

Highlights from Recent Literature

1 Analytical

1.1 Scanning Tunneling Microscopy of Monoatomic Gold Chains on Vicinal Si(335) Surface: Experimental and Theoretical Study

Electronic and topog. properties of the Si(335) surface, containing Au wires parallel to the steps was studied. M Krawiec, T Kwapinski, M Jalochowski from the Institute of Physics and Nanotechnology Center, M. Curie-Sklodowska University, Poland, Los Alamos National Laboratory, Preprint Archive, *Condensed Matter* 2005 **1-6**, arXiv:cond-mat/0510263, 11 Oct 2005. Scanning tunneling microscopy (STM) supplemented by reflection of high energy electron diffraction (RHEED) technique was used. The STM data show the space and voltage dependent oscillations of the distance between STM tip and the surface which can be explained within one band tight binding Hubbard model. The STM current was calculated using nonequil. Keldysh Green function formalism.

1.2 Wavelength-Dispersive XRF analysis of Purity of Gold

The wavelength dispersive XRF method was applied to the detection of the purity of Au (98.00-99.95%). Calibration curve was established by using GBW stds. and self-prepared working std. Y Wu, X Ye, M Fang from the Shanghai Research Institute of Measurement and Testing Techniques, Shanghai, 200233, Peoples Republic of China, Lihua Jianyan, Huaxue Fence 2003, **39(11)**, 639. The accuracy of detection, especially for samples with relatively low Au contents, was improved by background correction. The absorption-intensifying effect was eliminated by the Lachance-Trill concentration correction model. WDXRF is simple and rapid, and the difference between the results obtained by WDXRF and those by fire assay, AAS, or ICP-AES was <0.10%.

2 Catalysis

2.1 Water-Enhanced Catalysis of CO Oxidation on Free and Supported Gold Nanoclusters

The enhancement by water molecules of the catalytic activity of gas-phase and supported gold nanoclusters toward CO oxidation is investigated with first-principles calculations, A Bongiorno, U Landman from the Georgia Institute of Technology, School of Physics, Atlanta, USA, *Physical Review Letters* 2005, **95(10)**, 106102/1. Coadsorption of H₂O and O₂ leads to formation of a complex well bound to the gold cluster, even on a defect-free MgO(100) support. Formation

of the complex involves partial proton sharing between the adsorbates, that in certain configurations results in proton transfer leading to the appearance of a hydroperoxyl-like complex. The O-O bond is activated, leading to a weakened peroxy or superoxolike state, and consequently the reaction with CO to form CO₂ occurs with a small activation barrier of .apprx.0.5 eV. A complete catalytic cycle of the water-enhanced CO oxidation is discussed.

2.2 Reductive Routes to Stabilized Nanogold and Relation to Catalysis by Supported Gold

Evidence is presented and discussed for the involvement of ionic gold, probably Au(1+) in catalysis by supported gold. D Boyd, S Golunski, G Hearne, T Magadzu, K Mallick, M Raphulu, A Venugopal, M Scurrall from the Johnson Matthey Technology Centre, Reading, UK, *Applied Catalysis, A: General* 2005, **292**, 76. Various catalytic systems and various experimental techniques have been used for reactions involving carbon monoxide. Moessbauer effect spectroscopy on gold-titania and gold-titania-zirconia reveals the co-existence of Au(0), Au(I) and Au(III), but only the Au(I) content correlates directly with the activity of these solids for CO oxidation XPS data suggest that a small (ca. 6%) fraction of the gold present in gold-titania-zirconia catalysts is present in an electron deficient state relative to Au(0). For gold-iron oxide catalysts, high water-gas shift activity is obtained for samples in which a partial reduction of the gold, initially present as Au(III), has occurred. For gold-HY zeolites, in which the gold is initially introduced as Au(III) by ion-exchange from [Au(en₂)]³⁺, samples become catalytically active only after a considerable induction period has been exceeded. The induction period is shortened and the activity of the catalysts increased by pre-treatment with sodium borohydride, and some degree of reduction of the gold is assessed to have occurred. Further evidence that non-equiv. states of gold exist (i.e. metallic and ionic gold) in active CO oxidation catalysts based on gold-titania is provided by the fact that partial removal of gold occurs when the solids are treated with solutions containing cyanide ions under oxidative conditions. The specific activity per unit of gold increases with decreasing gold content when the gold content is lowered by such treatment. The results are consistent with the requirement for Au(I) involvement in the catalytic reaction, though a role for Au(0) is not ruled out.

2.3 Gold as a Catalyst

A review; this article describes possibilities of using gold as a catalyst. G Smit, from the Faculty of Philosophy, J. J. Strossmayer Univ. of Osijek, Osijek, 310000, Croatia, *Kemija u Industriji*, 2005, **54(9)**, 389. Because of its chemical inert character, gold was not considered as an active catalyst until the mid-eighties in the last century. Then, M. Haruta revealed in his article that gold is a very active catalyst for CO oxidation if it is dispersed at some suitable support (oxides of 3d-transition metals, hydroxides of alkali earth metals or activated carbon) with diameters of its particles smaller than

10 nm. What followed was an explosion of publications about gold catalysis. Before the great discovery was made by M. Haruta, gold catalysts were usually prepared by impregnation which did not provide samples with a dispersion as high as those for Pt-group metals because of a much lower m.p. of gold (1336 K). Therefore, new methods of preparation had to be found that would make a strong connection between supports and particles of gold. Very active gold catalyst will be prepared if it is dispersed at supports with sp. surface areas larger than $50 \text{ m}^2 \text{ g}^{-1}$.

The best catalysts were prepared with diameters of gold particles from 2-3 nm. It is possible to achieve this using the following methods: a) deposition-precipitation: immersing a metal oxide into an aqueous solution of $\text{HAuCl}_4 \cdot 3 \text{ H}_2\text{O}$ (pH 6-10) and aging for about one hour, b) co-precipitation: simultaneous precipitation of aqueous solutions of $\text{HAuCl}_4 \cdot 3 \text{ H}_2\text{O}$ and metal nitrate by Na_2CO_3 or NH_4OH , c) Iwasawa's method: reaction of Au-phosphine complexes with freshly precipitated supports of $(\text{Ti}(\text{OH})_4, \text{Mn}(\text{OH})_2, \text{Co}(\text{OH})_2, \text{Fe}(\text{OH})_3, \text{Zn}(\text{OH})_2, \text{Mg}(\text{OH})_2 \dots)$, d) co-sputtering: simultaneous sputter-deposition of gold and metal oxide on a suitable substrate to form a film in an atm. containing oxygen, e) chemical vapor deposition: adsorption and decomposition of an organogold compd. in a form of vapor onto a metal oxide. Methods a) and b) are most frequently used. $\text{HAuCl}_4 \cdot 3 \text{ H}_2\text{O}$ or phosphine complexes $\text{Au}(\text{PPh}_3)(\text{NO}_3)$ and $[\text{Au}_3(\text{PPh}_3)_3](\text{NO}_3)_3$ are usually used as gold precursors.

