

Highlights from Recent Literature

1 Analytical

1.1 Determination of As(III) and As(V) By Stripping Voltammetry Method using Home Made Gold Rotation Disk Electrode

The method for the detection of As(III) and As(V) in new type home-made Au electrode was established. T Le, N Thanh; A H Ba from the Department of Environmental Science, College of Natural Science, Ho Chi Min, Japan, *Tap Chi Phan Tich Hoa, Ly Va Sinh Hoc* 2005, **10**, 30. The method shows the good response for As(III) and As(V) concentration in $\mu\text{g/L}$ range. The method was checked by raw-material from EAWAG. The interference of some ions was researched and interference ions were successful removed.

1.2 Determination of the Thickness of Ultrathin Gold Films from X-ray Photoelectron Spectroscopy Data

A method based on XPS and taking into account photoelectron elastic scattering in solids and nondipolar transitions in photoionization is used to evaluate the thickness d of ultrathin Au films. V Nefedov, V Yarzhemsky, I Nefedova and R Szargan from the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991, Russia, *Inorganic Materials* 2005, **41(9)**, 945. Two procedures for varying the photoelectron path in a film are examined: by rotating the analyzer and the sample. Both approaches have significant advantages over the straight-line approximation which does not take into account elastic scattering and gives considerably overestimated d . Experimental data are simulated using the Monte Carlo method. The two procedures ensure roughly equal accuracies ($\approx 5\%$) in reproducing the film thicknesses used in simulations. The rotating analyzer method typically gives slightly higher values of d in comparison with the rotating sample method.

2 Catalysis

2.1 Synthesis of Carbon Nanotubes over Gold Nanoparticle Supported Catalysts

The synthesis of carbon nanotubes (CNTs) through the catalytic decomposition of acetylene was carried out over gold nanoparticles supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$. Monodispersed gold nanoparticles with 1.3-1.8 nm in diameter were prepared by the liquid-phase reduction method with dodecanethiol as protective agent. S Lee, M Yamada, M Miyake from the Japan Advanced Institute of Science and Technology (JAIST), School of Materials Science, Nomi,

Ishikawa, Japan, *Carbon* 2005, **43(13)**, 2654. The carbon products formed after acetylene decomposition consist of multi-walled carbon nanotubes with layered graphene sheets, carbon nanofilaments (CNFs), and carbon nanoparticles encapsulating gold particles. The observed CNTs have outer diameters of 13-25 nm under 850°C . The influence of several reaction parameters, such as kind of carriers, reaction temperature, gas flow rate, was investigated to search for optimum reaction conditions. The CNTs were observed at a relatively low temperature (550°C). The silica-alumina carrier showed higher activity for the formation of CNTs than others used in the screening test. With increasing temperature, the CNTs showed cured structures having thick diameters and inside compartments. When Au content on the support was over 5 wt.%, the gold nanoparticles coagulated to form large ones >20 nm in diameter and became encapsulated with graphene layers after decomposition of acetylene.

2.2 Gold on Titania Catalysts, Influence of Some Physicochemical Parameters on the Activity and Stability for the Oxidation of Carbon Monoxide

In the standard deposition-precipitation method for prepreg. Au/TiO₂ (P-25) catalysts, after addition of NaOH to the HAuCl₄ solution and introduction of the P-25, the suspension was heated to 343 K. As the pH was increased from 2 to 9, the gold uptake decreased but the specific activity rose as the particles became smaller. F Moreau, G C Bond, Institute for Materials Research, University of Salford, Greater Manchester, UK, *Applied Catalysis, A: General* 2006, **302(1)**, 110. Excellent catalysts were however made by conducting the whole preparation at room temperature, showing that heating to 343 K as was done earlier was quite unnecessary. No advantage was found in performing preparations in the dark. In a second preparation method HAuCl₄ solution was heated at 343 K before TiO₂ addition. This method of preparation, if carried out at pH 6, ensured total deposition of the gold, a relatively high activity for CO oxidation, and represents the best compromise from a practical standpoint. Catalysts made with a high-area anatase ($90\text{ m}^2\text{ g}^{-1}$) responded to the pH used in the preparation in a similar way as TiO₂ (P-25), but the pH for optimum activity covered a wider range (7-9). Preparations made with anatase of high surface area (240 or $350\text{ m}^2\text{ g}^{-1}$) gave complete recovery of gold from solution, but had only a low catalytic activity. Maximum specific rate was found with anatase of $37\text{ m}^2\text{ g}^{-1}$, the value being only slightly lower than the highest value given with the P-25 support. The safest way for preserving the activity of Au/TiO₂ catalysts is by keeping them below ambient temperature. The activity loss observed during long-term CO oxidation experiments could be restored by oxidation at 573 K. Sintered catalysts could be reactivated by treatment with aqua regia and re-deposition of the gold precursor at pH 9.

2.3 Gold Catalysts Supported on Ceria and Ceria-Alumina for Water-Gas Shift Reaction

Gold-supported catalysts on ceria and ceria-alumina with different ratios in the water-gas shift reaction were studied. It was shown that the addition of alumina leads to the deeper oxygen vacancies formation, detected by Raman and TPR measurements. D Andreeva, I Ivanov, L Ilieva, M Abrashev from the Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria, *Applied Catalysis, A: General* 2006, **302(1)**, 127. It was established an increase of the ceria dispersion and as well as slightly increase of the gold particle size. In the presence of alumina after catalytic operation the dispersion of gold and ceria practically does not change. The lower WGS activity on gold/ceria-alumina can be explained on the basis of reduction-oxidation cycle of the reaction. It was established no efficiency re-oxidation of the catalyst surface at the temperatures of the reaction test by the water vapor and we consider this as a main reason of the lower catalytic activity.

