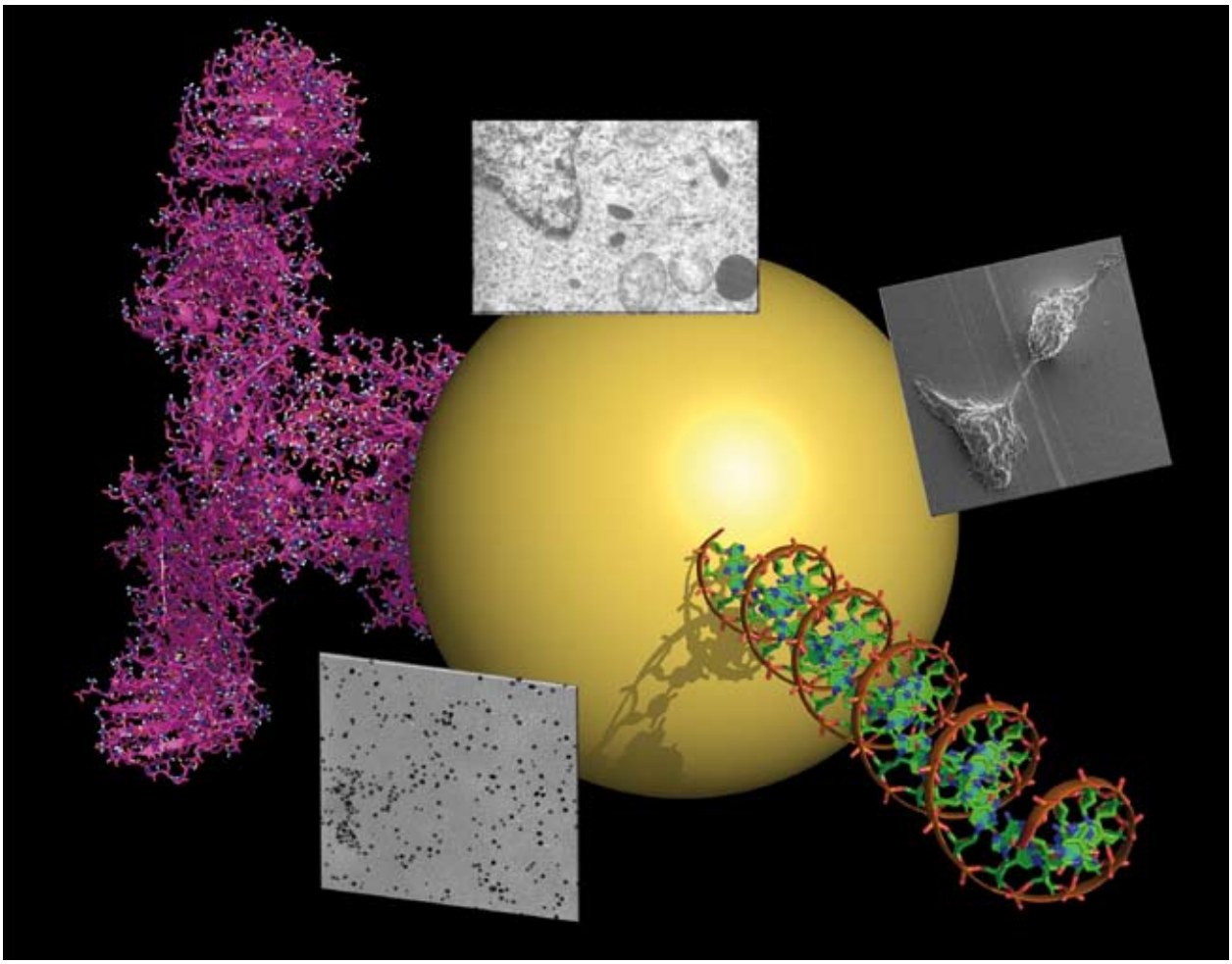

Gold—an introductory perspective†

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We introduce the collection of reviews in this thematic issue of *Chemical Society Reviews* that demonstrate and discuss the current cutting edge research in the field of gold chemistry and materials science as it stands today. We also highlight achievements in the fields of gold catalysis, gold nanoparticles and the preparative, structural and theoretical chemistry of gold, and discuss the remaining challenges and opportunities. Our aim is to inspire further discovery in these new and deeply fascinating fields.

