

Highlights from Recent Literature

1 Analytical

1.1 An FTIRAS Study of Nitrophenyl Mono- and Multilayers Electro-Deposited on Gold by Reduction of the Diazonium Salt

Formation of an organometallic junction by direct bonding of 4-nitrobenzene monolayer on Gold surface by diazonium chem. was demonstrated by Fourier transform reflection-absorption spectroscopy with s- and p-polarized radiation. A Ricci, C Bonazzola, E Calvo, from the Inquimae, DQIAyQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, *Physical Chemistry Chemical Physics* 2006, **8(37)**, 4297

1.2 Cyclic Voltammetric Response of Nicotinic Acid and Nicotinamide on a Polycrystalline Gold Electrode

The oxidation of nicotinic acid and nicotinamide on a polycryst. Gold electrode occurred at almost same potentials but their reduction did at different peak potentials. X Wang, N Yang, Q Wan from the Graduate School of Engineering, University of Fukui, Fukui, Japan *Electrochimica Acta*, 2006, **52(1)**, 361. The redox reaction mechanisms of nicotinic acid and nicotinamide were rationalized by the formation/disappearance of the new N-O bonds in the pyridine rings by cyclic voltammetry and bulk electrolysis. The anodic currents of nicotinic acid and nicotinamide were controlled by diffusion, while the cathodic ones by adsorption. The difference in the cathodic peak potentials of nicotinic acid and nicotinamide on the polycryst. Gold electrode is attributed to the effect of the electron densities of remote substituents on the pyridine rings. The cathodic peak currents at .apprx.0.20 V were linear with their concentrations in the range of 2.4 mM to 2.7 .mu.M and 2.4 mM to 3.3 .mu.M with detection limits of 0.27 and 0.33 .mu.M for nicotinic acid and nicotinamide, respectively Voltammetry was then adopted for the selective monitoring the content of nicotinic acid and nicotinamide in pharmaceuticals.

1.3 EXAFS Studies on Gold Nanoparticles over Novel Catalytic Materials

Novel nanogold catalytic systems made up of Gold nanoparticles (.apprx.2-6 nm) supported on Nb, Yb, La and Ce oxide materials were synthesized. XAS is uniquely suited for studying catalytic systems with low metal and high metal dispersion. D Akolekar, S Bhargava, G Foran, from the Catalysis and Advanced Materials Group, School of Applied Sciences, RMIT University, Melbourne, Goldstralia, *Radiation*

Physics and Chemistry 2006, **75(11)**, 1948. Gold L3 edge x-ray absorption spectroscopic measurements were carried out over supported Gold nanoparticles. The interesting results obtained from EXAFS and XANES confirms the typical characteristics and structure of Gold nanoparticles in these materials.

2 Catalysis

2.1 Gold catalyst research at The Institute of Isotopes, Budapest

Laszlo Gucci from the Department of Surface Chemistry and Catalysis, Institute of Isotopes of the Hungarian Academy of Sciences, Budapest, H-1525, Hungary, *Gold Bulletin (London, United Kingdom)* 2006, **39(3)**, 121, A review; gold catalyst research at The Institute of Isotopes, Budapest is discussed.

2.2 Supported Gold and Ruthenium Catalysts for the Oxidation of CO with Oxygen and Water Vapour

The activity of the Fe₂O₃-supported 0.5-5.0% transition group metal catalysts in the water gas shift reaction ((3:6:91 vol./vol.) CO-O-He, H₂O/CO=1.7 by moles, -80-500.degree.) fell in the descending order: Ru - Rh > Pt > Ir > Pd > Gold. W Jozwiak, E Kaczmarek, T Maniecki, A Basinska from the Inst. Chem. Ogolnej i Ekol., Politech. Lodzka, Poland, *Przemysl Chemiczny* 2006, **85(8-9, Pt. 1)**, 729. In the Ru and the Gold catalysts, supports suppressed the activity in the following orders: (Na, K)/Fe₂O₃ > Fe₂O₃ Cr₂O₃ > Al₂O₃ SiO₂ .apprx. O (inactive catalysts) and (Na, K)/Fe₂O₃ > Fe₂O₃ > TiO₂ > Al₂O₃, respectively Na and K (3.6% K) enhanced the activity to yield 50-80% CO conversions. Active centers included Ru.degree. and redox Fe²⁺ - Fe³⁺ of magnetite Fe₃O₄. Support's reduction, 3Fe₂O₃ + CO = 2 Fe₃O₄ + CO₂, is prerequisite for Ru/K/Fe₂O₃ to be active. Similarly, dehydroxylation of the K-coated Fe₂O₃ surface, 2Fe-OH - Fe₃+O + Fe₂+ + Vo + H₂O₂, is essential for Gold/K/Fe₂O₃ to be active.

2.3 Photocatalysis by ZnS Nanoparticles of the formation of ZnS/Gold Heterostructure in the reduction of complex ions of Gold

The photocatalytic activity of ZnS nanoparticles during the reduction of the KGold(CN)₂ complex was found. A Raevskaya, A Korzhak, A Stroyuk, S Kuchmii from the Piszarzhetskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev, *Theoretical and Experimental Chemistry* 2005, **41(6)**, 359. The spectral characteristics of the nanocomposite ZnS/Gold and also the principal kinetic relationships involved in its formation were studied. The photoreaction has equil. character resulting from oxidation of the obtained gold by holes in the valence band of the zinc sulfide.