Gold loading should not be more than 20 at.% [at. % Au = $100 \text{ Au}/(\text{Au} + \text{Fe})$], and during precipitation pH must be greater than 6. During deposition in alkalie solutions, AuCl_4^- transforms to $\text{Au}(\text{OH})_3\text{Cl}^-$ which ppts. as $\text{Au}(\text{OH})_3$. Calcination at temperatures above 473 K causes transformations of $\text{Au}(\text{OH})_3$ to Au_2O_3 and Au_2O_3 to metallic gold. Before characterization or activity test, gold catalysts are usually pretreated in different ways to achieve bigger activity and stability. But, the catalysts with best performance were prepared through different pretreatments (oxidation, reduction, no pretreatment). The investigations have tried to explain the roles of supports and gold particles. Those results made the divergences even bigger.

Some results have shown that there supports had no importance, whereas the others have shown that supports had a crucial role. As for the gold component, some scientists believe that metallic gold is the most active, whereas the others consider oxidized forms of gold more active. Many investigators think that perimeter of gold particles is a place that takes the main role for the most of reactions, so the main aim during preparation should be smaller gold particles. The role of humidity is very important because of practical use of those catalysts. However, the results about it are also divergent. Despite these differences and a restraining from making any generalizations, we can conclude that during the last decade a great introduction of gold as a heterogeneous and homogeneous catalyst for many reactions has been made. The most significant patents

and prototypes, like air purifn. from CO (Mintek), three-way catalyst (Toyota), fuel cells (Mitsubishi), addn. of alcs. to alkynes (BASF), show that an era of gold as a very important catalyst for conventional and unconventional processes has started.

2.4 Advances in Preparation and Application of Supported Gold Nano-Particles Catalyst with High Catalytic Activity

A review; the latest advances in preparation and application of supported gold nano-particles catalyst with high catalytic activity were reviewed. X Xin G Luo R Zhao from the Department of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing, 102617, Peoples Republic of China *SO Shiyou Huagong* 2005, **34(9)**, 898. Important factors which would affect catalytic activity of catalyst were discussed. Preparation methods for gold nano-particle catalysts were compared. Gold nano-particle catalyst with high catalytic activity could be prepared by selecting suitable preparation method and support, and by strictly controlling Au nano-particle size.

2.5 Catalytic Oxidation of CO by Aqueous Polyoxometalates on Carbon-Supported Gold Nanoparticles

Oxidation of CO was carried out at room temperature with the use of aqueous solutions of polyoxometalates over carbon-supported gold catalysts. W Kim, G Rodriguez-Rivera, S Evans, T Voitl, J Einspahr, P Voyles, J Dumesic from the Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI, 53706, USA *SO Journal of Catalysis* (2005), 235(2), 327. The turnover frequency (TOF) for CO oxidation reaches high rates of 4.7 s^{-1} for catalysts with average gold particle sizes of 5 nm, estd. by X-ray diffraction (XRD) and transmission electron microscopy (TEM), and with gold loading of 1 wt%, detected by elemental anal. Lower rates are observed at higher gold loadings, which may be attributed to mass transport limitations in the present system and to the presence of larger gold particles. Carbon-supported gold catalysts exhibit selective oxidation of CO vs. H_2 , and a small increase in the selectivity for CO vs. H_2 oxidation is observed as the gold particle size decreases from 12.1 to 5.6 nm.

2.6 Heterogeneously Catalyzed Hydrogenation using Gold Catalysts

A comprehensive overview in the field of heterogeneously catalyzed hydrogenations over gold surfaces and supported gold catalysts is given. P Claus from the Darmstadt University of Technology, Department of Chemistry, Institute of Chemical Technology, Darmstadt, Germany, *Applied Catalysis, A: General* 2005, **291(1-2)**, 222. It is also highlighted where the latter are superior to other hydrogenation catalysts. Basic principles including the adsorption and activation of hydrogen, structure-sensitivity, real structure of supported gold catalysts and attempts to

identify the active sites are discussed. In reactions exhibiting a selectivity problem, e.g. hydrogenation of two C=C bonds or C=C vs. C=O groups, the characteristic feature of gold catalysts is the preferred hydrogenation of one of these groups leading to monoenes, unsaturated alcohols and unsaturated ketones as reaction products important to the chemical industry.

2.7 DFT and In Situ EXAFS Investigation of Gold/Ceria-Zirconia Low-Temperature Water Gas Shift Catalysts: Identification of the Nature of The Active Form of Gold

A combined experimental and theor. investigation of the nature of the active form of gold in oxide-supported gold catalysts for the water gas shift reaction has been performed. In situ extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) experiments have shown that in the fresh catalysts the gold is in the form of highly dispersed gold ions. D Tibiletti, F Amieiro, R Burch, Y Chen, J Fisher, A Goguet, C Hardacre, P Hu, D Thompsett, CentACat and School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, UK *SO Journal of Physical Chemistry B* 2005, **109(47)**, 22553. However, under water gas shift reaction conditions, even at temperatures as low as 100°C, the evidence from EXAFS and XANES is only consistent with rapid, and essentially complete, reduction of the gold to form metallic clusters containing about 50 atoms.

The presence of Au-Ce distances in the EXAFS spectra, and the fact that about 15% of the gold atoms can be reoxidized after exposure to air at 150°C, is indicative of a close interaction between a fraction (ca. 15%) of the gold atoms and the oxide support. D. functional theory (DFT) calculations are entirely consistent with this model and suggest that an important aspect of the active and stable form of gold under water gas shift reaction conditions is the location of a partially oxidized gold (Au. δ +) species at a cerium cation vacancy in the surface of the oxide support.

It is found that even with a low loading gold catalysts (0.2%) the fraction of ionic gold under water gas shift conditions is below the limit of detection by XANES (<5%). It is concluded that under water gas shift reaction conditions the active form of gold comprises small metallic gold clusters in intimate contact with the oxide support.

2.8 Commercial Aspects of Gold Catalysis

A review; there is the potential to apply catalysis by gold in numerous com. applications. C Corti, R Holliday, D Thompson from the World Gold Council, International Technology, London, UK, *Applied Catalysis, A: General* (2005), **291(1-2)**, 253. These practical uses include catalysts for pollution and emission control, chemical processing of a range of bulk and speciality chemicals, the emerging hydrogen economy for clean hydrogen production and fuel cell systems, as well as for sensors to detect poisonous or flammable gases or substances in solution.

The purpose of this paper is to briefly review the major com. opportunities to apply heterogeneous gold catalysis and to highlight those areas that are considered to merit particular attention. It is considered that all involved in this exciting field need to carefully consider both the durability of catalysts under representative operating conditions and viable methods of catalyst preparation, in order to commercially apply the new science that has developed in recent years.

2.9 Low-Content Gold-Ceria Catalysts for the Water-Gas Shift and Preferential CO Oxidation Reactions

Low-content (<0.6 at.%) Au-ceria samples were prepared by single-pot synthesis using the urea gelation/co-precipitation method, and by NaCN leaching of high-content (5 at.%) Au-ceria materials prepared by deposition-precipitation. W Deng, J De Jesus, H Saltsburg, M Stephanopoulos from the Department of Chemical and Biological Engineering, Tufts University, Medford, MA, USA, *Applied Catalysis, A: General* 2005, **291(1-2)**, 126. These catalysts, containing cationic Au in ceria, are active for both the low-temperature H₂O-gas shift (WGS) reaction and preferential oxidation of CO (PROX). The surface O of ceria, as estd. by H₂-TPR, was used to normalize the WGS reaction rates.