Introduction

Gold has been a topic that has fascinated mankind since it was first discovered. It is the most noble of metals; it does not tarnish on exposure to the atmosphere and retains its beautiful lustre undiminished for millennia. It has been the source of many beautiful historical artifacts and works of art. It is also a metal with high monetary value and in these current times of high energy costs gold has increased in value dramatically. Hence, from the perspective of the monetary, art and historical communities, gold is an important metal, something that has high value and is readily traded (Fig. 1). Indeed the price of gold is a key indicator of the financial status of the world economy. However, for chemists, until recently, gold has presented very little fascination, although it did fascinate alchemists before the advent of modern chemistry (Fig. 2), the reason being that its chemical inertness as a bulk metal appeared to provide very limited opportunities to open up new and exciting chemistries. It was almost as though the known fact that gold is the most noble of metals precluded anyone from really searching for new interesting discoveries. In view of this, the chemistry of gold was relatively undeveloped, and typically in any chemistry text book, the chapter dealing with gold was the shortest. This is not now the case. The observation that gold, when sub-divided to the nanoscale, can be exceptionally active as a catalyst has spurred a great number of discoveries.[1,2] Indeed gold now fascinates materials scientists, catalysis, surface and synthetic chemists and theoreticians in great numbers. One reason for this, as pointed out by Corma,[3] in this issue, is that gold catalysis provides a link between model systems that can be produced by materials and surface scientists and the real systems used in catalyst discovery. The newly discovered chemistry of gold can be used on the one hand to gain a deeper understanding of catalysis and how, on the other, materials can be synthesized, and stabilized at the nanoscale.

After silicon, gold is probably the most frequently used element in nanoscale science today, and nanoparticles of gold have a much longer history than those of any other metal. Their presence in gold bhasma,[4] gold containing ashes prepared for medicinal purposes by usually secret recipes, dates back to the Vedic period of

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† Part of a thematic issue covering the topic of gold: chemistry, materials and catalysis.

Graham Hutchings is currently Professor of Physical Chemistry at Cardiff University having completed, in 2006, 9 years as Head of the School of Chemistry. His early career was spent in industry, in ICI at Teeside, and then in AECI, South Africa, where he made his initial discoveries concerning catalysis with gold. He moved to academia in 1984, and he has been mainly interested in the discovery of catalysts for oxidation and enantioselective reactions. He has held chairs in the University of Witwatersrand and the University of Liverpool before moving to Cardiff in 1997.

Mathias Brust is Professor of Chemistry at the University of Liverpool. He obtained his PhD in Physical Chemistry from this university in 1995, and then did postdoctoral research at the Universities of Buenos Aires, Texas at Austin and Liverpool. He was awarded an EPSRC Advanced Research Fellowship in 1998 and established his research group at Liverpool. He is mainly recognised for his contribution to the development of the Brust–Schiffrin method for the preparation of monolayer protected gold clusters. His research interests include aspects of metal nanoparticle chemistry, nanoelectronics and bionanotechnology. Current focus is on understanding interactions between metal nanoparticles and biological systems.

Hubert Schmidbaur is emeritus professor at Technische Universität München, where he had held the Chair of Inorganic and Analytical Chemistry for 30 years, after previous academic positions at Universität Marburg and Universität Würzburg. His visiting professorships included recent appointments at the University of Stellenbosch and the National University of Singapore. He is a member of several academies and learned societies and his research work was acknowledged by many awards. Gold chemistry has been one of his prominent fields of research. In 1996 he organized the first major conference on Gold Chemistry, Biochemistry and Technology in Hanau/Germany, the biggest centre of the gold industry in Europe.