2.4 Photocatalytic properties of TiO₂ modified with Gold Nanoparticles in the Degradation of oxalic acid in Aqueous Solution

The commercially available TiO₂-catalyst (Degussa P25) was supported by spray pyrolysis deposition method on the outer surface of the quartz tubes, incorporated in photocatalytic reactor. V Iliev, D Tomova, R Todorovska, D Oliver, L Petrov, D Todorovsky, M Uzunova-Bujnova, from the Institute of Catalysis, Bulgarian Academy of Sciences, Bulgaria, *Applied Catalysis, A: General* 2006, **313(2)**, 115. The crystal structure and the morphology of the films were studied. The immobilized TiO₂ is modified with nanosized gold particles by the photoreduction method to obtain different noble metal loading (0.05-0.4 wt.%). The characterization of the synthesized catalysts was carried out by the BET method, XPS, SEM, TEM and the adsorption of the model pollutant was detd. The degradation of oxalic acid has been studied in aq. solution photocatalyzed by band-gap-irradiated TiO₂, modified with nanosized gold particles. The presence of low amounts of gold on the TiO₂ surface leads to an increase of its photocatalytic activity. The max. value of the photocatalytic activity was registered with the .apprxeq.0.16 wt. % Gold on TiO₂ sample. At this concentration the activity of the Gold-modified TiO₂ is approx. double that of the semiconducting support. The adsorption properties of the catalysts, as well as the noble metal content on the surface of the support, influence the efficiency of the photocatalytic process. The reaction rate of photocatalytic degradation of the oxalic acid follows a zero kinetic order according to the Langmuir-Hinshelwood model.

2.5 Catalyst Containing Gold on Ceria-Manganese Oxide for Carbon Monoxide Oxidation in Hydrogen Stream for Fuel Cell Use

A patent for a Gold catalyst comprising gold on a support of ceria or ceria-manganese oxide is used for the oxidation of CO in a H₂ stream. Inventors are M Kroell, S Katusic, M Kraemer, J Chung, Y Chen from Degussa AG, Germany Patent No PI EP 1724012, A1 Nov 2006

2.6 The Effect Of Gold On The Reduction Behaviour Of Some Metal Oxide Catalysts

The results of some temperature programmed reduction experiments are analyzed. G Munteanu, E Segal, L Ilieva from the Murgulescu Institute of Physical Chemistry of the Romanian Academy, Bucharest, *Annals of West University of Timisoara, Series of Chemistry* 2005, **14(2)**, 141. One evidences the effects of the gold nanoparticles on the reduction behavior of several gold promoted metal oxide catalysts: .alpha.-Fe₂O₃, V₂O₅/TiO₂, V₂O₅/ZrO₂ and V₂O₅/CeO₂. The effects of gold particles on the values of the kinetic parameters are also analyzed

2.7 Catalytic Properties Of Carboxylic Acid Functionalized-Polymer Microsphere-Stabilized Gold Metallic Colloids

Polymer-microsphere-stabilized gold metallic colloids have been prepared by a novel strategy of simple and convenient reduction of the metallic salt through the stabilization of the active carboxylic acid group on the gel and surface layer of the microsphere. W Liu, X Yang, W Huang from the Key Laboratory of Functional Polymer Materials, the Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin, Peop. Rep. China, *Journal of Colloid and Interface Science* 2006, **304(1)**, 160. The nature of the interaction between the carboxylic acid and Gold nanoparticles was studied in detail by XPS. Preliminary results indicate that polymer-microsphere-stabilized gold colloids are active catalysts for the reduction of 4-nitrophenol to 4-aminophenol with sodium borohydride as reductant. The catalytic properties of the stabilized catalyst for recycling were also investigated.

2.8 Gold Catalysts: Nanoporous Gold Foams

Unsupported, nano-porous Gold foam with a sponge-like morphol. is formed by selective leaching of Ag from a Gold-Ag alloy. V Zielasek, B Juergens, C Schulz, J Biener, M Biener, A Hamza, M BGoldmer from the Institut fuer Angewandte und Physikalische Chemie, Universitat Bremen, Bremen, Germany, *Angewandte Chemie, International Edition* 2006, **45(48)**, 8241. This Gold foam is a highly active catalyst for CO oxidation at ambient pressure and temperature (down to -20.degree.), and has potential applications as membrane catalysts.