2.4 Pure Hydrogen Production on a New Gold-Thoria Catalyst for Fuel Cell Applications.

A new gold catalyst was synthesized by deposition-precipitation of gold hydroxide on thoria. The catalyst showed extremely high catalytic activity at the lowest possible temperature for carrying out of water-gas shift reaction (WGS) under experimental conditions. T Tabakova, V Idakiev, K Tenchev, F Boccuzzi, M Manzoli, A Chiorino, from the Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria, *Applied Catalysis, B: Environmental* 2006, **63(1-2)**, 94. The measured degree of CO conversion at 393 K (GHSV = 4000 h⁻¹) was 84%. The effect of space velocity and water vapor partial pressure on WGS activity was studied at different temperatures. The catalytic measurements testified high stability of Au/ThO₂. HRTEM combined with EDS, x-ray diffraction and H₂-TPR techniques were used for the catalyst characterization. Detailed FTIR measurements of adsorbed CO at different temperatures on oxidized and reduced catalyst were performed. FTIR spectra were also collected during CO + O₂ interaction at different temperatures, CO oxidation in the presence of hydrogen (PROX) and WGS. Preliminary catalytic tests for CO oxidation in hydrogen-rich gas stream revealed that Au/ThO₂ could be of interest as potential catalyst for the PROX process.

2.5 Quantitative Determination of Gold Active Sites by Chemisorption and by Infrared Measurements of Adsorbed CO

Quant. measurements of CO chemisorption in the range 140-180 K, supported by FTIR data on adsorbed CO, were performed on Au/TiO₂, Au/Fe₂O₃, and Au/CeO₂ catalysts. F Menegazzo, M Manzoli, A Chiorino, F Boccuzzi, T Tabakova, M Signoretto, F Pinna, N Pernicone, from the Dipartimento di Chimica, and Consorzio INSTM-UdR Venezia, Università di Venezia, Venice, Italy, *Journal of Catalysis* 2006, **237(2)**, 431. On the first two samples, which had similar particle size

distributions, an av. Au/CO chemisorption stoichiometry of about 3, referred to step-edge Au atoms, was found. On Au/CeO₂, where very small clusters and quite large particles are present, the CO-chemisorbed vol. was much higher than expected, due to the prevailing contribution of very small Au clusters. On the same sample, a change in the IR absorption coeff. was observed and was reasonably explained.

2.6 Effects of the Structure of Ceria on the Activity of Gold/Ceria Catalysts for the Oxidation of Carbon Monoxide and Benzene

Using precipitated cerium hydroxide dried at 100°C as a support, a highly dispersed CeO₂-supported Au catalyst was prepared. S Lai, Y Qiu, S Wang, from the Department of Chemistry and Centre for Surface Analysis and Research, Hong Kong Baptist University, Hong Kong, Kowloon Tong, Peop. Rep. China, *Journal of Catalysis* 2006, **237(2)**, 303. Compared with similarly prepared catalysts supported on low-surface area CeO₂, Au on this high-surface area support exhibited more resistance to sintering and was more active for CO and benzene oxidation. Benzene oxidation was very dependent on the CeO₂ structure. Temperature-programmed reduction showed the reducibility of surface O was higher for high-surface area CeO₂. It was proposed that creating surface O vacancies by CeO₂ surface reduction promoted O adsorption. Active O formed by dissociation of adsorbed O was the active species for benzene oxidation; the dissociation was promoted by Au nano-particles. When present together in the reactant mixture, benzene inhibited CO oxidation, but CO enhanced benzene oxidation; moisture promoted both CO and benzene oxidation.

2.7 Influence of Cation-Adsorption and Sonochemical Approaches on the Preparation of Gold Catalyst

Nanosize mesoporous ZrO₂ support was synthesized via a solid-state reaction route. X Xu, J Li, X Liu, Z Hao, W Zhao, from the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, Peop. Rep. China, *Journal of Nanoscience and Nanotechnology* 2006, **6(3)**, 872. A new preparation method involving cation-adsorption and sono-chem. procedure was developed for mesoporous ZrO₂ supported nano-gold catalyst

2.8 Gold Nano-Particles Stabilized in Mesoporous Mcm-48 as Active CO-Oxidation Catalyst

Gold in nano-crystal size is known as highly active CO-oxidation catalyst. Using simple deposition techniques gold has been deposited as ≈3nm particles inside the channels of mesoporous silica-TiO₂-MCM-48. M Bandyopadhyay, O Korsak, M van den Berg, W Gruenert, A Birkner, W Li, F Schueth, H Gies, from the Institut fuer Geologie, Mineralogie und Geophysik, Lehrstuhl Kristallographie, Fakultät fuer Chemie Ruhr-Universität Bochum, Ruhr-Universität Bochum, Bochum, Germany, *Microporous and Mesoporous Materials* 2006, **89(1-3)**, 158.

In the presence of gold nano-particles the catalyst converts CO to CO₂ at 50% level at -20°C. The composite is stable against sintering up to at least 200°C. XANES and EXAFS confirm the coexistence of elementary and ionic gold during the catalytic activity.

2.9 Remarkable Hydrodechlorination Activity over Silica Supported Nickel/Gold Catalysts

Gas phase hydrodechlorination (HDC) of 2,4-dichlorophenol was carried out using a co-impregnated Ni-Au/SiO₂ (Ni/Au at. ratio = 10) and the performance of the catalyst was compared to that of Ni/SiO₂. G Yuan, J Lopez, C Louis, L Delannoy, M Keane, from the Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY, USA, *Catalysis Communications* 2005, **6(8)**, 555. The Au lowered the temperature requirements for metal reduction and impacted on H₂ uptake/release. The Ni-Au/SiO₂ system showed higher HDC activity and unprecedented enhancement of HDC performance after thermal treatment. The catalyst performance is linked, on the basis of TEM-EDX data, to surface Ni-Au interactions. This effect did not extend to the gas phase phenol hydrogenation where Ni-Au/SiO₂ was less active and thermal treatment had no significant effect on activity/selectivity.