Cyclic temperature-programmed reduction with intermittent reoxidation showed that the surface structures of Au-ceria catalysts are highly reversible. Considerable re-oxidation by O or H₂O can occur even at ambient conditions. The stability of low-content Au-ceria catalysts for the PROX reaction in a realistic fuel gas mixture containing 1% CO - 0.5% O₂ - 50% H₂ - 10% H₂O - 15% CO₂ - He was excellent. No decrease in activity or selectivity was found in cyclic operation up to 150°.

2.10 Solvent-free Oxidation of Primary Alcohols to Aldehydes using Supported Gold Catalysts

Supported Au catalysts were studied for the oxidation of primary alcs. under solvent-free conditions in the absence of base. D Enache, D Knight, G Hutchings from the School of Chemistry, Cardiff University, Cardiff, UK, *Catalysis Letters* 2005, **103(1-2)**, 43. The primary alcs. are benzyl alc., octan-1-ol, and geraniol; the gold nanocrystal catalysts were prepared by coprecipitation, deposition precipitation, and impregnation of supports. For benzyl alc. and octan-1-ol, selective oxidation to the corresponding aldehydes was observed, particularly with Au/CeO₂, whereas for more acidic supports, e.g. Fe₂O₃, subsequent oxidation of the aldehydes to the corresponding acids occurred, forming the ester (benzyl benzoate, octyl octanoate, respecially) by reaction with the alc., by acid-catalyzed mechanism.

Alternatively, the mechanism of ester generation could involve hemiacetal formation between the aldehyde and residual alc., followed by direct oxidation to the observed ester. The reaction of geraniol is much more complex and the reaction was carried out in the presence and absence of acids to gain a full understanding of the interplay between

oxidation and isomerization reactions. Comparison with other active catalysts reveals that using Au catalysts in solvent free conditions gives high turnover frequency for the synthesis of the aldehydes with 100% selectivity (150 h⁻¹ and 26 h⁻¹ for benzyl alc. and octan-1-ol, respectively), which are comparable to the best reported to date for these reactions.

2.11 Influence of the Conditions of Thermal Treatments and of Storage on the Size of the Gold Particles in Au/TiO₂ Samples

The size of the gold particles is a very important parameter to get active catalysts. Only the methods able to produce small particles (<5 nm) supported on oxides, with a min. of chlorides, lead to performing catalysts, esp. for CO oxidation. R Zanella, C Louis from the Laboratoire de Reactivite de Surface, Universite Pierre et Marie Curie, Paris, France, *Catalysis Today* 2005, **107**. In addition to the preparation methods, the gold particle size depends on other parameters, for example, the conditions of thermal treatment. This work focused on the parameters of thermal treatment that influence the gold particle size in Au/TiO₂ samples prepared by different methods.

It was found that the gold particle size decreases when the gas flow increases, when the amount of sample decreases, or when H₂ or Ar is used instead of air. The particle size slightly increases with the treatment temp. The two first parameters cause more drastic changes in particle size than the treatment temp. Once gold metal particles are obtained, their size can evolve in the presence of light or in ambient air. It is proposed to store them in a desiccator, under vacuum and in the dark. Possible evolutions of the samples during characterization (exposure to electrons or photons beams) are also discussed.

2.12 Catalysts Based on Gold Nanosized Species Incorporated into Zeolites

Last year's nanosized gold particles attract much attention as a component of industrially perspective catalysts for some reactions as CO oxidation, NO reduction etc. The authors studied several systems including gold based on different synthetic zeolites pure or doped with another metal (Fe, Na). A Simakov, N Bogdanchikova, I Tuzovskaya, E Smolentseva, A Pestryakov, M Farias, M Avalos, from CCMC, Univ. Nacional Autonoma de Mexico, Ensenada, Mexico, Proceedings of SPIE-The International Society for Optical Engineering 2005, 5924 (Complex Mediums VI: Light and Complexity), 592410/1. It was shown by different techniques (XPS, UV-Vis spectroscopy, TPR) that intrinsic properties of zeolites used and gold system preparation method influence significantly on the contribution of different gold species (ions, clusters and particles).

For mixed Au-Me-zeolites activity level and dynamic of CO conversion with time in steam and temp. depends on nature of zeolite and specificity of Au-Me interaction. All binary metal systems were found to be activated in different degree during catalytic activity test due to mutual interaction of gold

with second metal. Extremely high level of CO conversion and low dependence of activity on temperature was observed for Au- Fe- H- and Na-Y zeolites. The change in contribution of gold nanoparticles was observed after sample contact with CO.

3 Chemistry

3.1 Kinetics and Mechanism of the Gold Corrosion Dissolution in Hypochlorite Solutions

Kinetics and mechanism of the gold metal dissolution by means of corrosion in chloride-hypochlorite solutions are studied. L Kozin, V Prokopenko, A Bogdanova from the Vernadskii Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine, *Protection of Metals* 2005, **41(1)**, 22. The dependency of the dissolution rate on the solution pH, sodium hypochlorite concentration, and temperature are detected conditions of the gold passivation surface during its corrosion in the studied solutions are discussed. The first-order rate consts. of the gold dissolution ($k_i = 0.079-0.4030 \text{ s}^{-1}$) at temperatures from 277 to 304 K and others are calculated. The equil. consts. of the dissolution reactions in acid and alkalie chloride-hypochlorite solutions are different: 1.2 .times. 10⁶ and 2.39 .times. 10², respectively the activation energy calculated from the temperature dependence of the rate consts. (53.43 kJ/mol) evidences a kinetic control of the gold dissolution quant. data on the composition of surface adsorption films, formed by oxidation gold dissolution products, are obtained using the Auger spectroscopy.

3.2 Mechanism of Dissolution of Gold in Chloride-Hypochlorite Solutions

The mechanism of metallic gold dissolution in chloride-hypochlorite solutions is discussed. L Kozin, V Prokopenko, A Bogdanova from the Institute of General and Inorganic Chemistry of NAS of Ukraine, Kiev, Ukraine, *Ekotekhnologii i Resursosberezhenie* 2004, **(6)**, 20. The conditions for the formation of passive adsorption layers on the gold surface during the dissolution in the solutions under the study are considered. The quant. data obtained by means of AES on the composition of the adsorption surface layers, i.e. the products of the reaction of the oxidizing Au dissolution are presented.

3.3 Gold Nanotriangles Biologically Synthesized using Tamarind Leaf Extract and Potential Application in Vapor Sensing

The size and shape dependent electronic and chemical properties of metal nanoparticles has drawn the attention of chemists, physicists, biologists, and engineers who wish to use them for the development of new generation nanodevices. In this article, the authors report the synthesis of gold nanotriangles using tamarind leaf ext. as the reducing agent. B Ankamwar, M Chaudhary, M Sastry from the

Department of Chemistry, Abasaheb Garware College, Pune, India, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry* 2005, **35(1)**, 19. On treating aqueous chloroauric acid solution with tamarind leaf ext., rapid reduction of the chloroaurate ions is observed leading to the formation of flat and thin single cryst. gold nanotriangles.

At. force microscopy analysis of the gold nanotriangles indicated that they ranged in thickness from 20 to 40 nm. These gold nanotriangles with unique and highly anisotropic planer shapes might find application in photonics, optoelectronics, and optical sensing. The authors investigated the effect of different organic solvent vapors like methanol, benzene and acetone on the cond. of tamarind leaf ext. reduced gold nanotriangles. I-V characteristics measurement of these nanotriangles was done in presence of these org. solvent vapors. The observed characteristics suggest the application of gold nanotriangles to future chemical sensors.