2.9 Homocysteine-Mediated Reactivity and Assembly of Gold Nanoparticles

This paper reports the findings of a study of the reactivity and assembly of gold nanoparticles mediated by homocysteine (Hcys), a thiol-containing amino acid found in plasma. I Lim, S Im W Ip, E Crew, P Njoki, D Mott, C J Zhong, Y Pan, S Zhou from the Department of Chemistry, State University of New York at Binghamton, Binghamton, NY, USA, *Langmuir* 2007, **23(2)**, 826. The aim is to gain insight into the interparticle interaction and reactivity, which has potential application for the detection of thiol-containing amino acids. By monitoring the evolution of the surface plasmon resonance absorption and the dynamic light scattering of gold nanoparticles in the presence of Hcys, the assembly is dependent on the nature and concentration of the electrolytes, reflecting an effective screening of the diffuse layer around the initial citrate-capped nanoparticles that decreases the barrier to the Hcys adsorption onto the surface, and around the subsequent Hcys-capped nanoparticles that facilitate the zwitterion-type electrostatic interactions between amino acid groups of Hcys bound to different nanoparticles. A key element of the finding is that the interparticle zwitterion interaction of the Hcys-Gold system is much stronger than the expectation for a simple Hcys or Gold solution, a new phenomenon originating from the unique nanoscale interparticle interaction. The strength and reversibility of the interparticle zwitterion-type

electrostatic interactions between amino acid groups are evidenced by the slow disassembly upon increasing pH at ambient temps. and its acceleration at elevated temperature. These findings provide new insight into the precise control of interfacial interactions and reactivities between amino acids anchored to nanoparticles and have broad implications in the development of colorimetric nanoprobcs for amino acids.

3 Chemistry

3.1 The Adsorptive Behavior of Quaternary Ammonium Gemini Surfactants at Bare Gold Electrode

The adsorptive behavior of three cationic Gemini surfactants C16H33Me2N-C4H8-NMe2C16H33(C16C4-C16), C12H25Me2N-C4H8-NMe2C12H25(C12-C4-C12), C8H17Me2N-C4H8-NMe2C8H17(C8-C4C8) at bare gold electrode was studied with cyclic voltammetry, a.c. impedance spectra (ACIS), and quartz crystal microbalance (QCM). J Li, F Zhao, B Zeng, from the College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Peop. Rep. China, *Wuli Huaxue Xuebao* 2006, **22(2)**, 249. The electrochem. probe catechol (CC) can exhibit two pairs of redox peaks at 0-0.8 V (vs. SCE) in 0.3 mol L⁻¹ KNO₃ solutions. When some cationic Gemini surfactants are introduced into the solutions, the 1st pair of peaks decreases, but the 2nd pair of peaks increases. At the same time, the anodic peaks move in pos. direction and the cathodic peaks shift in neg. direction. For the three Gemini surfactants, their influence on the voltammetric behavior of CC follows such order as C8-C4-C8 < C12-C4-C12 < C16-C4-C16. ACIS shows that in the presence of Gemini surfactants, the impedance of the electrode interface grows. For those surfactants, the impedance rises with increasing alkyl-chain length. Similar result was obtained in QCM experiment. Namely, when the alkyl-chain is longer, the Gemini surfactant makes the frequency change more. The adsorption modes of those Gemini surfactants are established according to the change of the 1st anodic peak area of CC. Their adsorption belongs to Langmuir adsorption.

4 Electrochemistry

4.1 Molecular Assemblies of Functional Molecules on Gold Electrode Surfaces Studied by Electrochemical Scanning Tunneling Microscopy: Relationship Between Function and Adlayer Structures

In this research, mol. assembly and function of aromatic thiols, porphyrins, phthalocyanines, and fullerenes on Gold single crystal surfaces were studied by electrochemical methods and scanning tunneling microscopy (STM). S Yoshimoto from the National Institute of Advanced Industrial Science and Technology (AIST), Central 6, 1-1-1 Higashi, *Tsukuba, Japan*, *Bulletin of the Chemical Society of Japan* 2006, **79(8)**, 1167.

Surface functions of promoter mols. such as pyridinethiols, pyrimidinethiols, and benzenethiol for cytochrome c electrochem. were characterized by electrochem. techniques. Adlayer structures of those mols. were studied by in situ STM, and mol. orientations for each mol. on the Gold surfaces were clarified at mol. level. Adlayers of porphyrins and phthalocyanines for electrocatalytic reduction of dioxygen were examined to elucidate the relation between activity and adlayer structure. Stable 2-dimensional arrays of Co porphyrins indicated 2-electron reduction of O₂ to H₂O₂, whereas 2-step 4-electron reduction of O₂ to H₂O occurred becGoldse of highly mobile porphyrinatoiron mols. on the surface. Also, well-defined adlayers of crown-substituted phthalocyanine for host-guest interface and binary array consisting of porphyrin and phthalocyanine for the design of supramol. nanoarchitectures were clearly visualized by STM. Finally, a unique approach for controlling mol. orientation was found by the formation of supramol. assemblies consisting of porphyrin and fullerene. The electrochemical redox reaction of carbonyl and ferrocene moieties was promoted by using the simple method for the construction of a 1:1 supramol. assembled film consisting of C60 deriv. and octaethylporphyrinatometal on Gold single crystal surfaces.

