

Highlights from Recent Literature

1 ANALYTICAL

1.1 Determination of mercury in gold bullion by flame and graphite furnace atomic absorption spectrometry

A procedure has been developed by M.W. Hinds of the Royal Canadian Mint, Ottawa, Canada to determine mercury in unrefined gold by flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) (*Spectrochim. Acta, Part B*, 1998, **53B**(6-8), 1063-1068). High acid content (60-80% of concentrated HCl in water) was needed to keep silver (usually present with gold deposits) in solution as a chloro-complex. Although mercury determinations by FAAS and GFAAS have poor sensitivity, the relatively high concentrations of mercury (0.02-0.2%) are well within the capabilities of these techniques. No significant difference was observed between concentration values obtained from these techniques and those obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES) with the same sample. The limit of detection (3 s) is *ca* 20 $\mu\text{g g}^{-1}$ for both GFAAS and FAAS determinations. However, FAAS is the recommended method due to simplicity of operation, higher sample throughput, low cost, and ease of method transfer to other laboratories.

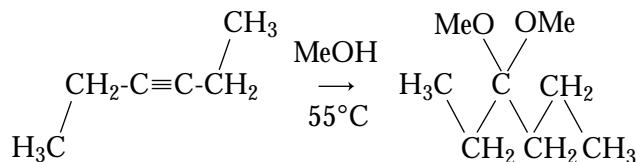
2 CATALYSIS

2.1 Homogeneous and Heterogeneous Liquid Phase Catalysis

Following the establishment of gold catalysts for gas phase reactions (see, for example, page 111 of this issue), two significant advances have been made in the use of gold catalyst systems in the liquid phase.

The first represents a major step forward for homogeneous catalysis using gold species. A group at BASF AG, Ludwigshafen, Germany (J.H. Teles, S. Brode and M. Chabanas, *Angew. Chem. Int Ed.*, 1998, **37**, 1415) have described the use of cationic gold(I) complexes of the type $[\text{L-Au}^+]$ (where L is a phosphine, phosphite or an arsine) for the addition of alcohols to alkynes. An example of such a reaction is given in the next column.

The turnover numbers for this type of reaction were found to be up to 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 (20 – 50°C) in the presence of acid co-catalysts.

The second example is provided by the work from the CNR laboratories in Milan (L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552). Gold on carbon catalysts have been used for the selective liquid phase oxidation of diols with dioxygen in alkaline solution under mild conditions (343 – 363 K). Ethane-1,2-diol gave 93% selectivity to glycolate at 80% conversion with a 1% gold on carbon catalyst. Glyoxal (OHC-CHO) is first formed and this rearranges via a Cannizzaro reaction to the glycolate ion (HO-CH-COO^-). As with gold catalysis in the gas phase, the gold particle size is important and the most selective catalyst had a diameter of 7nm, and was prepared by deposition precipitation, from HAuCl_4 and sodium carbonate followed by reduction with formaldehyde.

2.2 Heterogeneous Gas Phase Catalysis

Much of the exciting new work in this field is put into perspective by that described by M. Valden, X. Lai and D.W. Goodman, *Science*, 1998, **281**, 1647. Gold clusters ranging in diameter from 1 to 6 nm were prepared on single crystal surfaces of titania in ultrahigh vacuum to investigate the unusual size dependence of the low-temperature catalytic oxidation of carbon monoxide. A band gap starts to appear at 4 nm diameter, and increases in width as the size is further decreased. The results indicate that the pronounced structure sensitivity of CO oxidation on Au/TiO_2 originates from quantum size effects associated with the supported gold particles. The observed tailoring of the properties of small metal particles by altering the particle size and its support could prove to be important for other metals as well as gold and is likely to be useful in the design of nanostructured materials for catalytic applications.

3 CHEMISTRY

3.1 A Nitride Containing Infinite Zigzag Gold Chains

A new ternary calcium auride nitride with the formula $(\text{Ca}^{2+})_2\text{AuN}^{3-}$, has been prepared by the reaction of Ca_3N_2 powder with gold foil in the correct stoichiometric ratio under high pressure dry nitrogen (P.F. Henry and M.T. Weller, *Angew. Chem. Int. Ed.*, 1998, **37**, 2855). The structural characterization of the product from Rietveld refinement of powder neutron and X-ray diffraction data shows the presence of relatively short Au-Au bonds (2.857 Å) that form extended zigzag chains. These bond lengths are slightly shorter than those found in metallic gold (2.884 Å). Ca_2AuN is best described as CaN zigzag chains inserted into the CaAu structure, which also has zigzag chains although it has not as yet been fully characterized. Ca_2AuN is thus the first example of a ternary material containing zigzag gold chains and it is only the second example of a gold nitride.