2.10 Characterization and Catalytic Performance of Co/Sba-15 Supported Gold Catalysts For Co Oxidation

Cobalt-containing SBA-15 supported gold catalysts for low-temperature CO oxidation were prepared and characterized by N₂ adsorption/desorption, X-ray diffraction, transmission electron microscopy, inductively coupled plasma-atom emission spectroscopy and XPS techniques. X Xu, J Li, Z Hao, W Zhao, C Hu from the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, Peop. Rep. China, *Materials Research Bulletin* 2006, **41(2)**, 406. The effects of cobalt and gold content on the catalyst activity were investigated in detail. Among them, 2% Au/40% Co/SBA-15 shows the highest activity, its complete conversion temperature for CO is at 273 K. It was believed that both the dispersion of CO₃O₄ and the high surface areas caused by SBA-15 contribute to the good activities of cobalt-containing SBA-15 supported gold catalysts. Furthermore, the strong metal-support interaction between gold and cobalt oxides is greatly related to the catalytic performance.

2.11 Preparation of Alumina Supported Gold Catalysts: Gold Complexes Genesis, Identification and Speciation by Mass Spectrometry

All of the key stages in the synthesis of alumina supported gold catalysts are presented here in detail: from the evolution of a gold precursor-HAuCl₄ in aqueous solution, to its interaction with alumina. S Ivanova, V Pitchon, C Petit, H Herschbach, A Van Dorsselaer, E Leize, from the Laboratoire

des Matériaux, Surfaces et Procédés pour la Catalyse, Strasbourg, France, *Applied Catalysis, A: General* 2006, **298**, 203. The gold precursor hydrolyzes with the production of both neutral and charged species of type: [AuCl₃-x(H₂O)(OH)_x]⁰ and [AuCl₄-x(OH)_x]⁻ along with protons to maintain an elec. balance. This evolution depends on salt concentration, pH value and temperature. The [AuCl₄]⁻ species is the only one easy to quantify by UV-vis spectroscopy. Mass spectrometry is able to quantify gold species in the solution as a function of various parameters prior to and following addition of the support. This method allows detg. the nature and amount of species grafted on the surface of support. The increase in temperature generates an evolution towards species, which are charged and more hydrolyzed. The optimal conditions for quick and successful grafting are detd. to be gold salt concentration 10⁻⁴ mol L⁻¹ and temperature of gold solution 70°C. Under these conditions the gold complexes present in the solution, namely [AuCl₃(OH)]⁻ and trans-[AuCl₂(OH)₂]⁻, provoke the formation of monodentate surface species over alumina, while cis-[AuCl₂(OH)₂]⁻ and [AuCl(OH)₃]⁻ allow grafting in the bidentate mode. We will report how this preparation method leads to a quant. gold deposit. The resulted catalysts are active in the reaction of CO oxidation.

3 Chemistry

3.1 On the Temperature Stability of Gold Nanorods: Comparison Between Thermal and Ultrafast Laser-Induced Heating

The response of Au nanorods to both thermal and ultrafast laser-induced heating was examined. The thermal heating experiments show structural changes that occur on timescales ranging from hours to days. H Petrova, J Perez Juste, I Pastoriza-Santos, G Hartland, L Liz-Marzan, P Mulvaney, from the Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, USA, *Physical Chemistry Chemical Physics* 2006, **8(7)**, 814. At the highest temperature examined (250°C) the nanorods are transformed into spheres within an hour. However, no structural changes are observed in the laser-induced heating experiments up to temperatures of 700 ± 50°C. This is attributed to thermal diffusion in the laser experiments. Measurements of the period of the extensional mode of the nanorods using time-resolved spectroscopy show a significant softening at high pump laser powers. However, the decrease in the period is less than expected from bulk Young's modulus vs. temperature data.

3.2 Growth and Structure of Small Gold Particles on Rutile TiO₂(110)

The growth and structure of small Au_n particles (n=1-4) on a rutile TiO₂(110) surface have been examined using gradient cor. d. functional theory slab calculations. D Pillay, G Hwang, from the Department of Chemical Engineering and Institute

of Theoretical Chemistry, The University of Texas at Austin, Austin, TX, USA, *Physical Review B: Condensed Matter and Materials Physics* 2005, **72(20)**, 205422/1. The authors present potential energy maps for single Au atoms on the stoichiometric and reduced surfaces. This comparison shows that the presence of oxygen vacancies on $\text{TiO}_2(110)$ drastically alters the adsorption and surface diffusion of single Au atoms, and in turn the growth and structure of Au particles. On the reduced surface, the delocalization of electrons from oxygen vacancies provides a low-energy diffusion channel for Au adatoms along a $\text{Ti}(5c)$ row, while there is no preferential direction in Au diffusion on the stoichiometric surface. The small Au particles bind preferably to the vacancy site, with a sizable adsorption energy that oscillates with the no. of constituent atoms by virtue of spin pairing. Based on the comparison of supported and gas-phase Au particles, the authors also discuss the effect of the particle-substrate interaction on the structure of small Au particles grown on $\text{TiO}_2(110)$.

3.3 Controlled Growth of Sonochemically Synthesized Gold Seed Particles in Aqueous Solutions Containing Surfactants

Au seed particles stabilized by citric acid were prepared by the sonochem. reduction of Au(III) ions in aqueous solutions K Okitsu, B Teo, M Ashokkumar, F Grieser, from the Graduate School of Engineering, Osaka Prefecture University, Osaka, Japan, *Australian Journal of Chemistry* 2005, **58(9)**, 667. These seed particles were grown by the reduction of adsorbed Au(III) ions by ascorbic acid in aqueous solutions containing cationic surfactants, dodecyltrimethylammonium bromide (C12TAB), hexadecyltrimethylammonium bromide (C16TAB), and didodecyltrimethylammonium bromide (DDDAB). The rate of reduction of Au(III) ions during the seed-growth process was found to be strongly dependent upon the type and concentration of the cationic surfactants. The presence of Ag^+ in the growth solution containing DDDAB affected the size distribution of the gold particles.