4.2 Active Catalysts of Electrochemically Prepared Gold Nanoparticles for the Decomposition of Aldehyde iosition Alcohol Solutions

Sonoelectrochem. synthesized Gold nanoparticles with diameters of .apprx.20 nm were prepared from Gold sheets in NaCl aq. solutions without the addn. of any stabilizer. Y Liu, C Yu, K Yang from the Department of Chemical and Materials Engineering, Vanung University, Chung-Li City, Taiwan, *Electrochemistry Communications* 2006, **8(7)**, 1163. First, a Gold substrate was cycled in a deoxygenated aq. solution containing 0.1 M NaCl from -0.28 to +1.22 V vs. Ag/AgCl at 500 mV/s for 100 scans. The durations at the cathodic and anodic vertexes are 10 and 5 s, respectively. After this process, Gold-containing complexes were left in the solution then the Gold working electrode was immediately replaced by a Pt electrode, and a cathodic overpotential of 0.6 V from the open circuit potential (OCP) was applied under sonification to synthesize Gold nanoparticles. Encouragingly, the prepared Gold nanoparticles are active catalysts for the decomposition of 2000 ppm aldehyde in 40% (vol./vol.%) EtOH aq. solutions. After testing for 10 days, the aldehyde was decomposition by .apprx.50% in alc. solutions containing 25 ppm Gold nanoparticles under slight stirring. After testing for 10 days, the aldehyde was undetectable in Gin wines containing 60 ppm aldehyde by just adding 1 ppm Gold nanoparticles under slight stirring.

5 Electronics and Sensors

5.1 Screen Printed Carbon Electrode Modified With Poly(L-Lactide) Stabilized Gold Nanoparticles For Sensitive As(III) Detection

Poly(L-lactide) stabilized Gold nanoparticles (designated as PLA-GoldNP) with an av. particle size of .apprx.10 nm were used to modify a disposable screen-printed C electrode (SPE) for the detection of As(III) by differential pulse anodic stripping voltammetry. Y Song, G Muthuraman, Y Chen, C Lin, J Zen from the Department of Chemistry, National Chung Hsing University, Taichung, Taiwan, *Electroanalysis* 2006, **18(18)**, 1763. Gold modification was evaluated by cyclic voltammetry, whereas SEM and TEM revealed the size and distribution of Gold nanoparticles. The PLA-GoldNP/SPE was applied effectively to detect toxic As(III) in HCl medium. Under the optimal experimental conditions, a linear calibration curve up to 4 ppm with a detection limit ($S/N = 3$) of 0.09 ppb was obtained. The sensitivity was good enough to detect As(III) at levels lower than the current EPA std. (10 ppb). Most importantly, the PLA-GoldNP/SPE can be tolerable from the interference of Cu, Cd, Fe, Zn, Mn, and Ni and hence provides a direct and selective detection method for As(III) in natural waters. Practical utility of the PLA-GoldNP/SPE was demonstrated to detect As(III) in Blackfoot disease endemic village groundwater from southwestern coast area of Taiwan (Pei-Men).

5.2 Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition

Plasmonic metal nanoparticles have great potential for chem. and biol. sensor applications, due to their sensitive spectral response to the local environment of the nanoparticle surface and ease of monitoring the light signal due to their strong scattering or absorption. K Lee, M El-Sayed from the Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, USA, *Journal of Physical Chemistry B* 2006, **110(39)**, 19220. The Goldthors studied the dependence of the sensitivity of the surface plasmon resonance (frequency and bandwidth) response to changes in their surrounding environment and the relative contribution of optical scattering to the total extinction, on the size and shape of nanorods and the type of metal, i.e., Gold vs. Ag. Theoretical consideration on the surface plasmon resonance condition revealed that the spectral sensitivity, defined as the relative shift in resonance wavelength with respect to the refractive index change of surrounding materials, has two controlling factors: 1st the bulk plasma wavelength, a property dependent on the metal type, and 2nd on the aspect ratio of the nanorods which is a geometrical parameter. The sensitivity is linearly proportional to both these factors. To quant. examine the dependence of the spectral sensitivity on the nanorod metal composition and the aspect ratio, the discrete dipole approxn. method was used for the calcn. of optical spectra of Ag-Gold alloy

metal nanorods as a function of Ag concentration. The sensitivity does not depend on the type of the metal but depends largely on the aspect ratio of nanorods. The direct dependence of the sensitivity on the aspect ratio becomes more prominent as the size of nanorods becomes larger. However, the use of larger nanoparticles may induce an excessive broadening of the resonance spectrum due to an increase in the contribution of multipolar excitations. This restricts the sensing resolution. The insensitivity of the plasmon response to the metal composition is attributable to the fact that the bulk plasma frequency of the metal, which det. the spectral dispersion of the real dielec. function of metals and the surface plasmon resonance condition, has a similar value for the noble metals. However, nanorods with higher Ag concentration show a great enhancement in magnitude and sharpness of the plasmon resonance band, which gives better sensing resolution despite similar plasmon response. Also, Ag nanorods have an additional advantage as better scatterers compared with Gold nanorods of the same size.

5.3 Gold Nanoparticles: Enhanced Optical Trapping and Sensitivity Coupled with Significant Heating

Gold nanoparticles appear to be superior handles in optical trapping assays. Y Seol, A Carpenter, T Perkins from the JILA, University of Colorado, Boulder, USA, *Optics Letters* 2006, **31(16)**, 2429. The Goldthors demonstrate that relatively large gold particles ($R_b = 50$ nm) indeed yield a sixfold enhancement in trapping efficiency and detection sensitivity as compared to similar-sized polystyrene particles. However, optical absorption by gold at the most common trapping wavelength (1064 nm) induces dramatic heating (266.degree. C/W). The Goldthors detected this heating by comparing trap stiffness from three different methods in conjunction with detailed modeling. Due to this heating, gold nanoparticles are not useful for temperature-sensitive optical-trapping experiments, but may serve as local mol. heaters. Also, such particles, with their increased detection sensitivity, make excellent probes for certain zero-force biophys. assays.