4 Electrochemistry

4.1 Simultaneous Electrochemical Determination of Oxygen and Carbon Dioxide Gas Mixtures in a Non-Aqueous Solvent using Unshielded and Membrane Shielded Gold Microelectrodes

The simultaneous electrochemical reduction of O and CO₂ was studied at a com. available Au microelectrodes (5.0 μm, diam.) in DMSO solvent, using both voltammetric and potential step chronoamperometric techniques. In agreement with previous voltammetric studies, CO₂ is shown to react with the superoxide anion radical, formed from the electro-reduction of O (-1.2 V vs. Ag). S Floate, C Hahn, from the Nuffield Department of Anaesthetics, University of Oxford, Radcliffe Infirmary, Oxford, UK, *Sensors and Actuators, B: Chemical* 2005, **B110(1)**, 137. This cross-interference reaction complicates the simultaneous detection of O and CO₂. The simultaneous electro-reduction of O and CO₂ (-2.2 V vs. Ag) also presents detection difficulties, particularly at low levels of CO₂. By contrast, the use of potential step, chronoamperometric techniques effectively collapse the deleterious cross-interference reaction between superoxide and CO₂ (current enhancement <2%). Also, the concomitant electro-reduction of O and CO₂ reveals a linear dependence of the transient's current with O and CO₂ over a prescribed gas concentration range for both species. In addn. a prototype practical sensor that incorporates a polytetrafluoroethylene (PTFE, Teflon) membrane-covered Au microelectrode, for the simultaneous measurement of O and CO₂ over a wide concentration range, is described.

4.2 Gold-Nanoparticle-Dispersed Boron-Doped Diamond Electrodes for Electrochemical Oxidation of Oxalic Acid

Electrochemical behavior of Au-nanoparticle-dispersed diamond electrodes were studied for the oxidation of oxalic acid in phosphate buffer solution. T Ivandini, Y Naono, A Nakajima, Y Einaga from the Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama, 223-8522, Japan *SO Chemistry Letters* 2005, **34(8)**, 1086. Comparison is made with Au, as-deposited diamond and Au-implanted diamond. The electrodes combine the high catalytic activity of Au and the low background current of diamond electrodes. Also, the electrodes can overcome the problem of stability as it is found when using other electrodes.

4.3 Electrochemical Impedance Spectroscopy Study of Mixed Thiol Monolayers on Gold

Electrochemical impedance spectroscopy (EIS) measurement of the capacitance can be used to calc. the composition of mixed self assembled monolayers (SAMs) consisting of binary mixtures of octanethiol (OTT) with hexadecanethiol (HDT) and dodecanethiol (DDT) with 11-mercaptoundecanoic acid (MUA) on Au. Y Xing, S Li, A Lau, S O'Shea from the Department of Chemistry, National University of Singapore, Singapore, 117543, Singapore *SO Journal of Electroanalytical Chemistry* 2005, **583(1)**, 124. The authors monitor as a function of immersion time changes in composition of the mixed SAM and examine the displacement of one thiol in a SAM with another thiol from solution under the experimental conditions the composition of the mixed SAM formed by co-adsorption from a mixture of thiols in solution is detected by thermodyn., not kinetic, factors given sufficiently long immersion times (up to 10 days). Fully formed SAM consisting of a single component behave differently in that some pure SAM (e.g., DDT) are completely displaced when exposed to a competing thiol in solution, whereas others (e.g., MUA) can only be partially displaced, presumably because of strong interlayer cohesion between the carboxylate end groups.

5 Electronics and Sensors

5.1 Optical Fibre Sensors based on Vapochromic Gold Complexes for Environmental Applications

A new vapochromic material based on a gold-silver complex and diphenylacetyl, of formula [Au₂Ag₂(C₆F₅)₄(C₆H₅C.tplbond.CC₆H₅)], has been developed and used for the detection of some volatile org. compounds (VOCs). C Bariain, I Matias, C Fdez-Valdivielso, C Elosua, A Luquin, J Garrido, M Laguna from the Departamento de Ingenieria Electrica y Electronica, Universidad Publica de Navarra, Pamplona, 31006, Spain *SO Sensors and Actuators, B: Chemical* 2005, **B108(1-2)**, 535. The material is presented in the form of dark green powders. When the powders are in

presence of VOC, its color changes, yielding to a change in its optical properties. The sensor consists of an optical fiber pigtail onto the cleaved end of which the vapochromic material was deposited. The fiber has a core diam. of 200 μm and a plastic cladding. A com. available solvent, Liquicoat is used to create a solution, capable of being fixed onto the fiber. The fiber optic sensor is employed in a reflection scheme, so the other extreme of the optical fiber pigtail is connected to an optical coupler, completing the set-up with an optical source to generate the interrogating signal and an optical detector to measure the received intensity-modulated signal. The behavior of the sensor has been studied for different wavelengths for different concentrations of several VOC. Changes up to 2.5 dB in the reflected optical power were detected.

5.2 Flashbond. Thermosonic Au-bonding on Flash-gold in the Chip-on-Board Technology

The industrial research project FLASHBOND is presented. It was investigated whether thin Au films (0.05-0.3 μm) fulfill the quality and reliability requirements for surfaces of printed circuit boards. F Rudolf from IAVT, TU Dresden, Germany, *Produktion von Leiterplatten und Systemen* 2005, **7(8)**, 1441. These Au films were deposited by thermosonic wire bonding. A possible wear through of the Au layer is discussed. The aim of the FLASHBOND project is the development of industrial applicable solutions for the thermosonic Au wire bonding. The Au solutions have to be integrated into the fabrication processes for chip-on-board components and modules. The organization of FLASHBOND and the technol. transfer are discussed. The FLASHBOND project is divided in 3 parts: (i) optimization of the bonding parameters, (ii) detection of the reliability of the wire-bonded contacts, and (iii) material analyses to study the influence of flash Au on the contact properties.

5.3 Method of Creating Gold Contacts Directly on Printed Circuit Boards and Product Thereof

A method of creating domed shaped contacts on a printed circuit board includes etching or drilling a central opening in each copper pad, and then screening a mound of silver epoxy into the opening. J Walter, W Sinclair from Aries Electronics, Inc., USA, Patent No EP 1599077, A1 November 2005. The silver epoxy above the pad slumps to form a domed bump. The silver epoxy is then cured and is coated, in turn, by a layer of electroless nickel and gold. The resulting gold plated contacts are of monolithic structure and function to facilitate connection to a mezzanine board.