Fig. 1 Gold is a widely traded metal in the banking world and is held as national reserves at central banks.

ancient India but it may well be possible to find even earlier evidence for anthropogenic gold nanoparticles given that the element itself has been known since prehistoric times. The oldest well-documented example is their use for decorative purposes in the comparatively recent Lycurgus cup from the 4th century AD, which is now exhibited in the British Museum and represents a fine illustration of Roman glass making skills.[5]

The art of handling gold in the form of nanoparticles matured to a science with Faraday's now legendary 1857 report in which he conjectured that the gold was present in solution in a "finely divided metallic state".[6] Following his pioneering discoveries, the first half of the 20th century saw a steady growth of knowledge in the field of colloid science, with gold again playing a prominent role. These developments were however marginalised by the revolutionary advances in physics that were taking place at the same time and by the repercussions these had on other sciences, in particular chemistry. Hence, Wolfgang Ostwald's "world of neglected dimensions",[7] *i.e.* the size domain between the molecular and that accessed by optical microscopy, did not receive any heightened attention until the advent of nanotechnology in the last two decades of the 20th century, when many of the old phenomena and concepts were revisited in the light of a more modern understanding of science. The importance of gold in nanotechnology, then and now, chiefly stems from its unique stability as a pure metal. Most other metals under ambient conditions are rapidly covered by a passivating oxide film, which makes them unsuitable for the fabrication of metallic nanoscale features, in which the majority of atoms are located at the surface. Hence, gold is a preferred metal for research in nanoelectronics. In the same way, nanoparticles of most other metals oxidise rapidly when exposed to air leaving gold the material of choice for most applications that involve colloidal metals.

The wealth of size-, shape- and environment-dependent optical properties of gold nanoparticles, here subject to a review by García de Abajo and colleagues,[8] is another decisive factor for the choice of gold in nanotechnological applications such as bio-labels, sensors, actuators and optical coatings. With the exception of silver, no other metal matches gold in terms of controllability and responsiveness of optical properties.

The fascination with gold catalysis, gold nanoparticles and gold chemistry has prompted an avalanche of research activity. Twenty years ago there were relatively few papers concerned with gold being published, whereas in the past year alone there were over 1200 papers and patents published on the topic of gold catalysis. In this issue of *Chemical Society Reviews* we have brought together a collection of reviews that demonstrate and discuss the current cutting edge research in the field of gold chemistry and materials science as it stands today. Our aim is to seek to inspire further discovery in this new and deeply fascinating field.

Achievements and successes

Catalysis

Catalysis by gold is now viewed as perceived wisdom, *i.e.* that gold, either in nanocrystalline form as colloids or supported in some way, or as discrete cationic complexes, offers a myriad of possibilities to activate and react molecules. The initial discovery of the catalytic efficacy of gold[1,2] was made out of the backdrop of some confusion. On the one hand there were distinct observations that would have, and, indeed, should have, encouraged any catalytic chemist to look further. Most notable of these is the work by Bond and co-workers[9,10] on hydrogenation where it was observed that very small particles of Au were very active. However, many reports stated that gold had no particular catalytic efficacy, and that observed activity may just be due to impurities.[11] Over the past twenty years there have been a number of discoveries which demonstrate that gold is the catalyst of choice for a number of reactions; *i.e.* gold is not just a good catalyst, it is the best. Sometimes gold has to be alloyed with other metals, *e.g.* Pd, to observe some of the effects, but in many cases it is gold alone that demonstrates this unique activity. Notable examples are:

- Low temperature CO oxidation[12]
- Acetylene hydrochlorination[13]
- Addition of nucleophiles to acetylenes[14]
- Selective hydrogenation of N–O bonds[15]
- Alcohol oxidation to acids[16] and aldehydes[17]
- Direct formation of hydrogen peroxide[18]

The reviews by Nolan,[19] Hashmi[20] and co-workers demonstrate the efficacy of gold when used as cationic complexes as homogeneous complexes for a wide range of chemical transformations, indeed that these catalysts can play an increasingly important role in organic synthesis. The reviews by Corma,[3] Rossi[21] and co-workers demonstrate the extensive applications of nanocrystalline gold as a heterogeneous catalyst. These