4 Electrochemistry

4.1 Gold Nanoparticles Dispersed Polyaniline Grafted Multiwall Carbon Nanotubes as Newer Electrocatalysts: Preparation and Performances for Methanol Oxidation

New electrocatalysts were prepared by dispersing Au nanoparticles onto polyaniline (PANI)-grafted multi-wall C nanotube (MWNT-g-PANI) matrix by a 2-step electrochem. process. P Santhosh, A Gopalan, K Lee, from the Advanced Analytical Science and Nanomaterials Laboratory, Department of Chemistry Education, Kyungpook National University, Taegu, S. Korea, *Journal of Catalysis* 2006, **238(1)**, 177. In the 1st step, PANI chains are grafted onto amine-functionalized MWNT (MWNT- NH_2) by electro-polymg. a mixture of aniline and MWNT- NH_2 (dispersed in cetyltrimethyl

NH_4Br) using cyclic voltammetry. In the 2nd step, Au nanoparticles are dispersed into the film of MWNT-g-PANI by electrochem. reduction of HAuCl_4 . MWNT-g-PANI-modified electrodes with varying amts. of Au nanoparticles were prepared. Films of MWNT-g-PANI-Au were analyzed by field emission TEM (FETEM). The FETEM images indicate that Au particles of 8-10 nm are uniformly distributed in the MWNT-g-PANI. XRD provide support for the existence of Au nanoparticles. The electrocatalytic properties of the MWNT-g-PANI-Au electrode toward oxidation of MeOH and adsorbed CO (COads) were studied by chronoamperometry and COads stripping voltammetry and compared with the properties of MWNT-Au and pristine Au electrodes. MWNT-g-PANI-Au catalysts exhibit good electrocatalytic activity toward the oxidation of MeOH and COads. Oxidation of MeOH occurs at a much lower oxidation potential (780 mV) at the MWNT-g-PANI-Au electrode with high current densities compared with the MWNT-Au electrode (890 mV) and pristine Au electrode (930 mV), due to the dispersion of Au nanoparticles into the 3-dimensional network of MWNT-g-PANI. The results suggest that the MWNT-g-PANI-Au electrode has better oxidation kinetics for the oxidation of COads to CO_2 than the MWNT-Au and pristine Au electrodes. The MWNT-g-PANI-Au catalyst can be used in direct MeOH fuel cells.

4.2 Electrochemical Oxidation of 4-Chloroguaiacol on Gold or Lead Oxide Electrodes

The electrochem. behavior of 4-chloroguaiacol (4-CG) on pre-treated gold electrodes was investigated by cyclic voltammetry. Y Samet, R Abdelhedi, A Savall from the Laboratoire de Radio-analyses et d'Environnement, Ecole Nationale d'Ingenieurs de Sfax, BPW, Sfax, 3038, Tunisia, *Journal de la Societe Chimique de Tunisie* 2002, **4(12)**, 1615. Electrolytic solutions are water-acetone mixts. with 0 - 40 vol % acetone and containing 0.5 mol dm^{-3} of sulfuric acid. The cyclic voltammogram shows one irreversible anodic peak and a pre-peak. The effect of experimental conditions on the ratio of these two peaks was examined. The proposed mechanism is based on the hypothesis of a two-electron discharge leading to three phenoxonium cation mesomers, which hydrolysis would lead to 4-chlorocatechol, methoxyhydroquinone and 5-chloro-3-methoxycatechol. The process of electrode passivation during 4-CG electrooxidation at the gold electrode was studied with respect to 4-CG concentration and for different conditions of the electrode pre-treatment. Preliminary study shows that 4-CG is quant. oxidized by electrolysis at PbO_2 anode in sulfuric acid aqueous solutions (pH = 2). Maleic, fumaric, formic and oxalic acids are among the formed products.

4.3 Study on Growth of Conducting Cotapc on the Gold Electrode

The electropolymn. of Co tetraaminophthalocyanine on Au electrode was studied by cyclic voltammetry and electrochem. quartz crystal microbalance (EQCM). X Zhang,

C Ren, M Ying, from the Zhejiang Wanli University, Zhejiang, Peop. Rep. China, *Chuangan Jishu Xuebao* 2004, **17(2)**, 306. The effects of various parameters (such as solvents, electrolytes, scan rates, the CoTAPc concentration, etc.) on the polymer growth were also studied. The redox characterization and the stability of the conducting film on repeat charging and discharging were checked in aqueous and nonaqueous solutions. The ion transportation played an important role in these processes.

4.4 Formation of One-Dimensional Crooked Gold Nanocrystals by Electrochemical Technique with Surfactant Solution

This study demonstrates the synthesis of 1-dimensional (1D) crooked Au (Au) nanocrystals by an electrochem. method with surfactant. For example, the primary surfactant may be cetyltrimethylammonium bromide (CTAB), and the auxiliary surfactant may be tetradodecylammonium bromide (TTAB) with isoPrOH (IPA) solvent. C Huang, Y Wang, P Chiu, J Lin, from the Department of Applied Physics, National University of Kaohsiung, Kaohsiung, Taiwan, *Chemistry Letters* 2006, **35(1)**, 30. The formation of crooked Au nanocrystals was induced by aggregation of many small Au nuclei between the several large Au nanoparticles during growth, causing the small Au nuclei to link to the large Au nanoparticles forming crooked Au nanocrystals.

4.5 Gold Nanoparticle-Assisted Electroreduction of Oxygen

The electrocatalytic effect of nano-sized Au particles towards reduction of O was studied in neutral aqueous media. C Raj, A Abdelrahman, T Ohsaka, from the Department of Chemistry, Indian Institute of Technology, Kharagpur, India, *Electrochemistry Communications* 2005, **7(9)**, 888. The self-assemblies of -NH₂ terminated short chain disulfide, cystamine (CYST) and arom. dithiol, 1,4-benzenedimethanethiol (BDMT) were used for anchoring nanostructured citrate-stabilized Au particles. The cyclic voltammetric peak for the reduction of O at cystamine monolayer-modified Au electrode (CYST-Au) is rather broad and it appears at ≈ -0.5 V vs. Ag/AgCl, which is 250 mV more neg. than that at the bare Au electrode. The BDMT monolayer-modified Au electrode (BDMT-Au) does not show any characteristic peak for the reduction of O, as the monolayer completely blocks the permeation of O to the electrode surface. Reduction of O at less neg. potential was observed when Au nanoparticles were anchored on these thiol monolayer-modified electrodes. The Au nanoparticle on the electrode surface efficiently catalyzes the reduction of O to H₂O₂. Compared to the bare polycryst. Au electrode, a significant increase in the cathodic peak current and a 130-mV pos. shift in the cathodic peak potential were observed at the Au nanoparticle-anchored electrodes.