6 Medical and Dental

6.1 Synchrotron X-Ray Synthesis of Colloidal Gold Particles for Drug Delivery

The Goldthors reported a simple approach to generate gold colloids from HAuCl₄ containing aq. solution by synchrotron x-ray irradiation at room temperature Y Yang, C Wang, Y Hwu, J Je from the Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taichung, Taiwan, *Materials Chemistry and Physics* 2006, **100(1)**, 72. Gold colloids were readily formed with reasonable yield. It was also obsd. that the addn. of NaHCO₃ tremendously modified the size and size distribution of gold nanoparticles. The Goldthors preliminary

drug carrying experiment showed that thus produced gold nanoparticles could successfully carry anti-tumor drug and possess potential for drug delivery applications.

6.2 D-Penicillamine Adsorption on Gold: An in Situ ATR-IR Spectroscopic and QCM Study

The adsorption of penicillamine from ethanol on gold was studied in situ by attenuated total reflection IR (ATR-IR) and quartz crystal microbalance (QCM) experiments. M Bieri, T Buergi from the Faculte des Sciences, Institut de Microtechnique, Universite de Neuchatel, Neuchatel, Switzerland, *Langmuir* 2006, **22(20)**, 8379. Both ATR-IR and QCM reveal a fast mass uptake. In ethanol, the mol. adopts a zwitterionic form. Upon adsorption, part of the mols. deprotonate at the amine group, which is a relatively slow process that goes along with a strong shift of the $\nu_{\text{as}}(\text{COO}^-)$ mode. Both ATR-IR and QCM confirm a physisorbed layer. ATR-IR also shows that the latter consists of zwitterionic mols. only, whereas both zwitterionic and anionic species are found in the chemisorbed layer. The IR spectra of the physisorbed and chemisorbed layers are rather different, and the mols. within both layers seem to be oriented with respect to the surface. The ATR-IR spectra also indicate that all three functional groups of penicillamine (i.e., thiol, carboxylate, and amine) interact with the surface, and d. functional theory calcns. support this finding. QCM also shows that the mol. uses considerably more space on the surface than mols. of similar size, which supports a three-point interaction. The latter leads to a strong anchoring of the mol. to the metal, which may explain the exceptional capability of penicillamine to bind metals.

7 Metallurgy, Materials and Coatings

7.1 An Investigation of the Gold-Rich Alloys in Gold-Ag-Zr Ternary System

On the basis of Gold-Ag, Gold-Zr and Ag-Zr binary phase diagrams, the 700.degree.C isothermal section of the gold-rich field in Gold-Ag-Zr ternary system was established by X-ray diffraction anal., electron probe microanalyses (EPMA) and optical microscopy. K Zhang, J Li, L Chen from the Kunming Institute of Precious Metals, Kunming, Yunnan, Peoples Republic of China, *Gujinshu* 2006, **27(1)**, 10. It was found that there is the long single-phase region, Gold(Ag) or Ag(Gold), along the Gold-Ag binary isomorphous system on the gold-silver-rich side of the 700.degree.C isothermal section. It was confirmed that the partial 700.degree.C isothermal section consists of four single-phase regions: solid solution Gold(Ag) or Ag(Gold), Gold4Zr, Gold3Zr, and Gold2Zr; four binary-phase regions: Gold4Zr + Gold(Ag), Gold3Zr + Gold(Ag), Gold4Zr + Gold3Zr, and Gold3Zr + Gold2Zr; and two ternary regions: Gold4Zr + Gold3Zr + Gold(Ag) and Gold3Zr + Gold2Zr + Gold(Ag). No new ternary compd. was formed in the gold-rich field.

7.2 Doping-Induced Simultaneous Improvement of Strength and Ductility in Ultrafine Grained Gold Wires

The room temperature tensile properties of ultrafine-grained 25- μm diam. gold wires were evaluated as a function of calcium doping of 21-87 wt. ppm. at strain rates between 10⁻³ and 10⁻¹/s. Y Chew, C Wong, C Breach, F Wulff, T Lew from the Materials and Applications Center, Kulicke and Soffa (S.E.A.) Pte. Ltd., Singapore, Singapore, *Journal of Materials Research* 2006, **21(9)**, 2345. Paradoxically, increased Ca content simultaneously increased the strength and ductility of the Gold wires. However, based on SEM and tensile characterization, the grain size distribution, strain-hardening rate, and strain-rate sensitivity of the Gold wires did not change with Ca content, and showed that neither grain refinement nor plastic instability is likely to be responsible for the concurrent improvement in strength and ductility.