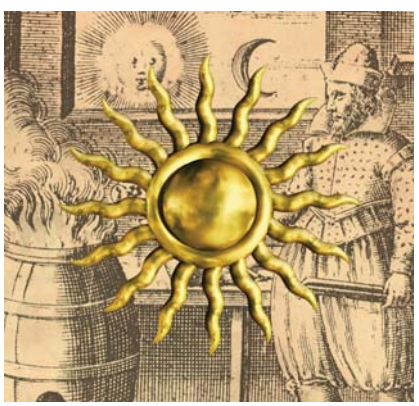

Fig. 2 Gold was the fascination of many alchemists. Copyright Murray Robertson.

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reviews[3,19–21] focus on the discovery of these catalysts and the current state of understanding.

Parallel to the numerous studies using high area catalysts, a number of elegant studies have been carried out, primarily from the surface science and *in situ* spectroscopic communities, typically using model systems, that have focused on trying to gain a deeper understanding of how and why gold can function as such an effective catalyst for such a broad range of reactions. These model systems are exceptionally elegant and their key features are brought out in reviews by Goodman,[22] Gates[23] and co-workers. As these model studies have developed so has the possibility of gaining an understanding through the detailed use of theoretical approaches, and the intricacies of these methods are set out in a review by Willock and co-workers.[24] The collection of reviews therefore presents the cutting edge of gold catalysis as it stands today, but we must recognize it is a fast moving field.

Gold nanoparticles

The reviews in this volume that deal with the nanoscience of gold cover many of the exciting advances that followed the explosive growth in scientific interest in nanoscale phenomena in the early 1980s. The discovery of the phosphine-stabilised Au_{55} cluster by the Schmid group in Essen in 1981 and the notion that such materials could, in principle, be used as building blocks for nanoscale devices marks the beginning of a paradigm shift from classic colloidal science to chemical nanotechnology.[25,26] The highlights of the ongoing Au_{55} story are here comprehensively presented in a critical review by Günter Schmid himself,[27] including the most recent developments at the interface of nanotechnology and medicine. The discovery of Au_{55} coincided with the enormously influential invention of the STM[28] (and soon after the AFM[29]) by Binnig and Rohrer, which made the nanoscopic world much more widely accessible to direct inspection than had previously been the case, when the rather expensive TEM was the only technique capable of comparable resolution. The combination of new abilities, namely, to chemically make well-defined nano-objects and to routinely image and manipulate them on surfaces, together with the commercially inspired quest for the miniaturization of electronic devices demanded by Moore's law, have probably been the major reasons for the huge and unabated interdisciplinary interest in nanometre scale phenomena that followed. The concept of the nanoparticle as a building block for larger structures and possibly devices has fascinated and inspired scientists ever since, and its fulfilment still represents a huge challenge. Two reviews cover this theme from two different angles. Prasad and colleagues[30] describe in detail the state-of-the-art in the field of self-organised two-dimensional superlattices, which were first reported by Bawendi *et al.* for CdSe[31] and by Whetten *et al.* for thiolate-capped gold nanoparticles[32] as building blocks. Well-defined but not necessarily ordered assemblies of gold nanoparticles linked to each other by polymeric templates are the subject of Rotello and co-workers' review,[33] which also includes a number of applications of such materials, for example as chemical vapour sensors, first reported by Snow and Wohltjen in 1998.[34]

While many important studies have been carried out using either traditional preparations of gold hydrosols, such as the classical Turkevich citrate reduction route[35] and its modifications,[36] or Au_{55}, the relative lack of stability of these particles sets limitations to the experimental conditions that could be employed. Most of these problems were overcome by thiolate-stabilisation of the particles based on Nuzzo and Allara's discovery of self-assembled monolayers of thiols on gold surfaces.[37–40] Following a suggestion by Royce Murray, such particles are now widely referred to as monolayer protected clusters (MPCs).[41] Thiolate-stabilisation also enabled the Murray group to thoroughly investigate the electrochemical charging behaviour of MPCs, which led to an elegant demonstration of electrochemical Coulomb staircase charging at room temperature.[42] This area of research is comprehensively reviewed in the contribution by Quinn and colleagues.[43]