5 Electronics and Sensors

5.1 Functionalized Gold Nanoparticles as Phosphorescent Nanomaterials and Sensors

Ligand-capped Au nanoparticles were synthesized by capping monothiol derivs. of 2,2'-dipyridyl onto the surface of Au nanoparticles (Au-BT). The av. size of the metal core is ≈ 4 nm, with a shell of ≈ 340 bipyridine ligands around the Au nanoparticle. B Ipe, Y Itty, T Karuvath, G Kakkudiyil from the Photosciences and Photonics, Regional Research Laboratory (CSIR), Trivandrum, India, *Journal of the American Chemical Society* 2006, **128(6)**, 1907. The high local concentration of the chelating ligands (≈ 5 M) around the Au nanoparticle makes these particles excellent ion sponges, and their complexation with EuIII/TbIII ions yields phosphorescent nanomaterials. Absorption spectral studies confirm a 1:3 complexation between EuIII/TbIII ions and bipyridines, functionalized on the surface of Au nanoparticles. The red-emitting Au-BT:EuIII complex exhibits a long lifetime of 0.36 ms with 6 line-like emission peaks, whereas the green-emitting Au-BT:TbIII complex exhibits a lifetime of 0.7 ms with 4 line-like emission peaks. These phosphorescent nanomaterials, designed by linking BT:EuIII complexes to Au nanoparticles, were further used as sensors for metal cations. A dramatic decrease in the luminescence was observed upon addition of alk. earth metal ions (Ca²⁺, Mg²⁺) and transition metal ions (Cu²⁺, Zn²⁺, Ni²⁺), resulting from an isomorphous substitution of EuIII ions, whereas the luminescence intensity was not influenced by the addition of Na⁺ and K⁺ ions. Direct interaction of bipyridine-capped Au nanoparticles with Cu²⁺ ions brings the nanohybrid systems closer, giving 3-dimensional superstructures. Strong interparticle plasmon interactions were observed in these closely spaced Au nanoparticles.

5.2 Characterisation of Intermetallic Growth in Copper and Gold Ball Bonds on Aluminium Metallization

While the characterization of intermetallic coverage and intermetallic phase (IP) growth in Au ball bonding on Al is quite well understood, there is relatively little literature concerning the morphol. and growth of IP's between Cu balls bonded on Al pad metalization. F Wulff, C Breach, D Stephan, K Saraswati from the Materials & Applications Centre, Kulicke and Soffa (S.E.A.) Pte. Ltd, Singapore, Singapore, *Proceedings of Electronics Packaging Technology Conference, 6th, Singapore, Singapore, Dec. 8-10, 2004* 348. The difference between Cu-Al IP growth compared with the well known Au-Al IP's was studied mainly of larger wire diameter (35-50 μ m) in the early 1980's. Cu wire ball bonding was established for many years mainly for high power devices at wire diameters ≥ 38 μ m and fine wire for discrete device applications. However, there is now interest in fine pitch Cu wire ball bonding at smaller wire diameters of 25 μ m and smaller for high pin count applications, driven mainly by cost reduction. Development and optimization of robust Cu wire bonding

processes for such applications requires an assessment of intermetallic coverage and Cu-Al intermetallic growth after isothermal aging. This paper describes the problems associated with coverage detection, some characteristics of Cu-Al and Au-Al intermetallic compounds and characterizes the difference in the IP growth between Au-Al and Cu-Al. The relative merits of Au and Cu ball bonding are also briefly discussed.

5.3 Pulsed Laser Deposited Platinum and Gold Nanoparticles as Catalysts for Enhancing the CO Sensitivity of Nanostructured SnO₂ Sensors

The authors, R Dolbec M El Khakani from the Matériaux et Télécommunications, INRS- Energie, Varennes, QC, Can. *Sensor Letters* 2005, **3(3)**, 216, report on the influence of Pt and Au catalyst nanoparticles on the sensitivity towards CO of nanostructured SnO₂-based sensors. The Pt and Au nanoparticles presenting various nanostructural characteristics were deposited on the top of the SnO₂ sensing films by means of pulsed laser deposition (PLD). It is shown, for the first time, that Au nanoparticles can be as efficient as Pt nanoparticles for enhancing the sensing performance towards CO. While the catalytic activity of Pt nanoparticles is shown to present a sharp size effect (with a max. peaking around 2 nm), the Au nanoparticles are found to exhibit a rather high reactivity over a wider range of particles size ranging from ≈9 to 30 nm.

6 Medical and Dental

6.1 Stability of Gold Nanoparticle-Bound DNA Toward Biological, Physical, and Chemical Agents

Positive charged trimethylammonium-modified mixed monolayer protected clusters (MMPCs) interact with DNA by complementary electrostatic binding, serving as efficient DNA delivery systems. G Han, C Martin, V Rotello from the Department of Chemistry, University of Massachusetts, Amherst, MA, USA, *Chemical Biology & Drug Design* 2006, **67(1)**, 78. The stability of gold nanoparticle-bound DNA toward biol., phys., and chem. agents is investigated. The MMPC-bound DNA is efficiently protected from DNase I digestion and experiences nicking/cleavage-induced morphol. changes with higher concns. of DNase I. Significant protection of MMPC-bound DNA was also observed in a phys. sonication assay. However, the MMPC-bound DNA was found to show enhanced cleavage upon exposure to chem. induced radicals. The latter may indicate that bound DNA is bent and wrapped on the surface of the cationic MMPC.