3.2 A New Type of Metal Sandwich Structure

A new type of metal sandwich structure $[\text{Ag}\{\{\text{Au}(\mu\text{-N}^3, \text{C}^2\text{-bzim})\}_3\}_2]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ ($\text{N}^3, \text{C}^2\text{-bzim} = 1\text{-benzylimidazolate}$) has been described by A. Burini, J.P. Fackler, R. Galassi, B.R. Pietroni and R.J. Staples, *Chem. Commun.*, 1998, 95-96. It was obtained by reacting the neutral triangular cluster $[\text{Au}(\mu\text{-N}^3, \text{C}^2\text{-bzim})_3]$ with Ag^+ . This is the first sandwich silver cluster of a trinuclear cyclic gold(I) complex and the units stack with two short intermolecular Au...Au distances of ca 3.2 Å.

3.3 Preparation and Characterization of $\text{Tl}_2\text{Au}_4\text{S}_3$

S. Löken, C. Felser and W. Tremel, *Chem. Commun.*, 1998, 1603 have described the synthesis of $\text{Tl}_2\text{Au}_4\text{S}_3$, obtained by reacting gold with fluxes of Tl_2S and sulfur. Its crystal structure is characterized by sheets of buckled 16-membered rings of Au and S atoms with short Au-Au contacts (3.010 Å) between the sheets. Acute Au-S-Au angles (91.8°) at the corners of the boat-like rings lead to an Au-Au distance of 3.350 Å within the rings.

3.4 Synthesis of $\text{Cs}_4\text{Au}_7\text{Sn}_2$

A gold-tin framework structure with Au_7 -clusters and Sn_2 dumb-bells has been described by U. Zachwieja and J. Wlodarski, Fachbereich Chemie, Universität Dortmund, Germany (*Z. Anorg. Allg. Chem.*, 1998,

624(9), 1443-1446). Silver-coloured, brittle single crystals of $\text{Cs}_4\text{Au}_7\text{Sn}_2$ were synthesized by reaction of CsN_3 with gold sponge and powdered tin at 920 K. The structure of the compound was determined from x-ray single-crystal diffraction data. Au and Sn form a framework structure that consists of interconnected $[\text{Au}_7]$ clusters and Sn_2 dumb-bells. The Cs atoms occupy channel-like cavities within the Au Sn partial structure.

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 Introducing Chemical Transport Selectivity into Gold Nanotubule Membranes

This paper, by J.C. Hulteen, K.B. Jirage and C.R. Martin, *J. Am. Chem. Soc.*, 1998, **120**, 6603, describes the introduction of chemically-based transport selectivity into polymeric membranes that contain a collection of monodisperse gold nanotubules with internal diameters of molecular dimensions <1 nm. By chemisorbing thiols (R-SH) onto the gold tubule surfaces, the rate and selectivity of transport in these membranes is dramatically altered by the chemical nature of the R group.

4.2 One- and Two-Dimensional Quantum Transport in Thin Gold Wires

S. Friedrichowski and G. Dumpich, Experimentelle Tieftemperaturphysik, Gerhard-Mercator-Universität-GH-Duisburg, Germany (*Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**(15), 9689-9692) have reported on magnetoresistance (MR) measurements of thin gold wires of various widths, between 50 nm and 50 µm prepared by electron-beam lithography. The MR was measured at 1.5-25 K using a 4He-bath cryostat where magnetic fields of up to $B = 5$ T can be applied perpendicular to the film plane. The MR data of the various gold wires was analysed using detailed theoretical calculations concerning 1-dimensional and 2-dimensional quantum transport. The authors determined the phase coherence length and its temperature dependence, and found that it was almost independent of whether the gold wires show 1-dimensional or 2-dimensional quantum transport behaviour. This confirmed the analysis of the MR data and showed that the phase coherence length displays intrinsic scattering properties.