6 Medical and Dental

6.1 Protein-Coating Evaluation Method of Colloidal Gold Nanoparticles

Colloidal gold nanoparticles might be of use as nano scale delivery systems of various therapeutic materials in the future. Recent studies have reported the feasibility of

colloidal gold nanoparticles as gene delivery systems or protein delivery systems. In this study, the authors aimed to develop a short-step method useful for screening the optimal coating conditions of colloidal gold nanoparticles with proteins. M Kim, N Young, M Sang, J Kim, C Mogg, K Han-Gon, O Jung-Ae, Y Oh from the College of Medicine, Pochon CHA University, S. Korea, *Yakche Hakhoechi* 2004, **34(6)**, 465. They observed that colloidal gold nanoparticles have properties of changing its unique color when they were exposed to NaCl solution taking advantage of the color changing properties of colloidal gold nanoparticles,

They applied the color testing method of colloidal gold nanoparticles solutions for evaluating the protein coating nature. Using bovine serum albumin as a model protein, they tested the protein coating of colloidal gold nanoparticles via the color change upon NaCl addn. The optimal coating concentration and coating conditions of colloidal gold nanoparticles with bovine serum albumin were fixed using the color testing methods. They suggest that the color testing method might be applied to optimize the coating condition of colloidal gold nanoparticles with other therapeutic proteins.

6.2 Thermosensitive Nanospheres with a Gold Layer Revealed as Low-Cytotoxic Drug Vehicles

In this paper, the pos. effect of a gold layer on cell viability is demonstrated by examg. the results given by 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium (MTS) assay and two-color cell fluorescence viability (TCCV) assay. J Qin, Y Jo, J Ihm, D Kim, M Muhammed from the Materials Chemistry Division, Royal Institute of Technology, Stockholm, Sweden, *Langmuir* 2005, **21(20)**, 9346. These cytotoxicity tests were performed with human cervical adenocarcinoma cells (HeLa cell line) and transformed African green monkey kidney fibroblast cells (Cos-7 cell line). To fabricate the nanostructures as drug vehicles, first, poly(L,L-lactide-co-ethylene glycol) (PLLA-PEG) and poly(N-isopropylacrylamide-co-D,D-lactide) (PNIPAAm-PDLA) were synthesized, and then two kinds of thermosensitive nanospheres comprising "shell-in-shell" structures without a gold layer (PLLA-PEG@PNIPAAm-PDLA) and with a gold layer (Au@PLLA-PEG@PNIPAAm-PDLA) were constructed by a modified double-emulsion method (MDEM). Both of them displayed a unique thermosensitive character exhibiting the lower crit. soly. temperature (LCST) at 36.7°C which was confirmed by UV-vis spectroscopy and differential scanning calorimetry (DSC). The release profiles of entrapped bovine serum albumin (BSA) were monitored at 22 and 37°C, respecially, to reveal the thermal dependence on the release rate. In cell viability tests, both PLLA-PEG@PNIPAAm-PDLA and Au@PLLA-PEG@PNIPAAm-PDLA showed excellent cell viability, and furthermore, Au@PLLA-PEG@PNIPAAm-PDLA, particularly at high doses, exhibited more enhanced cell viability than PLLA-PEG@PNIPAAm-PDLA. This effect is mainly attributed to the gold layer which binds the protein molecules first and consequently facilitates

transmembrane uptake of essential nutrients in the cell media, resulting in favorable cell proliferation.

6.3 Safety of Gold in Stapes Surgery

Gold prostheses in middle ear surgery were found to have a higher extrusion rate than prostheses made from titanium. Incidences of deafness after insertion of a gold piston into the vestibule during stapes surgery were obsd. The aim of this study was to find out to what degree gold cations can diffuse from the prosthesis piston into the perilymph. P Kwok M Schuster, K Boch, P Jacob, O Gleich, J Strutz from the Ear, Nose and Throat Department, University of Regensburg, Regensburg Germany, *Biomaterials* 2005, **26(34)**, 7132. For this, gold prostheses were incubated in artificial perilymph for 4 mo, after which the gold content of the perilymph was analyzed. As gold exhibits a special behavior in complex fluids like the perilymph, a new analyzing method was developed. The results show that gold does leak out of the pistons, that it can be reliably measured and that the amt. of gold reaching the perilymph depends on the contact area. As the amt. of gold measured in the perilymph stays far below the toxic level, it is very unlikely that the gold cations diffusing from a stapes prosthesis into the perilymph have a toxic effect on the inner ear hair cells. Inflammatory or allergic reactions to gold induced by direct tissue contact, however, cannot be excluded

6.4 Colloidal Gold Nanoparticle Modified Carbon Paste Interface for Studies Of Tumor Cell Adhesion and Viability

A non-toxic biomimetic interface for immobilization of living cells and electrochemical exogenous effect study of cell viability was constructed by mixing colloidal gold nanoparticles in carbon paste. A new approach to study the effects of anti-tumor drug and other exogenous factors on cell viability was proposed. D Du, S Liu, J Chen, H Ju, H Lian, J Li from the Key Laboratory of Analytical Chemistry for Life Science (Education Ministry of China), Nanjing University, Nanjing, Peoples Republic of China, *Biomaterials* 2005, **26(33)**, 6487. The nanoparticles were efficient for preserving the activity of immobilized living cells and preventing their leakage from the electrode surface. The immobilized living AsPC-1 cells (pancreatic adenocarcinoma cells derived from ascites) exhibited an irreversible voltammetric response related to the oxidation of guanine. The presence of guanine was verified by liq. chromatog.-mass spectrometry. The contents of guanine in cytoplasm of each AsPC-1 and normal pancreatic cell were detected to be 370 and 22 amol, resp. The cytotoxic effect of adriamycin resulted in a decrease in peak current of guanine. The optimal exogenous factors that affected cell viability, including pH, temperature and salt concentration of electrolyte, were just consistent with cell growth conditions in culture. This simple and rapid method could be applied for the electrochemical investigation of exogenous effect and characterization of the viability of living cells.

7 Metallurgy, Materials and Coatings

7.1 Resistivity Induced by a Rough Surface of Thin Gold Films Deposited on Mica

A review. A central question regarding thin metallic films is how does the roughness of the film affect its elec. transport properties, when its thickness is comparable to or smaller than the electron mean free path. The drive to build ever-faster circuits generates the drive for miniaturization and VLSI, which poses a pressing need to reach full understanding of electron-rough surface scattering. The authors review progress in the field that has taken place over the last 5 years. R Munoz from the Department of Physics, Blanco Encalada 2008, Universidad de Chile, Santiago, 6511226, Chile, *Journal of Molecular Catalysis A: Chemical* (2005), **228(1-2)**, 163. From the theor. point of view, the so-called mSXW theory [Munoz et al., *J. Phys.: Condens. Matter* **11**(1999) L299] was recently published. The increase in resistivity induced by electron-surface scattering is computed using Kubo's linear response theory. The cond. of the film is detected by the spectral function characterizing the 1-particle Green's function describing the electron gas confined within the film.

The effect of the rough surface is to modify the self-energy of the electron gas. The cond. of the film turns out to depend on the height-height autocorrelation function (ACF) that describes the rough surface. It can be written in a closed form if the ACF is described either by a Gaussian or by an exponential. From the experimental point of view, the tendency to use parameters provided by theory as quantities that must be fitted to describe thin-film resistivity data was replaced by direct measurements of the surface roughness. The 1st measurement of the ACF of the rough surface of a 70-nm thick Au film deposited on mica was recently published [Munoz et al., *Phys. Rev. B* **62**(2000) 4686]. The measurement was performed with a scanning tunneling microscope (STM).

Using the data recorded with the STM and the mSXW theory, the authors reproduced the thickness as well as the temperature dependence of the best resistivity data available for Au films on mica. Theory reproduced the data to within a few percent without adjustable parameters. The authors report also the 1st measurement of the increase in resistivity induced by electron-surface scattering in Au films deposited on mica, performed at low temperatures and high magnetic fields.