6.2 3D Crosslinkers Based on Gold Nanocrystals for Collagen Drug Delivery Materials

The collagen matrix is one of the most promising biomaterials for both targeted drug delivery systems, and

scaffolding and mech. parts fabrication. K Slowinska, L Castaneda, S Pluskat, S Yadav, from the Department of Chemistry and Biochemistry, California State University, Long Beach, CA, USA, *PMSE Preprints* 2006, **94**, 346. The authors present novel type of a crosslinking agent, which can produce unique collagen matrix arrangement and thus improves properties of the matrix. The crosslinking agent is based on a monolayer protected gold nanocrystal. The 3-dimensional structure of an Au nanocrystal is capable of forming the multiple crosslinks from a common center. The agent is synthesized in a 2 step synthesis to express multiple aldehyde groups at the surface of an Au nanocrystal. The no. of the aldehyde groups on Au surface can be controlled. The collagen matrix modified with this novel crosslinking agent is studied in terms of its structure with transmission electron microscope. The thermal stability is examined with differential scanning calorimetry. To assess the biocompatibility of the matrix, cytotoxicity assays are conducted.

6.3 Assessing contamination paths of the German Adult Population with Gold and Platinum. The German environmental survey 1998 (Geres III)

Background: Even though increased environmental platinum levels were found since the introduction of automobile catalytic converters, little is known about the pathways of corporal uptake and the bioavailability of platinum in the general adult population. J Benemann, N Lehmann, K Broman; A Marr, M Seiwert; C Schulz, K Joeckel, from the Institute for Medical Informatics, Biometry and Epidemiology, Medical Faculty, University of Duisburg-Essen, Essen, Germany, *International Journal of Hygiene and Environmental Health* 2005, **208(6)**, 499. The aim of this study is to identify and quantify the main exposure pathways of gold and platinum in the general adult population. Methods: The German Environmental Survey 1998 (GerES III) collected population-based data on the corporal gold and platinum burden from a large sample of 1080 persons, 18-69 years of age. Urinary metal concentration was analyzed by SF-ICP-MS. Exposure data were assessed by standardized questionnaires. Data were log transformed and analyzed using multiple linear regression analysis with respect to exposure variables. Results: The R² of the linear regression model of urinary gold and platinum (ng/l) burden is 0.349 and 0.235, resp. In both models, the no. of teeth with noble metal dental alloy restorations (NMDAR) is the most important exposure pathway. One vs. no tooth with NMDAR is associated with an increase of 23.7% in urinary gold and 35.6% in platinum concentration. Chewing gum intensifies the release of gold and platinum from NMDAR: every addnl. day per wk when gum is chewed is associated with an increased gold (5.6%) and platinum (6.9%) burden. Furthermore, elevated urinary gold and platinum concns. were found for higher creatinine concns., more frequent coffee consumption and for people from the upper social class. Gold burden is also increased in

people with arthritis. Platinum burden is also increased in people living in western or northern Germany. Traffic-related variables had no significant effect on platinum burden.

6.4 Therapeutic Possibilities of Plasmonically Heated Gold Nanoparticles

A review. Nanoparticles of gold, which are in the size range 10-100 nm, undergo a plasmon resonance with light. D Pissuwan, S Valenzuela, M Cortie from the Institute for Nanoscale Technology, University of Technology Sydney, Broadway, Australia, *Trends in Biotechnology* 2006, **24(2)**, 62. This is a process whereby the electrons of the gold resonate in response to incoming radiation causing them to both absorb and scatter light. This effect can be harnessed to either destroy tissue by local heating or release payload mols. of therapeutic importance. Gold nanoparticles can also be conjugated to biol. active moieties, providing possibilities for targeting to particular tissues. Here, the authors review the progress made in the exploitation of the plasmon resonance of gold nanoparticles in photo-thermal therapeutic medicine.

6.5 Colloidal Gold Nanoparticles: a Versatile Platform for Developing Tumor Targeted Cancer Therapies

Colloidal gold nanoparticles represent a versatile biomedical platform. The authors' efforts have focused on the development of these nanoparticles into, a platform technology for developing tumor targeted drug delivery vectors. G Paciotti, L Myer, D Kingston, T Ganesh, L Tamarkin, from the CytImmune Sciences, Inc., Rockville, MD, 20850, USA SO NSTI Nanotech 2005, NSTI *Nanotechnology Conference and Trade Show, Anaheim, CA, United States, May 8-12, 2005*, **1**, 7. In the current communication, the authors describe the development of 2 colloidal gold nanoparticle drugs. The first drug, Aurimmune-T, is a multivalent drug assembled on 25 nm colloidal gold nanoparticles and designed to sequester TNF in solid tumors. While developing Aurimmune-T the authors recognized that TNF not only serves as the therapeutic responsible for anti-tumor efficacy but also a tumor targeting ligand. Support for this hypothesis is presented in the description of the second nanoparticle drug, AuriTax, a colloidal gold-based TNF targeted paclitaxel drug.

6.6 Gold Nanoparticles as Carriers for Efficient Transmucosal Insulin Delivery

Nanomaterials have gained tremendous importance in biol. and medicine because they can be used as carriers for delivering small mols. such as drugs, proteins, and genes. H Joshi, D Bhumkar, K Joshi, V Pokharkar, M Sastry from the Nanoscience Group, Materials Chemistry Division, National Chemical Laboratory, Pune, India, *Langmuir* 2006, **22(1)**, 300. The authors report herein the binding of the hormone insulin to gold nanoparticles and its application in transmucosal delivery for the therapeutic treatment of diabetes mellitus. Insulin was loaded onto bare gold

nanoparticles and aspartic acid-capped gold nanoparticles and delivered in diabetic Wistar rats by both oral and intranasal (transmucosal) routes. The authors principle observations are that there is a significant reduction of blood glucose levels (postprandial hyperglycemia) when insulin is delivered using gold nanoparticles as carriers by the transmucosal route in diabetic rats. Furthermore, control of postprandial hyperglycemia by the intranasal delivery protocol is comparable to that achieved using the standard s.c. administration used for type I diabetes mellitus, thus showing considerable promise for further development.