8 Nanotechnology

8.1 Topological Characterization of Crystallization of Gold Nanoclusters

Y Chui, R Rees, I Snook, B O'Malley, P Salvy, from the Applied Physics, School of Applied Science, RMIT University, Melbourne, Goldstralia, *Journal of Chemical Physics* 2006, **125(11)**, 114703/1. The Goldthors use a new topol. structure measure to analyze the local environment of 923 atom gold clusters quenched from the melt, at various quench rates, by mol. dynamics. Y Chew, C Wong, C Breach, F Wulff, T Lew from the Materials and Applications Center, Kulicke and Soffa (S.E.A.) Pte. Ltd., Singapore, Singapore, *Journal of Materials Research* 2006, **21(9)**, 2345 The crystn. and geometrical rearrangements of the core atoms upon freezing can be clearly obsd. using our structure measure which is based on planar graphs. The results support the hypothesis that crystn. is initiated from the surface and proceeds into the cluster core.

8.2 Synthesis of Multiple Shapes of Gold Nanoparticles With Controlled Sizes in Aqueous Solution Using Ultrasound

Effects of concentration of stabilizer (Na dodecylsulfate: SDS) and ultrasonic irradiation power on the formation of Gold nanoparticles (Gold-NPs) were studied. Gold-NPs with multiple shapes and size were synthesized by controlling the concentration of stabilizer and ultrasonic irradiation power. J Park, MAtobe, T Fuchigami from the Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Technology, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama, Japan, *Ultrasonics Sonochemistry* 2006, **13(3)**, 237. The shapes and size of Gold-NPs were controlled by changing either the ratio of Gold(III) ion/SDS or the power of ultrasonic irradiation. The multiple shapes and size distribution of Gold-NPs are dependent on not only the ratio of Gold(III) ion/SDS but also ultrasonic irradiation power. The

sonochem. synthesized Gold-NPs were characterized by TEM and UV-visible spectroscopy.

8.3 Alternative Approaches to Fabrication of Gold-Modified TiO₂ Nanotubes

Three approaches, impregnation-reduction, deposition and direct assembly, are used to fabricate gold-modified TiO₂ nanotubes. B Zhu, Z Sui, S Wang, X Chen, S Zhang, S Wu, W Huang from the Department of Chemistry, Nankai University, Tianjin, Peoples Republic of China, *Materials Research Bulletin* 2006, **41(6)**, 1097. Prepared materials are characterized with powder X-ray diffraction (XRD), SEM, TEM, high-resolution TEM, UV-visible absorption spectroscopy and BET, etc. The gold-modified TiO₂ nanotubes prepared via various procedures exhibit distinct difference in structure. By impregnation-reduction approach, gold-modified TiO₂ nanotubes with large gold particles are fabricated. The gold particles are either deposited on, or encapsulated in, TiO₂ nanotubes. However, by using gold hydrophilic colloidal dispersion as gold precursor, gold particles in the modified TiO₂ nanotubes are very small. Gold particles adhere only to the outer surface of TiO₂ nanotubes after the deposition process, whereas they adhere to both the outer and inner walls with the direct assembly process. A possible mechanism is proposed to illustrate the formation of gold-modified nanotubes that are prepared by the direct assembly process.

8.4 Tailoring The Shape of Colloidal Gold Particles with Nanosecond-Pulsed Laser Light

Modification of metal nanoparticles with laser light has been a well-known technique for several years. In this paper, we present our recent studies on tailoring the shape of colloidal gold particles with nanosecond-pulsed laser light. F Vogel, F Hubenthal, F Traeger from the Institut fuer Physik, Center for Interdisciplinary Nanostructure Science and Technology, CINSaT, Univ. Kassel, Kassel, Germany, *Proceedings of SPIE-The International Society for Optical Engineering* 2006, 6324(Plasmonics: Nanoimaging, Nanofabrication, and Their Applications II), 63240G/1. The underlying method is based on the shape and size dependent optical properties of metal nanoparticles, i.e. the excitation of surface plasmon polariton resonances. Thus, laser irradiation with a pre-detd. photon energy excites and heats nanoparticles of certain shapes and sizes selectively. This heating leads to diffusion and, for sufficiently high fluences, to evapn. of surface atoms. In our experiments, colloidal gold particles were prepared by chem. reduction of a gold salt resulting in nanoparticles with different sizes and shapes. Subsequently, the colloidal gold particles were irradiated with nanosecond-pulsed laser light. In all cases, a significant reduction of the line width of the surface plasmon polariton resonance has been obsd. This reflects a narrowing of the shape distribution of the particles. For example, irradiation with a photon energy of 2.16 eV and a fluence of (58 .+- . 2) mJ/cm² leads to a reduction of the width of the surface plasmon resonance from 0.30 eV to 0.22 eV (HWHM) due to a reshaping of the nanoparticles.

This has also been confirmed by TEM measurements. Also, a size reduction of the nanoparticles has been obsd.