4.3 Current-Induced Surface Dislocations on Thin Gold Films

The appearance and evolution of dislocations on the surface of flame-annealed gold films due to current

stressing (electromigration) have been studied using scanning tunneling microscopy by N. Shimoni, O. Biham, and O. Millo (Racah Institute of Physics, The Hebrew University, Jerusalem, Israel) in *Surf. Sci.*, 1998, **414**(1/2), L925-L931. Many line dislocations are present on the surface of such films, probably formed during the annealing process. Yet, at room temperature with no current stressing, the formation of new surface dislocations is rare. When a current is applied through the film, new line dislocations often emerge. The new dislocations run predominantly in directions close to that of the current, and usually appear in correlation with the onset of the current.

4.4 Self-Assembled Monolayers based on Chelating Aromatic Dithiols on Gold

N. Garg and L.T. Randall, *Langmuir*, 1998, **14**, 3815, have described how self-assembled monolayers (SAMs) were generated by the adsorption of xylene- α_1, α_2 -dithiol and 1,2-bis(mercaptomethyl)-4,5-dialkyl benzene derivatives, $[\text{CH}_3(\text{CH}_2)_m]_2\text{C}_6\text{H}_2[\text{CH}_2\text{SH}]_2$ ($m = 0, 4, 12, 13, 14, 15$), on the surface of gold. These monolayers were characterized by optical ellipsometry and contact angle goniometry. Comparison of the thicknesses and wettabilities of the new SAMs to those generated from normal alkanethiols suggests that the new chelating diols generate densely packed and highly oriented monolayer films on gold. Preliminary studies of film desorption in solution suggest that the new SAMs are more stable than normal SAMs on gold.

4.5 In-Plane Resistivity of Ultrathin Gold Films: A High Sensitivity, Molecularly Differentiated Probe of Mercaptan Chemisorption at the Liquid-Metal Interface

Y. Zhang, R.H. Terrill and P.W. Bohn (Department of Chemistry, Beckman Institute and Materials Research Laboratory, University of Illinois at Urbana-Champaign, USA, *J. Am. Chem. Soc.*, 1998, **120**(38), 9969-9970) have reported a resistivity measurement of mercaptan adsorption at the gold-liquid interface for gold films with thicknesses between the percolation threshold (*ca* 5 nm) and the electron mean free path (*ca* 80 nm). A simple four-probe resistance measurement reveals an increase of *ca* 4% in the in-plane resistivity of a *ca* 40 nm thick gold film upon adsorption of mercaptan monolayers. The effect is independent of the length of the alkyl chains of the chemisorbed alkanethiols, $\text{C}_n\text{H}_{2n+1}\text{SH}$ but is dependent on the molecular character of the adsorbate.

4.6 A New Class of Self-Assembled Monolayers: *closo*- $\text{B}_{12}\text{H}_{11}\text{S}_3$ - on Gold

It has been shown that *closo*- $\text{B}_{12}\text{H}_{11}\text{S}_3$ -self-assembled monolayers (SAMs) form spontaneously when gold substrates are exposed to solutions of $\text{Cs}_2[\text{closo}-\text{B}_{12}\text{H}_{11}\text{SH}]$ (L.J. Yeager, F. Saeki, K. Shelly, M.F. Hawthorne and R.L. Garrell, Department of Chemistry and Biochemistry, University of California, Los Angeles, USA; *J. Am. Chem. Soc.*, 1998, **120**(38), 9961-9962). The authors demonstrate that the adsorption process is remarkably similar to that of organothiol self-assembly on gold; adsorption occurs through the sulfur atom and is accompanied by cleavage of the S-H bond and the formation of a strong polar covalent sulfur-gold bond.

5 ELECTROCHEMISTRY

5.1 Voltammetry of Hydroxide Ion in Aqueous Solutions on Gold Microelectrodes

In a paper by M.E. Abdelsalam, G. Denault, M.A. Baldo and S. Daniele, *J. Electroanal. Chem.*, 1998, **449**, 5, a well-defined wave for the oxidation of hydroxide ions was recorded with gold microdisc electrodes either in sodium sulfate or sodium perchlorate solutions, made basic with sodium hydroxide. The wave appeared at *ca* 1.3 volts *vs* SCE, just before the background discharge. A plot of the limiting current corresponding to this wave against the radius of a series of microdisc electrodes gave a straight line which indicated that the process is diffusion controlled. Similarly, the limiting current was found to depend linearly on pH over the range 9 – 12.5. It is claimed that the results presented in this paper provide the first experimental evidence for the diffusion-controlled electrochemical oxidation of hydroxide ions in aqueous solutions. On large electrodes, however, the mass transfer is not as effective and a large OH^- concentration is required to overcome the background current due to oxide film growth (see also, L.D. Burke and P.F. Nugent, *Gold Bull.*, 1997, **30**, 43; *Gold Bull.*, 1998, **31**, 39).