7 Metallurgy, Materials and Coatings

7.1 Influence of the Nanoscale Structure of Gold Thin Films Upon Peroxidase-Induced Chemiluminescence

Au films with different nanoscaled roughness were elaborated by a pulsed-laser deposition technique to evaluate their ability to form biochip substrates. G Lu, B Cheng, H Shen, Z Chen, G Yang, C Marquette, L Blum, O Tillement, S Roux, G Ledoux, A Descamps, P Perriat from the Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, Peop. Rep. China, *Applied Physics Letters* 2006, **88(2)**, 023903/1. The crystal structure, microstructure, and optical absorption were studied by x-ray diffraction, at. force microscopy, and UV-visible absorption spectrum. Controlling the temperature of the substrate during the deposition process allows one to obtain samples with different roughness and grain sizes. The temperature can then be adjusted to elaborate thin films, which have either the optical behavior of bulk metal or that of individual clusters. This optical behavior strongly influences the chemiluminescence at 425 nm of luminol brought to the vicinity of peroxidase supported by biomols. phys- or chemisorbed on the films. The signal intensity increases of almost 1 order of magnitude when the film presents a significant surface resonance plasmon.

7.2 Copper(I), Silver(I) and Gold(I) Carboxylate Complexes as Precursors in Chemical Vapor Deposition of Thin Metallic Films

A review. Volatile precursors of Cu, Ag and Au for CVD of metallic layers are described. There is considerable research interest in CVD because it provides advantages such as selective deposition, control of film d. and thickness, etc. over other phys. deposition techniques. Cu, Ag, and Au compounds used as CVD precursors can be divided into three types: inorg., coordination and organometallic. A Grodzicki, I Lakomska, P Piszczek, I Szymanska, E Szlyk from the Faculty of Chemistry, Nicolaus Copernicus University, Torun, 87-100, Pol. *SO Coordination Chemistry Reviews* 2005, **249(21-22)**, 2232. Organometallic compounds are often used as CVD precursors, however they usually are air and moisture sensitive, also they were characterized by low

thermal stability. Inorg. compounds, which are usually air stable and easy to obtain, exhibit low volatility and require lower deposition pressures and higher vaporization temperatures. Therefore, the authors present here results on: (a) synthesis and characterization of inorg. and coordination precursors, (b) applications in CVD of metallic layers, (c) studies on the impact of CVD parameters on the quality of nanolayers, (d) gas phase compn. and reactions during fabrication of the metallic films. Carboxylates of Cu(I), Ag(I) and Au(I) and their complexes with tertiary phosphines are described as a new class of CVD precursor. The mol. structures are discussed based on x-ray structural analysis and spectroscopic methods. ^1H , ^{13}C , ^{31}P , ^{19}F , ^{63}Cu NMR ^{31}P CP MAS NMR, along with variable temperature NMR and IR were used for characterization of new Cu(I), Ag(I) and Au(I) complexes $[\text{M}(\text{COOR})(\text{L})]$ where $\text{R} = \text{CH}_3, \text{CMe}_3, \text{C}_2\text{F}_5, \text{C}_2\text{H}_5, \text{Me}_3\text{SiCH}_2, \text{Pr}, \text{C}_3\text{F}_7, \text{Me}_3\text{SiC}_2\text{H}_4, \text{Bu}, \text{C}_6\text{F}_{13}, \text{C}_7\text{F}_{15}, \text{C}_8\text{F}_{17}, \text{C}_9\text{F}_{19}, \text{C}_6\text{F}_5, \text{C}_6\text{H}_2\text{Me}_3, \text{L} = \text{PR}'$ where $\text{R}' = \text{Me}, \text{Et}, \text{Ph}, \text{OMe}, \text{OEt}, \text{OPh}$, or $\text{L} = \text{diphosphines-dppm}, \text{dppe}$. The analyses of thermal decomposition and MS data were used for elucidation of the decomposition mechanisms, description of the transport in the gas phase and deposition processes. The mol. structures of the precursors are discussed in relation to the quality of the obtained metallic nanolayers.

7.3 Evaluation of gold and aluminum wire bond performance for high temperature (500°C) silicon carbide (SiC) power modules

This paper describes an investigation of aluminum and gold wire bonding processes for high temperature electronics. H Mustain, A Lostetter, W Brown from the Department of Electrical Engineering, University of Arkansas, USA, *Proceedings Electronic Components & Technology Conference 2005*, **55th(Vol. 2)**, 1623. Ultrasonic wire bonding of 8 and 15 mil aluminum wire and 3 mil gold wire on various metalized substrates was investigated. Aluminum wire bonds to nickel-plated aluminum nitride (AlN) and silicon nitride (SiN) substrates were thermally cycled between -55°C and 400°C , and gold wires bonded to gold-coated AlN and SiN substrates were thermally cycled between -55°C and 500°C . The thermal cycling was accomplished according to MIL-STD-883E criteria. An environmental scanning electron microscope (ESEM) was used to examine the wire/pad and pad/substrate interface areas before and after the thermal cycling. After thermal cycling, the samples were subjected to destructive pull testing at room temperature. The results of the testing revealed no significant degrdn. of the bonds after thermal cycling.

8 Nanotechnology

8.1 Reversible Binding of Gold Nanoparticles to Polymeric Solid Supports

Gold nanoparticles (NPs) are essential components in the design of various functional systems of nanometer

dimensions. O Abed, M Wanunu, A Vaskevich, R Arad-Yellin, A Shanzer, I Rubinstein, from the Departments of Materials and Interfaces and Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel, *Chemistry of Materials* 2006, **18(5)**, 1247. Their properties are detd. by their size and the chem. compn. of their capping layer. We have recently presented a scheme for controlled modification of Au NP capping layers by reversible binding to a polymeric solid support via boronic acid chem. Octanethiol-stabilized Au NPs were bound reversibly to a polymeric resin derivatized with boronic acid groups. Specially synthesized bifunctional linker mols. carrying a diol on one end and a thiol on the other were bound to the boronic moieties on the resin via the diol group, enabling attachment of Au NPs to the linker-loaded resin through the thiol moiety of the linkers. The resin-bound NPs could be released back to solution by cleaving the boronate ester between the resin and the linker, leaving one (or a few) linker mol.(s) on the NPs. The released NPs retained their properties (optical, soly.) and could be rebound to boronic resins through the linker mols. on their surface. This process of reversible NP binding to a polymeric solid support is studied here in detail. Several boronic-modified resins and linker mols. were prepared and investigated. The chem. conditions for cleavage of the boronate ester were found to be different for NP-free and NP-loaded resins, varying with the type of diol on the linker mols. Reversible NP binding to high-surface-area solid supports may be useful for preparative reactions on NPs, including controlled NP modification, design of synthetic schemes for modification of NPs under protected conditions, and prevention of NP-NP interactions during chem. manipulation.