Most current uses of gold nanoparticles in the 1 to 100 nm range utilise some type of ligand-stabilisation usually *via* thiol moieties, for example, cysteine residues in peptides and proteins.[44] The ability to obtain extremely stable gold nanoparticles also in aqueous solution has led to a renaissance in the use of gold for life science applications. In this area, colloidal gold, in particular if modified with antibodies, had already played a significant role as a specific labelling agent for electron microscopic studies of tissues and cells before nanotechnology came into fashion.[45] The two reviews by Parak and co-workers[46] and by Wilson[47] give a flavour of the most important biomedical applications of gold nanoparticles, in particular, of the more recent developments ranging from point of care diagnostics to advanced methods of controlled intracellular delivery. The number of recently proposed applications in this rapidly developing field is so large that it is impossible to do justice to all of them within the scope of two topical reviews. Without doubt, life science and medical applications represent the largest area of growth for nanoparticle research, and our recently developed ability to precisely design and control the chemical and biochemical surface functionalities of stable nanoparticles has already resulted in exciting new opportunities of monitoring and manipulating biological processes.

A clear highlight in the history of gold nanoparticles is the X-ray structure of a thiolate-protected Au_{102} cluster reported late last year by Kornberg and co-workers.[48] This, together with a Au_{25} structure published a little later by Murray and co-workers,[49] provided for the first time direct and clear evidence for the existence of MPCs as precisely defined chemical compounds with a sum formula and a molecular structure. Interestingly, both structures reported seem to support the notion that both the number of gold atoms and that of ligand molecules are determined by the electronic configuration of the cluster rather than by its geometry. Stability seems to arise from achieving a closed shell of free 6s electrons confirming the heuristic power of the artificial atom concept. It is to be expected that more structures will be determined and that a new class of chemical compounds will be established over the next few years. The review by Häkkinen[50] provides insight in the atomic and electronic structures of gold clusters including a full consideration of these most recent experimental findings.

Finally what if anything is missing in this collection of reviews? The diversity of reviews before us shows that the field is interdisciplinary and that it has to do as much with biology, medicine, physics and engineering as with chemistry. Perhaps the solid state physics community could have been represented more strongly. Gold nanoparticles play an important role in the development of nanoelectronic devices such as single electron transistors, and ensembles of particles on insulator surfaces display fascinating collective phenomena, for example, reversible metal–insulator transitions.[51] Another area that has not been included here is the spectroscopic study of single gold particles, for which several optical techniques are now available.[52,53] These can provide insight into the optoelectronic, mechanical and chemical properties of individual particles. Another area that is rapidly expanding and has not been included here is the chemical functionalisation of MPCs. Practically all classes of compounds have been attached to the surface of gold nanoparticles, and a correspondingly wide range of potential applications have been proposed.[54]

Preparative, structural and theoretical chemistry of gold

In the 21st century, gold chemistry is now based on solid ground regarding the preparation and characterization of a wide variety of fundamental compounds with gold atoms in a broad range of oxidation states and coordination numbers or with gold clusters as core units. It is this broad basis laid by extensive experimental work carried out in the past few decades which has made all novel applications of gold metal and gold complexes possible.[55]

For a long time, alchemists and chemists had known and used only three *oxidation states* of gold (Au^0, Au^{1+}, Au^{3+}), whereas for modern gold chemistry the range has finally been extended to the lower and upper limits of Au^{1-} and Au^{5+}, respectively, and now includes not only Au^{2+} but also a variety of mixed oxidation states in polynuclear units or gold clusters, wires, surfaces, and nanoparticles covered with self-assembled monolayers.