5.2 Gold Nanoelectrodes of Varied Size: Transition to Molecule-Like Charging

R.W. Murray, R.L. Whetton *et al*, *Science*, 1998, **280**, 2098, in a collaborative paper involving authors from the University of North Carolina, Chapel Hill and the Georgia Institute of Technology, USA, have described a transition from metal-like double-layer capacitive charging to redox-like charging in electrochemical

ensemble Coulomb staircase experiments on solutions of gold particles of varied core size. The monodisperse gold nanoparticles are stabilized by short-chain alkane thiolate monolayers and have 8 to 38 kilodaltons core mass (1.1 to 1.9 nm in diameter). Larger cores display coulomb staircase behaviour consistent with double-layer charging of metal-electrolyte interfaces, whereas smaller core nanoparticles exhibit redox chemical character, including a large central gap. The change in behaviour is consistent with new near-infrared spectroscopic data showing an emerging gap between the highest occupied and lowest unoccupied orbitals of 0.4 to 0.9 eV.

6 ELECTRONICS

6.1 Quantized Conductance through Individual Rows of Suspended Gold Atoms

As the scale of microelectronic engineering continues to shrink, interest has focused on the nature of electron transport through essentially 1-dimensional nanometer-scale channels such as quantum wires and carbon nanotubes. H. Ohnishi and K. Takayanagi of the Takayanagi Particle Surface Project, ERATO, Japan Science and Technology Corporation, Tokyo, have reported (*Nature (London)*, 1998, **395**, 780-783) that quantum point contacts (QPCs) are structures (generally metallic) in which a 'neck' of atoms just a few atoms width in diameter (that is comparable to the conduction electrons' Fermi wavelength) bridges two electronic contacts. They can be prepared by contacting a metal surface with a scanning tunneling microscope (STM) and by other methods, and typically display a conductance quantized in steps of $2e^2/h$ ($\sim 13 k\omega^{-1}$), where e is the electron charge and h is Planck's constant. Here the authors report conductance measurements on metal QPCs prepared with an STM that the authors can simultaneously image using an ultrahigh-vacuum electron microscope, which allows direct observation of the relation between electron transport and structure. The authors observe strands of gold atoms that are about one nanometer long and consist of one single chain of gold atoms suspended between the electrodes. The authors verify that the conductance of a single strand of atoms is $2e^2/h$ and that the conductance of a double strand is twice as large, showing that equipartition holds for electron transport in these quantum systems.

6.2 Thermal Reshaping of Gold Nanorods in Micelles

M.B. Mohamed, K.Z. Ismail, S. Link and M.A. El-Sayed of the Laser Dynamics Laboratory School of

Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, USA (*J. Phys. Chem. B*, 1998, **102**(47), 9370-9374) have prepared gold nanorods from aqueous solutions by an electrochemical method and are shape controlled by using capping micelles as described by Y. Yu *et al* (*J. Phys. Chem. B*, 1997, **101**(34), 6661). TEM images were determined for these gold nanorods, taken from solutions heated to various temperatures at 25-160°C. Size and shape analysis of their TEM images showed that the mean aspect ratio of the nanorods in solution decreases with increasing temperature, mostly as a result of reduction in their length.

Heating the dried nanorods themselves on a TEM slide to much higher temperatures did not produce any shape changes. The observed relative instability of the longer nanorods in the micellar solutions can probably be attributed to the relative instability of the micelles capping the longer gold nanorods. Following the change with time of the longitudinal surface plasmon absorption band of the gold nanorods at five different temperatures, the activation energy for the thermal decomposition of the micelles is 21.0 ± 1.0 kcal mol⁻¹. The most stable rod-shaped micelle has an aspect ratio of 2.0. The craft decomposition (dissolution) temperature of these micelles is *ca* 155°C. This study provides a new method in which the thermal stability of micelles of various shapes may be used to change the size distribution of metal nanorods in solution. However, TEM or the absorption maximum of the longitudinal plasmon resonance of gold nanorods can be used as a sensitive monitor in studying the physical properties of the host micelles themselves.