7.2 Comparison of Nanometer-Scale Gold Structures Electrodeposited on Au and Pt Seed Electrode

Y Lee, S Ahn, Y Roh from the School of Information and Communication Engineering, Sungkyunkwan University, Suwon-City, Jangan-Ku, S. Korea, *Surface and Coatings Technology* 2005, **193(1-3)**, 137, report a new method to fabricate nanometer-scale gaps between two Au metal electrodes electrodeposited on either Au or Pt seed layer. The techniques used in this work are conventional

photolithog., where specifically designed photomask and lift-off methods and pulse/DC electroplating are used. In addn., the effects of pulse plating variables are investigated with respect to DC plating. The results obtained from the electroplated Au films on the Au seed layer are compared with those on the Pt one. The method is simple, inexpensive, faster, and robust, and gaps between metal electrodes could be easily controlled to nanometer-scale dimensions.

7.3 The Effect of Gold on The Phase Transitions of Titania

The microstructure and phase transformation behavior of sol-gel derived Au-TiO₂ was studied. X-ray powder diffraction (XRD), and BET surface area measurements were used to understand the microstructural development of Au-TiO₂ systems for possible regulation of the phase composition of TiO₂. For TiO₂, brookite transforms to anatase at T <600°; brookite transforms to rutile and anatase transforms to rutile at T .gtoreq.600° were observed for Au-TiO₂, brookite transform to anatase which transforms to rutile. M Debeila, M Raphulu, E Mokoena, M Avalos, V Petranovskii N Coville M Scurrrell from the Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, B.C., Mexico, *Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing* (2005), **A396(1-2)**, 61. Au enhanced the brookite-to-anatase phase transformation at T .ltoreq.500°, but retarded the anatase to rutile phase transformation.

There is no evidence of the substitution of Ti⁴⁺ ions by Au/or Au ions in TiO₂ and thus Au is bound mostly on the surface of TiO₂, consistent with SEM measurements. Although, Au retards the anatase to rutile phase transformation, it is unable to maintain the porous structure of TiO₂, leading to a collapse in the BET surface area to .ltoreq.1 m² g⁻¹ at 700°. The possibility of incorporation of Au³⁺ in the TiO₂ matrix in an interstitial site is discussed. The phase transformations are discussed in terms of the nucleation mechanisms previously proposed.

8 Nanotechnology

8.1 Effects of Intensity and Energy of CW UV Light on the Growth of Gold Nanorods

Growth of gold nanorods (AuNRs) by photochemical reduction of HAuCl₄ in a micelle solution of hexadecyltrimethylammonium bromide (CTAB) and tetraoctylammonium bromide (TOAB) is studied. O Miranda, A Temer from the Department of Chemistry, Villanova University, Villanova, PA, , USA, *Journal of Physical Chemistry B* 2005, **109(33)**, 15724. The effects of 300 and 254 nm UV light sources and their photon flux on the anisotropic growth of gold nanoparticles are investigated by controlling duration of irradiation and the no. of lamps within a photochemical reactor. The resulting AuNRs were characterized by absorption spectroscopy, FTIR, and TEM. Experimental results

indicate that a higher d. of longer colloidal AuNRs form by increasing the no. of incident photons (lamps) at 300 nm while the 254 nm lights produce a lower yield of shorter AuNRs. The yield of AuNRs also depends on the duration of irradiation which was found to be 6.00 h for 300 nm and 5.00 h for 254 nm radiation. Acetone is found to play a major role in the synthesis of AuNRs. Two mechanisms are proposed for the synthesis of Au nanoparticles in the presence and absence of acetone. Irradiation of samples for an excess time produces a lower concentration of AuNRs and a higher yield of spherical particles. This effect is attributed to atom-by-atom dissolution of AuNRs into Au-spherical particles.

8.2 Modification of Gold Nanoparticle Composite Nanostructures using Thermosensitive Core-Shell Particles as a Template

The formation of thermosensitive hybrid core-shell particles via in-situ synthesis of gold nanoparticles using thermosensitive core-shell particles as a template is reported. D Suzuki, H Kawaguchi, Haruma from the Faculty of Science Technology, Keio University, Yokohama, Japan *Langmuir* 2005, **21(18)**, 8175. The template core-shell particles, with cores composed mainly of poly(glycidyl methacrylate) and shells composed mainly of poly(N-isopropylacrylamide), were synthesized in an aqueous medium, and functional groups such as thiol groups were incorporated into each particle. These particles containing thiol groups were effective for the in-situ synthesis of gold nanoparticles in long-term storage. The obtained hybrid particles exhibited a reversible color change from red to purple, which originated from the surface plasmon resonance of gold nanoparticles and which was temperature-dependent in the range 25-40°. In addition to their thermosensitive property, the hybrid particles exhibited the unique characteristic of uniform distribution on a solid substrate. The particles obtained by this approach have potential thermosensitive applications such as in sensors and photonic or electronic devices.

8.3 Optimization of High-Yield Biological Synthesis of Single-Crystalline Gold Nanoplates

Single-cryst. gold nanoplates were obtained by reducing an aqueous chloroauric acid solution with the ext. of *Sargassum* sp. (brown seaweed) at room temperature B Liu, J Xie, J Lee, Y. Ting, J Chen from the Singapore-MIT Alliance, National University of Singapore, Singapore, *Journal of Physical Chemistry B* 2005, **109(32)**, 15256. The resulting gold nanoplates were characterized by UV-visible spectroscopy, x-ray diffraction, at. force microscopy, and TEM. The formation of gold nanoplates depended on a no. of environmental factors, such as the time taken to age the seaweed ext., pH of the reaction medium, reaction temperature, reaction time, and initial reactant concentrations. The size of the gold nanoplates can be controlled to between 200 and 800 nm by manipulating the initial reactant concentrations. The yield of the flat gold

nanocrystals relative to the total no. of nanoparticles formed was as high as .apprx.80-90%.

8.4 An Experimental and Theoretical Study of the Self-Assembly of Gold Nanoparticles at the Surface of Functionalized Multiwalled Carbon Nanotubes

This paper reports the findings of a detailed study of the self-assembly of gold nanoparticles at the surface of carbon nanotubes (CNTs). T Sainsbury, J Stolarczyk, D Fitzmaurice from the Department of Chemistry, University College Dublin, Ireland, *Journal of Physical Chemistry B* 2005, **109(34)**, 16310. The study included the development of a predictive model for the interactions (charge transfer, van der Waals, osmotic, elastic, nonelastic, and covalent) between tetraoctylammonium bromide-stabilized (TOAB) gold nanoparticles and alkyl- and alkylthiol-modified multiwalled carbon nanotubes (MWCNTs). It also included the measurement of the coverage of gold nanoparticles at the surface of the above MWCNTs as a function of increasing alkyl chain length.

One key finding is that it is possible to predict with a high degree of accuracy using the above model the measured coverage of gold nanoparticles adsorbed, either noncovalently or covalently, at the surface of a MWCNT. Another key finding is that, as predicted, under well-defined conditions the measured coverage of nanoparticles is very sensitive to the nature of the modified CNT surface and the contiguous environment, providing valuable insights that will underpin the rational design of functional nanoscale devices assembled from nanoparticle and CNT building blocks.