Theoretical chemistry of gold has played an important supportive role in the recent almost explosive development of gold chemistry. Step by step, theoretical physicists and quantum chemists transmitted to chemists the message that *relativistic phenomena* allow us to really understand the "nobility" of gold as the "king of the elements".[56–58] Not only its extreme electrochemical potential among the metals is readily explained by the maximum in the relativistic contraction of the valence orbitals reached by gold atoms, but also the high electron affinity of gold atoms which explains the unusual stability of the transition metal *anion* Au^{1-}.[59]

Mainly the extensive structural work using single crystal X-ray diffraction has unravelled yet another phenomenon initially not predicted by simple valence rules, the *aurophilicity effect*.[60,61] Gold(I) compounds in which the metal centre is in a seemingly closed shell electron configuration are not expected to show any affinity for one another. And yet there is ample experimental evidence for attractive intra- and intermolecular interactions which co-determine the configurations and conformations of molecules and the aggregation of molecular units into oligomers or multidimensional aggregates. These interactions give rise to specific physical effects which determine *e.g.* the photophysical properties of the complexes, which are often found to be highly emissive (luminescent).[62] Albeit metallophilicity has been recognized to be a more general effect, it appears to be strongest and most obvious for gold(I) owing not only to its strongest relativistic contraction but also to the low coordination number (CN 2) and therefore reduced steric hindrance for complexes with the metal in this oxidation state.

The aurophilicity phenomena were found to be ubiquitous not only in the molecular chemistry of gold, but also in the *solid state chemistry* of genuine inorganic solids. Salts and complexes with the classical di(cyano)aurate anions as the counterion or ligand, respectively, can serve as prototypes for this kind of system.[63]

The low coordination number and linear geometry of gold(I) compounds has further been found to be an excellent basis for the construction of one-dimensional *polymers* with gold atoms at regular intervals, or of *macrocycles* which—supported by aurophilic bonding—can become part of *catenated* and even *braided* or *double-braided systems*.[64]

Gold has offered to chemists and physicists a particularly broad range of cluster units $[Au_n]^{m+}$, with homometallic examples covering virtually any integer n from 2 to very high numbers. With $n \neq m$, these clusters have mixed valence states for the gold atoms contained therein, and these may be further modified by the introduction of heteroatoms in heterometallic or—more generally—heteroelemental clusters.[65] Clusters with small numbers n can be treated as quantum dots, while for large n the clusters range into the *nano* region. Gold nanoparticles with their variable and unique properties have become a major playground in modern *nanoscience*.

From a qualitative point of view, many of the new phenomena encountered in gold chemistry are experimentally well diagnosed and theoretically fully interpreted, but quantitative data, *e.g.* on bond energies and their dependence on the interatomic distances and on the substitution pattern, are still scarce. This makes any stringent evaluation of physical properties still rather difficult, and further studies are required. Once these limitations have been overcome, rapid progress could be made in the most promising applications of new gold-containing compounds in materials and nano science (photophysical and magnetic response, non-linear optics, mesogenic phases *etc.*).

Gold compounds have been used in *medicine* for almost a century and a few gold drugs have been very successful in chrysotherapy of arthritis and rheumatism. Cancer therapy with gold has also been a prominent research topic for many years and a breakthrough similar to the discovery and development of *cis*-platin and related compounds may be close.[66] Trials with new ligand systems are under way in several laboratories, but no clear trend has yet become discernible. Since gold salts in principle are highly toxic like most salts of its neighbours in the periodic table, most notably mercury, lead, and thallium, there will always be limits to any high-dose or long-term applications. However, a new area of gold chemistry in medicine may arise in diagnostics and therapy from the

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application of gold nano-particles which are insoluble and hence of low toxicity.

Most of the emerging new classes of gold compounds and their unique features of structure and bonding are highlighted in the collection of articles presented in this special issue of *Chemical Society Reviews*.

Remaining challenges

Catalysis by gold is now a maturing field and we are moving from the time of catalyst discovery using relatively non-complex methods of synthesis to more specific preparations and design, aided by detailed understanding of how nanoparticles and complexes can be prepared, aided by collaborations between material scientists and chemists, as well as the insights gained from model and theoretical studies. New methods are being refined and so this will fuel further progress.