9 Refining

9.1 Advances in Gold Recovery From Sulphide Ores Using Thiocyanate and Activated Carbon

Conventional hydrometallurgical systems for gold recovery from its ores include the use of cyanide as the leaching agent, followed by adsorption of the Gold(CN)₂- complex on activated carbon. G Munoz, J Simba, from the Department of Extractive Metallurgy, Escuela Politecnica Nacional, Quito, Ecuador, *Conference Proceedings - International Precious Metals Institute, 29th, Orlando, FL, United States, June 11-14, 2005* 030/1-030/10 Publisher: International Precious Metals Institute, Pensacola, Fla. These processes require that the leaching and recovery systems should be highly alk. Gold deposits are also rich in sulfides, which give acidic characteristics to the ores. For these reasons, the search for a suitable lixiviant in an acid environment was of great interest. The use of thiocyanate as a leaching agent under acidic conditions for gold dissolution and its recovery from solution using activated carbons are presented.

9.2 Prospects for Recovery of Difficult Gold Forms from Man-Made Placer Deposits

The article is devoted to the problem of gold recovery from man-made placer deposits. By the example of man-made placer deposits of the Solovoyovsky gold-bearing site (processed by dredge in 1968), morphol. and grain-size distribution characteristics of gold were studied on the basis of prospect-hole and furrow sampling of sand-clay gold refuse dumps. Y Mamayev, V Litvintsev, G Ponomarchuk, T Bانشchikova, V Podshivalov, S Alkov, *Obogashchenie Rud (Sankt-Peterburg, Russian Federation)* 2005, **(5)**, 42. The major proportion of valuable component is composed by size fractions that are not recovered by conventional methods, and alternative technologies for recovery of the size fractions in question are discussed.

9.3 Fundamentals and Applications of Alkaline Sulfide Leaching and Recovery of Gold

A review. C Anderson, E Dahlgren, M P Miranda, D Stacey, M Jeffrey, I Chandra from, the Center for Advanced Mineral and Metallurgical Processing, Montana Tech, Butte, MT, USA, *Conference Proceedings - International Precious Metals Institute, 29th, Orlando, FL, United States, June 11-14, 2005*, 024/1-024/19 Publisher: International Precious Metals Institute, Pensacola, Fla. The latter part of the 20th century saw great advances in the treatment of refractory gold ores coupled with increased reliance on the use of cyanide for gold processing. Now, in many parts of the world, there is social pressure to limit or eliminate the use of cyanide. As well, treatment of some refractory ores or concs. which have excessive cyanide consumption, gold cyanide pregrobbing

or significant sulfide content remain difficult. This paper will outline the history of the development of alk. sulfide leaching as an ancillary process to nitrogen species catalyzed (NSC) pressure leaching. Electrochem. fundamentals and the applicable thermodyn. of the alk. sulfide hydrometallurgical system will be outlined. As well, examples of refractory gold recovery with alk. sulfide hydrometallurgy such as an arsenopyrite gold conc. application, a chalkopyrite gold concentration application, a pregrobbing gold ore application, and a cyanide consuming gold ore application will be delineated in this paper.

9.4 Study on Gold(I) Extraction From Gold-Containing Polysulfide Solution With The Mixed Solvent of N1923-TBP

The effects of different neutral solvents, such as tri-n-octylamine, 4,4'-bis-(dimethylamino) thiobenzophenone, methyl-iso-Bu ketone, CHCl₃, and tri-Bu phosphate (TBP), on the extn. of Gold(I) from Gold-containing polysulfide solution with primary amine N1923 were studied. X Luo, Q Yan, H Peng from the Jiangxi University of Science and Technology, Ganzhou, Peop. Rep. China, *Youse Jinshu, Yelian Bufen* 2004, **(6)**, 30. TBP showed synergistic effect with N1923. The initial concentration of Gold(I) in water phase had no effect on the Gold extn. in N1923-TBP mixed solvent. Diluents (kerosene, n-octane, and benzene) for org. phase affected the extration of Gold in N1923-TBP mixed solvent. Diluents with aroms. extd. Gold at higher pH as compared to that without aroms. The main extracting agent in the mixed N1923-TBP solvent was N1923 at pH <9, but was TBP at pH >9.

9.5 Recovery of Gold from Slag Bb Pressure Oxidation-Cyanide Leaching Method

A process for recovering Gold from a slag was developed by pressure oxidation-cyanide leaching. The leaching rate for Gold was >70% at liq./solid ratio 1.5:1 and pH >11 for 3 h. The process showed good economic benefit. G Xue, Y Yu from the Chinese People's Armed Police Force, Yantai, Peop. Rep. China, *Kuangchan Zonghe Liyong* 2004, **(6)**, 48.

9.6 Development and Implementation of Processes for Recovery of Fine and Very Fine Native Gold from Placers Using a Fundamentally New Type of High-Performance Jigging Machines

Technologies for fine and extra fine native gold recovery from placer deposits based on application of gravity sepn. methods and featuring rational usage of strakes, jigging machines, spiral devices, concentration tables, centrifugal concentrators in combination with optimum methods of sands prepn. for concentration, developed by the .mchlt. Irgiredmet.mchgt. Institute, are presented. O Zamyatin, V Mankov, *Obogashchenie Rud (Sankt-Peterburg, Russian Federation)* 2005, **(6)**, 48. The results of their introduction at various facilities are described.