8.5 Shape Controlled Growth of Gold Nanoparticles by a Solution Synthesis

The shape of gold nanoparticles was successfully tuned among penta-twinned decahedrons, truncated tetrahedrons, cubes, octahedrons, hexagonal thin plates by introducing a small amount of salt into a N,N-dimethylformamide (DMF) solution containing poly(vinyl pyrrolidone) (PVP), and changing the temperature or the concentration of the gold precursor. Y Chen, C Xin, Nie, Z Jiang, Z Xie, J Lin, from the State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen, Peoples Republic of China, *Chemical Communications* (Cambridge, United Kingdom) 2005, **(33)**, 4181.

8.6 Surfactant-Free Synthesis and Functionalization of Gold Nanoparticles

A new, facile and generally applicable synthesis of functionalized gold nanoparticles is presented. It is based on the surfactant-free generation of weakly stabilized nanoparticles by the reduction of HAuCl_4 with sodium naphthalenide in diglyme. M Schulz-Dobrick, K Sarathy, M Jansen from the Max Planck Institute for Solid State Research, Stuttgart, Germany, *Journal of the American Chemical Society* 2005, **127(37)**, 12816. These nanoparticles were

found to lack long-term stability. However, stabilization in both unpolar and polar solvents could straightforwardly be achieved by subsequent addn. of various capping ligands. The resulting ligand-capped gold nanoparticles were investigated by TEM microscopy, UV-vis, and FT-IR spectroscopy. Particle core size can be tuned by the amt. of reduction agent. The strict sepn. of the reduction step and the functionalization step in this one-pot synthesis offers an easy and fast access to highly functionalized gold nanoparticles.

9 Refining

9.1 Method for Processing Products Containing Non-Noble Metal Chalcogenides, Platinum Group Metals and Gold

The invention by V F Malakhov, V N Efimov, A V Moskalev Patent No PI RU 2260629, C2, 20050920 is suitable in noble metal metallurgy, namely separation of platinum group metals and gold from non-noble metal chalcogenides. The method comprises steps of (a) treating material with nitric acid solution till oxidation-reduction potential 500-700 mV; (b) extg. non-sol. residue; (c) melting it at adding sodium-containing fluxes, carbon-containing reducing agent and copper- and/or iron-containing industrial process product obtained at hydrolysis or cementation treatment of solutions of refining production; and (d) settling and cooling melt till its solidification. Then sepd. bottom phase of heavy alloy is disintegrated to powder. Method allows to extrn. to target alloy up to 94% of platinum and palladium, $\backslash > 97\%$ of rhodium, iridium and ruthenium. Disintegrated alloy may be processed as conc. of refining production. The method results in increased content of noble metal in the bottom phase, and low cost of next refining process.

9.2 Solvent Extraction of Gold from Alkaline Cyanide Solution With a Tri-N-Octylamine/Tri-N-Butyl Phosphate/N-Heptane Synergistic System

Solvent extrn. of $\text{KAu}(\text{CN})_2$ from alkalie cyanide solution by using the pre-acidified tertiary amine, tri-n-octylamine (TOA) as extractant with the addn. of tri-Bu phosphate (TBP) as a synergist in n-heptane solution has been studied. J Jiang, Y He, H Gao, J Wu, J Jiang, Jianzhun from the Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, Peoples Republic of China *SO Solvent Extraction and Ion Exchange* 2005, **23(1)**, 113. The influence of several variables such as the molar ratio of TOA to $\text{KAu}(\text{CN})_2$, vol. percentage of TBP, phase ratio of the org. phase to the aqueous phase, and the pH of the aqueous phase were investigated. At a certain pH range, while TBP was $> 20\%$ (vol./vol.) and the molar ratio was > 1 , the organic phase can extract gold from the aqueous phase completely.

The relationship between the extrn. percentage of gold against the molar ratio and the log D - log TBP concentration

plot indicate that the stoichiometry of the extd. species is a 1:1:3 complex, namely, $[TOA \cdot H^+ \cdot Au(CN)_2^-] \cdot 3TBP$ (D = distribution ratio of $Au(CN)_2^-$). Dynamic laser scattering revealed that the org. phase tends to self-assemble to form aggregations when the concentration of gold in the org. phase reaches a certain limiting value. Stripping of the loaded org. phase by NaOH and inorg. salts, such as NH_4SCN , $NaClO_4$ and potassium halides, has also been investigated.

9.3 Leaching of Ovacik gold ore with Cyanide, Thiourea and Thiosulphate

The leaching kinetics of Ovacik Turkish gold ore have been investigated, and major parameters have been detected by using cyanide, thiourea and thiosulfate. M Tanriverdi, H Mordogan, U Ipekoglu from the Mining Engineering Department, Faculty of Engineering, Dokuz Eylul University, Turkey, *Minerals Engineering* 2005, **18(3)**, 363. The dissolution of gold is discussed in terms of extn. rates and reagent consumption during leaching.

9.4 Kinetic Model for Anodic Oxidation of Gold in Thiosulfate Media Based on the Adsorption of $MS_2O_3^-$ Ion-Pair

It has been the general practice among researchers to use the molar concentration of thiosulfate salts to be the same as that of $S_2O_3^{2-}$ ions involved in various equil. or rate expressions for interpreting gold oxidation kinetics. G Senanayake from the A.J. Parker Cooperative Research Centre for Hydrometallurgy, Department of Mineral Science and Extractive Metallurgy, Murdoch University, Australia, *Hydrometallurgy* 2005, **76(3-4)**, 233. However, chemical speciation anal. based on the assocn. of thiosulfate ion with monovalent cations (ion-pair formation) shows that the concentration of free $S_2O_3^{2-}$ ions is lower than that of assocd. $MS_2O_3^-$ ions with M being Na, K and NH_4 . Anal. of literature data on electrochemical oxidation rates of gold in non-ammoniacal alkalie sodium thiosulfate solutions based on the adsorption of $NaS_2O_3^-$ shows that the rate const. for gold oxidation is $4.2 \cdot 10^{-4} \text{ mol/m}^2\text{-s}$

9.5 Reasons for Resulting in High Gold Grade of Cyanidation Tailings and Improvement Measures Adopted

The company 1st plant used an all-slime cyanidation and zinc dust precipitation in floating gold ores. With increase of primary ore output and cutting down in mill head grade, the original process was not applicable and was reformed in 2001. L Zhang, Z Dai from the Songxian Jinniu Con., Ltd, Songxian, Henan Province, Peoples Rep. China, *Huangjin* 2004, **25(7)**, 33. The reformed process was flotation-cyanidation, zinc dust precipitation and flotation of cyanidation tailings to recover lead. The excessive concentration of flotation reagents led to the high gold grade in cyanidation tailings during following production. This problem could be solved by increasing the draining

quantity of barren solution or the quantity of fresh water used in the conc. pulps. The measures increased the gold cyanide recovery from 85% to 94%.

9.6 Use of Magnetic-Pulse Processing to Intensify Cyanidation Of Refractory Gold-Bearing Concentrate

The possibility of utilizing a preliminary magnetic-pulse treatment for modification of process characteristics of a partially refractory Au-pyrite flotation conc. during its hydrometallurgical processing was studied. G Skrylova, from TSNIGRI MPR Ross., Russia, *Rudy i Metally* 2004, **(4)**, 65. The preliminary treatment of the conc. was shown to enable an increase in the Au recovery in cyanidation of the conc. The Au recovery from the conc. increased by 3.7, 0.9-4.7, and 2.2-2.6% during 12, 48, and 72 h cyanidation respectively.