From a catalysis perspective, the key remaining challenge concerns the nature of the active site for supported gold nanoparticles. This has proved to be a highly controversial topic and a number of key debates concern the electronic nature of the active species. These are discussed in the reviews by Goodman,[22] Gates[23] and co-workers. On the one hand cationic gold species either in solution[14,19,20] or supported[13] are known to be active for the addition of nucleophiles to acetylenes, the debate concerns whether this is the case in other reactions, notably the oxidation of CO. The real nature of the problem, however, is, in contrast to the well defined molecular complexes used in homogeneously catalysed reactions,[14,19,20] real high area heterogeneous catalysts comprise a wide range of structures, all of which could be active in the catalysed reaction to some extent. The recent developments in aberration corrected scanning transmission electron microscopy are now starting to show the full complexity of these real heterogeneous catalysts. This is particularly well exemplified by some recent elegant microscopy of the Au/TiO_2 catalyst[67] which is known to be highly active for CO oxidation.[22] Using aberration-corrected microscopy, Pennycook and co-workers have shown that there is a very broad distribution of clusters and small nanoparticles co-existing in an active catalyst. On the one hand this is a great advantage if one is trying to discover an active catalyst, at that stage of catalyst design it is preferable to make a catalyst with a wide range of potentially active structures, since then you have the chance that some might be active. However, from a mechanistic standpoint we need to pinpoint which of the species present in real catalysts are indeed active. Also, are these the same species for all the reactions? After all gold is proving to be effective in a broad range of reactions,[3,19–23] but it is unclear whether there are a range of different sites where the activity can be fine-tuned to a specific reaction. This has not yet been achieved and represents the major challenge for gold catalysis today. Indeed, we anticipate that model catalyst[22,23] and theoretical studies[24] will prove to be crucial in gaining this understanding; but there is also a crucial role to be played by materials scientists since by combining their expertise with that of catalyst chemists we will start to synthesise specific structures in real high area catalysts and specifically test their catalytic efficacy. The elegant model and theoretical studies will lead the way in this new era of gold catalysts that we envisage.

Fortunately, there are many remaining challenges, and the field of gold chemistry and, in particular, gold nanoparticle research with all its surprising recent developments is anything but mature. One of the most urgent needs, for which practical solutions should be expected in the near future, is to achieve precise preparative control of particle shape. The review by Liz-Marzan and colleagues[68] illustrates the opportunities of chemically creating a vast range of different geometries as well as the considerable practical difficulties still associated with it. The control of particle size, on the other hand, has advanced quite significantly both by the development of a number of size separation methods,[69] and by preparative protocols that lead to near monodisperse products.[70] In practice, however, obtaining monodispersity and controlling particle size remains an experimental difficulty that requires a lot of experience and can be cumbersome and time consuming. Future developments that facilitate size control are thus still needed.

Very little work has been done regarding the conformation of the ligand shell and its dynamics in MPCs. An elegant NMR study by Rotello and co-workers in 2000 demonstrated that the ligand shell is highly adaptive in the sense that individual ligand molecules can regroup and even self-organise to form a receptor site in the presence of a suitable molecular template.[71] Unfortunately, very little similar work followed from these initial studies, and one should hope that the exciting opportunities of creating dynamic adaptive nanostructures will be recognised by future research. Apart from creating supramolecular functionality, the ligand shell appears to have other unexpected conformational properties with potentially far reaching consequences. Recent work by Stellacci and co-workers suggests possibilities of structuring the ligand shell by slight alterations of its composition, for example, to obtain meridians of ligands, the presence of which causes the cluster to adopt a bipolar symmetry.[72] This revives the important question of whether the building block concept can be taken to the next level by creating a version of nano-*Lego*® with asymmetric blocks that only fit together in a well-defined head-to-tail fashion. Stellacci *et al.* also recently suggested that the ligand shell conformation determines whether or not the particles are taken up by living cells.[73] This clearly presents fascinating perspectives and deserves further studies to be substantiated.