9.7 About The Theoretical Bases of Gold Dissolution

Certain problems of electrochem. reactions, put into the base of gold dissolution in cyanide media, and also the problems of influence of spatial configuration of complex gold anions, forming at the process of adsorption of cyanide on gold, which by modern thoughts can det. metal dissolution rate, are discussed in this article. M Ignat'ev from the Inst. Metall. i Obogashch., MON RK, Kazakhstan, *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'ya* 2005, **(6)**, 28. Utilization of heterotrophic bacteria provides for lowering of surface tension, appearing between phases and for improvement of cyanide access to ore metals, during leaching, thanks to synthesis of surface-active substances (in reaction medium). In the results, effectively of cyanide used increase, which makes possible reduction of its expenditure two times with simultaneous increase of gold extn. by 16-20%.

9.8 Implementation of A New Leaching Approach for the Treatment of Kcgm Gold Flotation Concentrate

A new leaching approach was implemented at Kalgoorlie Consolidated Gold Mines Gidji plant on a cyanide leach of ultra-fine ground sulfide conc. G Deschenes, S Ellis, J McMullen, M Habner from the Mining and Mineral Sciences Laboratories, CANMET, Natural Resources Canada, Ottawa, *Publications of the Goldstralian Institute of Mining and Metallurgy* 2005, 9/2005(First Extractive Metallurgy Operators' Conference, 2005), 35. High lime concentration and lead nitrate were used to overcome the refractoriness of the fine sulfides (high reactivity of fine sulfides with gold tellurides). The leach pretreatment stage was detrimental and was shut down. Lime titrn. was introduced as part of the process control. Leaching could be performed at low dissolved oxygen (3-5 ppm) to avoid sulfide oxidation and assocd. high cyanide and lime consumption. Plant results showed decreased cyanide consumption of 40% and an accelerated leaching rate, whereby most of the gold was dissolved in 24 h compared to 72 h used previously. Similar work was performed at the KCGM Fimiston plant, which leached a combined ultra-fine ground sulfide concentration along with the slimes fraction from hydrocycloning the bulk flotation conc. While significant improvements have been demonstrated, further work is progressing at KCGM to decrease the ultra-fine conc. leach tail grades further, and also to improve the understanding of conc. refractoriness and factors responsible for differences between lab. and plant leach results. Established profits since implementation of the new approach are in the range of \$A3.5 million/yr.

9.9 Selective Elution of The Gold Cyanide Complex from Anion Exchange Resin Using Mixed Solvents

The use of mixed solvents for the elution of the cyanide complexes of copper and gold from Purolite A500, a strong-base anion exchange resin, was investigated. R Rajasingam,

N Jayasinghe, F Lucien, T Tran from the School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, Goldstralia, *Minerals Engineering* 2006, **19(9)**, 896. The mixed solvents investigated include acetone-water, dimethylsulfoxide-water and N-methyl-2-pyrrolidone-water. The three types of counterions employed in each of the mixed solvents are CN⁻, Cl⁻ and OH⁻. The effects of counterion concentration and mixed solvent composition on elution of the complexes are examined. High recoveries of the gold cyanide complex are achieved in the mixed solvents at relatively low counterion concentrations. In contrast, the recoveries of the copper cyanide complexes are 1-3 orders of magnitude lower for the given initial loading of the metals on the resin. The selectivity of the elution process for gold is discussed in terms of the degree of solvation of the various anions in the mixed solvents. The possibility of using mixed solvents to develop an elution process that is selective for gold over multivalent cyanide complexes is considered.

9.10 A Green Technology for Recovery of Gold from Non-Metallic Secondary Sources

A process for the recovery of gold from processed gold-plated printed circuit boards, gold-coated bangles and gold-coated mirrors is described. S Syed from the Corrosion Research Group, King Abdulaziz City for Science and Technology, Atomic Energy Research Institute, Riyadh, SGolddi Arabia, *Hydrometallurgy* 2006, **82(1-2)**, 48. It is based on heating the solid waste along with an eco-friendly or green reagent, 20 vol.% formic acid solution to the boiling temperature to sep. the inorg. components from epoxy resin in gold-coated mirrors. Dissolution of base metals is accomplished by using a strong oxidizing agent, 20%(w/v) potassium persulfate, which is also eco-friendly or green, and heating to the boiling temperature Recovery of gold is achieved by melting. The recovery efficiency is on a par with the cyanidation process. The process can be scaled up and adopted.

10 General

10.1 Preparation of Gold And/Or Silver Nanostructures and Films for Cancer Therapy and Measuring a Change of Refractive Index

A patent by inventors F Frederix, B Van de Broek from the Interuniversitair Microelektronica Centrum, Belg. Patent No. PI EP 1741717,A1 Jan 2007 describes metal nanostructures comprising a nanometric metal core of Gold, Ag or an assembly or alloy of Gold and Ag, and one or more mols. attached to one or more surfaces of the nanometric metal core, wherein each mol. has the structural formula W-X-Y-Z, wherein W is an atom or a chem. group bound to said nanometric metal core, X is a hydrophobic spacer, Y is a hydrophilic spacer and Z is either H or a reactive group able to bind a reactive substrate or biomol. Nanostructures include pyramidal or branched shapes and monolayers of nanostructures. Such metal nanostructures are active under IR irradiation and are useful in making pharmaceutical compns. for the thermotherapeutic treatment of cancer. Films of the nanostructures are useful for measuring a change of refractive index.