9.7 Gold Recovery by Microwave Augmented Ashing of Waste Activated Carbon

Gold ore processing plants that utilize carbon adsorption technologies generate a waste activated carbon which contains high gold values, and the recovery of this gold represents a significant source of extra revenue. R Amankwah, C Pickles, W Yen from the Mining Engineering Department, Queen's University, Kingston, ON, Can. *SO Minerals Engineering* 2005, **18(5)**, 517. Microwave energy was utilized to combust the waste activated carbon, and the resulting ash was treated by conventional cyanide leaching to recover the gold. First, the real and imaginary permittivities of the activated carbon were measured by the cavity perturbation technique and were high, and thus the carbon was expected to be a microwave absorber. Second, the microwave heating behavior of the activated carbon was studied as a function of incident microwave power, processing time, sample mass and particle size. The sample temperature increased with increasing incident microwave power, processing time, sample mass and decreasing particle size.

For a 3 g sample with a particle size of $\sim 90 \mu\text{m}$, temperatures of $>1000^\circ$ can be attained at an incident microwave power of 1000 W and for a 5 min processing time. The effects of air flow rate, microwave power and processing time on combustion of the activated carbon were studied. By introducing air into the microwave combustion chamber, the carbon was completely oxidized, and the residue was a gold-containing ash, which was treated for gold recovery by the conventional cyanide leaching process. Over 95% gold extn. was achieved within 8 h. The microwave combustion of gold-containing waste activated carbon is a tech. viable and novel process for gold recovery.

9.8 Role of Copper(II), Carbonate and Sulfite in Gold Leaching and Thiosulphate Degradation by Oxygenated Alkaline Non-Ammoniacal Solutions

Researchers have been unable to incorporate the copper(II)-thiosulfate complexes in Eh-pH or species distribution

diagrams due to the unreliability of the reported stability consts. G Senanayake from the A.J. Parker Cooperative Research Centre for Hydrometallurgy, Department of Extractive Metallurgy and Mineral Science, Murdoch University, Australia *SO Minerals Engineering* 2005, **18(4)**, 409. A concurrent thermodyn. and kinetic anal. of literature data is described to show that the reaction between copper(II) and thiosulfate ions takes place via the formation of an unstable $\text{Cu}(\text{S}_2\text{O}_3)_n(\text{H}_2\text{O})-2(2n-1)$ complex followed by its first or second order decomposition.

The oxidation of thiosulfate to tetrathionate, predominantly via the second order disproportionation with a rate const. of 1.2 .times. 10⁵ mol/L-s produces $\text{Cu}(\text{S}_2\text{O}_3)_-$, which is stabilized as $\text{Cu}(\text{S}_2\text{O}_3)_n-(2n-1)$ with n being 2 or 3. This anal. allows the calcn. of two stability consts. 102.4 and 105.2 for $\text{Cu}(\text{S}_2\text{O}_3)_0$ and $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$, respectively, which predict the predominant species: $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$ (pH < 9), $\text{Cu}(\text{OH})_2$ (9 < pH < 11) and $\text{Cu}(\text{OH})_3^-$ (pH > 11). The disproportionation of $\text{Cu}(\text{S}_2\text{O}_3)_0$ and $\text{Cu}(\text{S}_2\text{O}_3)_-$ leads to the precipitation of Cu, CuS and Cu₂S. The calculated equil. consts. predict that copper(II) complexes such as $\text{Cu}(\text{S}_2\text{O}_3)_0$, $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$, $\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_3^-$ can leach gold to produce $\text{Au}(\text{S}_2\text{O}_3)_3^{2-}$, $\text{Au}(\text{OH})_0$, and $\text{Au}(\text{OH})_2^-$, where the latter two are converted to the more stable $\text{Au}(\text{S}_2\text{O}_3)_3^{2-}$ complex. The rate of thiosulfate oxidation by oxygen during gold leaching from copper gold ores in alkalie media is on the order of 10⁻⁶ mol/L-s, irrespecially of the presence or absence of ammonia.

This is three orders of magnitude smaller than the rate of oxidation of thiosulfate by copper(II) in acid media, indicating the involvement of mixed complexes of the type $\text{Cu}(\text{II})(\text{L})_n(\text{S}_2\text{O}_3)_m(\text{O}_2)$ in ammoniacal (L = NH₃) and non-ammoniacal (L = OH⁻) media, compared to the disproportionation of $\text{Cu}(\text{II})(\text{S}_2\text{O}_3)_1^{1-}$ in acid media with no oxygen. The gold leaching in oxygenated alkalie thiosulfate media obeys a shrinking core kinetic model with an apparent rate const. of the order 10⁻⁵/s. In the presence of 0.4 M total carbonate in alkalie media, the predominant copper(II) complex is $\text{Cu}(\text{CO}_3)_2^{2-}$. This minimizes thiosulfate degrdn. to tetrathionate via the disproportionation of $\text{Cu}(\text{II})(\text{S}_2\text{O}_3)_1^{1-}$. However, carbonate enhances the overall thiosulfate consumption and trithionate and sulfate formation, leading to a lower gold extn. In a thiosulfate-deficient leach liquor, such as that produced in the presence of carbonate, gold precipitation takes place via disproportionation reactions. The addn. of sulfite reproduces thiosulfate from tetrathionate, but slowly ppts. gold.

9.9 Arsenic Removal from High Arsenic Bearing Gold Sulfide Concentrate

A roasting method is described for the removal of arsenic levels of .apprx.10% from a gold conc. involving a weakly reducing amount in a rotary pipe furnace. L Yaozhong, R Smith from the Department of Chemistry, Yunnan Normal University, Kunming, Peoples Republic of China, *Transactions of the Institutions of Mining and Metallurgy, Section C:*

Mineral Processing and Extractive Metallurgy 2004, **113(3)**, C189. Under the optimized conditions of 650-700°, 15-16% CO₂ contg. coal gas and reaction time 30-40 min, the removal of arsenic was >95%, and the removal of sulfur was 25-28% of the amt. present. The resulting concentrations are acceptable for nonferrous smelting plants. With further oxidation and roasting, the content of residual sulfur in the roasted conc. decreased to <4%. Even without fine grinding, the cyanide leaching recovery of gold from the roasted conc. was >92%.

10 General

10.1 Manufacture of Writable and Printable Colloidal Gold Solution

Aqueous colloidal Au solution, useful for manufacture of jet-printing ink with long shelf life, comprises (a) Au nanoparticles, (b) a compd. having a polar tertiary amino group conjugated via a hydrophobic arom. residue with a weaker alkalie group, e.g., 4-dimethylaminopyridine, and (c) a stabilizer comprising a mercapto group and an acidic group, in particular a sulfonic acid group, such as SHCH₂CH₂SO₃H. □. M Berkei, M Korsten, F Ibarra, S Haubold, Patent No. US 2005204956 A1, September 2005.

10.2 Red Color Pigment using Gold Nanoparticles

A review on red pigment for polymers using gold nanoparticles. Y Nakao from the National Institute of Advanced Science and Technology, Japan, *AIST Today* (Japanese Edition) 2005, **5(1)**.