6.3 Gold Cluster Formation using an Atomic Force Microscope and its Applications to Gallium Arsenide Whisker Growth

Gold clusters have been formed on the GaAs(111)B substrate by the field evaporation of gold atoms using an atomic force microscope (AFM) in a study by M. Shirai, K. Hiruma, K. Kenji, T. Katsuyama, H. Koyanagi and S. Hosaka of the Central Research Laboratory, Hitachi Ltd., Tokyo, 185, Japan (*Superlattices Microstruct.*, 1998, **24**(2), 157-162). The clusters obtained appeared as mounds with typical diameters of 100-150 nm and heights of 1.5 nm. Also, gallium arsenide whiskers were grown after annealing by using these clusters as seeds. However, the sites of the whiskers did not correspond to the sites of the gold clusters existing before annealing and growth. Gold cluster formation by the AFM method did some damage to the substrate and permitted gold to diffuse into the substrate at relatively low temperatures.

7 METALLURGY

7.1 Solubility Data for Gold-Alkali Metal Systems

H.U. Borgstedt and C. Guminski from the Kernforschungszentrum Karlsruhe, Germany have published a series of short review articles on the gold-alkali metal systems, Au/Li, Au/Na, Au/K, Au/Rb and Au/Cs (*Solubility Data Ser.*, 1996, **64** (Metals in Liquid Alkali Metals, Pt. 2), 84-103. These include descriptions of the phase diagrams, location of liquidus lines, mutual solubilities of the elements involved, thermodynamic modelling, *etc.* The information available for each system is critically assessed and interpreted, for example by re-drawing some of the phase diagrams, with a view to identifying areas where better definition is required. The reviews help to define the existing state of knowledge and to identify desirable areas for future investigation.

8 REFINING

8.1 Gold Uptake by Plants

In a paper from Massey University, Palmerston North, New Zealand (C.W.N. Anderson, R.R. Brooks, R.B. Stewart and R. Simcock. *Nature*, 1998, **395**, 563) experiments are described in which plants, grown on soil treated with ammonium thiocyanate as a chelating agent, absorb gold. The Indian mustard plant species *Brassica juncea* gave the highest individual value for accumulation of gold, *ie* 57 μg gold per g dry weight. Values were very variable, however. The view is expressed that it is therefore technically feasible to grow a 'crop of gold' upon auriferous substrates. The thiocyanate kills the plants after about a week, but this is not really a problem because these plants grow very quickly (see *Chem. and Ind. (London)*, 1998, 829) The gold can be recovered by burning the dead plants and refining the ash. A forthcoming article by these authors will be published shortly in *Gold Bulletin*.

8.2 Extraction of Gold from Cyanide or Chloride Media by Cyanex 923

This paper, by F. Alguacil, C. Caravaca and S. Martinez, of CSIC, Ciudad Universitaria, Madrid, *J. Chem. Technol. Biotechnol.*, 1998, **72**, 339-346 describes a new phosphine oxide extractant, known as Cyanex 923, which has been applied in the recovery of gold from either cyanide or chloride aqueous media. $\text{Au}(\text{CN})_2$ is extracted by this reagent throughout the whole pH range. The presence of lithium salts in the media improves the degree of extraction. The extraction mechanism proposed can be explained in terms of a solvating reaction, the species formed in the organic phase being $\text{Li}^+\text{Au}(\text{CN})_{2.3}(\text{R}_3\text{PO})$. The stripping can be performed by low ionic strength solutions such as dilute KCN, and the reaction is enhanced by an increase in temperature. In chloride media, gold(III) is extracted in the entire range of acid concentrations. The amount of extraction agent required to achieve the same level of extraction in this medium is much lower than in the cyanide media. The temperature has a negative effect on the extraction. Another difference observed between the two media, is that the presence of ionic salts in chloride media has no influence on the extraction, and this may be attributed to the fact that the extracted species, HAuCl_4 , is a protonated rather than of an ionic species.

8.3 Thermodynamic Analyses of FeAsS, FeS₂ and Au in NaOCl-NaOH Solution and One-Step Leaching of Gold

The reaction thermodynamics of arsenopyrite, pyrite and gold with sodium hypochlorite in sodium hydroxide media and the solution chemistry of H_3AuO_3 at different pH values have been analysed by D. Wang, A. Mao, G. Qiu and J. Xu, of the Beijing General Research Institute for Nonferrous Metals, Beijing, P.R. China in a paper published in *Youse Jinshu* 1998, **50**(1), 40-44. The obstruction of the metal hydroxide solid layer formed during oxidation of sulfide minerals in alkaline media was eliminated by grinding in a porcelain ball mill, 91.9% of the gold was extracted by one-step leaching in 20 minutes from concentrations containing arsenic in the Guangxi Zhuang Autonomous Region.