Cellular uptake of nanoparticles in general is still poorly understood, and in view of using nanoparticles as intracellular probes as carriers for drug and gene delivery, research is needed to establish the factors that determine the uptake mechanisms and the intracellular fate of nanoparticles. In this context it is also important to develop nanoparticles that can carry and release molecular payloads in a controlled fashion. Early examples of how such systems may be devised are presented in the review by Parak and co-workers.[46]

Another area that deserves future attention is the reactivity of the ligand shell of MPCs. These clusters represent unique opportunities for the development of *ikebana* chemistry, which could be defined as the controlled arrangement of selected functional groups on the surface of a nanoparticle. This will lead to the ability to tune the reactivity of the functional groups involved and may

present opportunities for the development of new catalysts that operate in a way similar to enzymes.

Opportunities

In the field of catalysis there appear to be many opportunities for the application of the unique advantages offered by gold in a commercial context. For example, as noted by Corma,[3] Rossi[21] and coworkers there are a number of possibilities in the field of selective chemical synthesis, notably the direct formation of hydrogen peroxide and the selective oxidation of OH functional groups. In the latter case, catalysis by gold can play an increasingly important role in the use of bio-renewable feedstocks such as sugars and glycerol. The high specificity of supported gold catalysts in reactions of acetylenes may also provide a key opportunity. For example, although acetylenes are highly reactive for addition reactions using gold, the reactions of alkenes is not observed to any extent. This presents the possibility of excellent selectivity in process streams which contain both acetylene and alkenes, and it can be expected that this feature can be exploited. Recent studies show that this expectation is realistic.[74] However, the real opportunity will come from a combination of expertise that will encompass much of the chemistry described in this issue. Namely, the combination of synthesis, using the unique aspects of gold chemistry, together with leads provided by model surface and theoretical studies to prepare a new range of high activity bespoke catalysts.

It is always very difficult to predict opportunities for the future, in particular, if commercial aspects are to be considered for gold chemistry in general and gold nanoparticles in particular. Hence, we will simply try to extrapolate from some of the challenges mentioned in the previous section. Once perfect control over particle size, shape and *Lego*®-type polarity has been achieved, the question arises whether nanoscale self-assembly can be carried out as a branch of preparative chemistry, which would use a kit of particles of different shapes, sizes and binding affinities instead of molecules to assemble structures and devices. Even if this vision were to become reality, it is not obvious which practical applications would arise from it. At present it is difficult to imagine that conventional computer architectures and manufacturing methods, for example, could seriously be challenged by a chemical bottom-up approach to device manufacture. We would, however, dare to predict that *Lego*® nanotechnology, if it can be realised, would enable applications that have not yet been invented and thus cannot be described here. It would be an enabling technology *par excellence* comparable in importance with polymer chemistry, or the invention of the integrated circuit, and obviously not limited to the use of gold as a construction material.

Gold nanoparticles have shown a potential for adaptive chemistry. This means that one could envisage the combinatorial discovery of artificial receptors, sensors and enzymes by shuffling around different ligands (including peptides, for example) with different functional groups on the particle surface. The parameter space for such a journey of discovery would be enormous. Unfortunately, this is just an idea, and probably nobody currently works on the combinatorial design of ligand shell functionality. An area of intense activity, on the other hand, concerns the interactions of nanoparticles with living organisms. Answering pressing questions regarding the potential toxicity of nanoparticles is only one motivation for such studies, which could on the medium to long term result in novel therapeutic opportunities to cure many diseases including cancer,[75] and may lead to the general concept of intracellular surgery carried out by precisely programmed invasive nanoparticles. In the near future, however, we will first see an increasing use of gold nanoparticles in diagnostic applications, for example, in simple home diagnostic devices of the type currently used for pregnancy tests.

Nanotechnology is also generally predicted to be instrumental in addressing great challenges such as securing our future energy supply.[76] Gold will have its place in researching more efficient nanostructured systems for solar energy conversion and in optimising fuel cell catalysts.

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