8.2 Support Effects on the Nucleation, Growth, and Morphology of Gold Nano-Clusters

The nucleation, growth, and morphol. of gold (Au) clusters on an irreducible oxide (SiO_2), highly reduced TiOx ($x \approx 1$), and less reduced TiOx ($x \approx 2$) were studied by scanning tunneling microscopy (STM) with the goal of understanding the relation between the nucleation, growth, and morphol. of Au clusters and the reducibility of the oxide support. B Min, W Wallace, D Goodman, from the Department of Chemistry, Texas A&M University, College Station, TX, USA, *Surface Science* 2006, **600(2)**, L7. Au clusters show preferential nucleation and growth on a TiOx surface compared to a SiO_2 surface. Higher densities of Au clusters were found on highly reduced TiOx, suggesting that reduced Ti sites play a role as an active site for the nucleation and growth of Au clusters.

8.3 Synthesis of Gold-Silver Alloy Nanoparticle and its Light-Scattering Property

A gold-silver alloy nanoparticle was synthesized with trisodium citrate by one-step reduction method, and a series of alloy nanoparticles of different gold and silver mole ratios were obtained. H Yin, X He, H Liu, W Li, L Chen from the Department of Chemistry, Nankai University, Tianjin, 300071, Peop. Rep. China, *SO Fenxi Huaxue* (2005), **33(7)**, 939.

Various techniques, such as UV-visible spectrophotometry, synchronous light-scattering spectrophotometry, emission spectrophotometry, transmission electron microscopy, were used to characterize the nanoparticles. The diameter of alloy nanoparticle (gold and silver mole ratio 1:1) was 48.7 nm, it was global and compact. Compared with gold nanoparticle (518 nm) and silver nanoparticle (425 nm), it had a unique UV-vis absorption peak at 459 nm. Its max. light-scattering wavelength was 590 nm. There was a linear relationship between the max. light-scattering wavelength (λ_{\max}) and the molar fraction of silver (XAg) in alloy nanoparticles, $\lambda_{\max} = 619.5 - 153.4 X_{\text{Ag}}$, $r = -0.9927$. The relationship of intensity of scattered light (I_g) and the mole ratio of silver (XAg) was also linear, linear equation was $I_0 = 272.1 + 625.7 X_{\text{Ag}}$, and $r = 0.9957$. In the emission spectrum of alloy nanoparticles, multiple frequency and fractional frequency lights were obtained. It was shown that the gold-silver alloy nanoparticle had a nonlinear optic property.

8.4 Preparation and Characterization of Gold Nanoparticles and their Application in Biochemical Analysis

A review. Chem. and phys. preparation methods of Au nanoparticles are introduced. S Sun, Z Jiang from the Department of Resource and Environmental Science, Guangxi Normal University, Guangxi, Peop. Rep. China, *Gujinshu* 2005, **26(3)**, 55. The spectral and microscopic characterization techniques are presented.

8.5 Synthesis of Monodisperse Stable Gold Sols with the Use of High-Molecular and Low-Molecular Stabilizers

The methods of nanosized gold particles formation are developed using AuCl₄⁻ reduction with NaBH₄ in the presence of high-mol. (HM) and low-mol. (LM) stabilizers compatible with living organisms. V Lazarchik, O Vrublevskaya, T Vorobyova from the Research Institute of Physico-Chemical Problems, Belarusian State University, Minsk, Belarus, *Physics, Chemistry and Application of Nanostructures: Reviews and Short Notes to Nanomeeting 2005*, [International Conference], Minsk, Belarus, May 24-27, 2005, 390. The most stable sols with 2-3 nm particles and high monodispersivity are formed with HM stabilizers such as PVA, gelatin, PVP. Correlations were found between stability of sols and the χ -potential. The most stable sols have the χ -potential of 60-76 mV.

8.6 Synthesis and Stabilization of Gold Nanoparticles in Reverse Micelles of Aerosol OT and Triton X-100

Mechanisms of the formation and stabilization of Au nanoparticles in reverse micelles of micro-emulsions based on Triton X-100 (TX-100) and Aerosol OT (AOT) were studied. M Spirin, S Brichkin, V Razumov from the Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia, *Colloid Journal* 2005,

67(4), 485. The instability of AOT-based microemulsions is caused by the oxidative degrdn. of Au nanoparticles in micelle H₂O pools. Methods are proposed for the stabilization of these microemulsions. The mean size of Au nanoparticles synthesized in TX-100 reverse micelles in the presence of Na sulfite is markedly smaller than that of particles prepared in AOT reverse micelles. This is explained by the fact that Au clusters are formed in the micelle shell rather than in the H₂O pool. In the shell, the clusters are stabilized by oxyethylene groups of TX-100 mols.

8.7 Low-Temperature Metallic Alloying of Copper and Silver Nanoparticles with Gold Nanoparticles through Digestive Ripening

A simple alloying procedure is described in which noble metal alloy nanoparticles are produced in gram quantities via digestive ripening. A Smetana, K Klabunde, C Sorensen, A Ponce, B Mwale from the Departments of Chemistry and Physics, Kansas State University, Manhattan, KS, USA, *Journal of Physical Chemistry B* 2006, **110(5)**, 2155. This process involves mixing of sep. prepared colloids of Au and Ag or Cu particles and then heating in the presence of an alkanethiol (dodecane thiol) under reflux. The result after 1 h is alloy nanoparticles. Particles synthesized according to this procedure were characterized by UV-vis spectroscopy, EDX analysis, and high-resolution electron microscopy, the results of which confirm the formation of alloy particles. The particles 5.6 ± 0.5 nm diameter for Au-Ag and 4.8 ± 1.0 nm diameter for Cu-Au undergo facile self-assembly to form 3-dimensional superlattice ordering. During this digestive ripening process, the org. ligands display an extraordinary chem. in which atom transfer between atomically pure copper, silver, and gold nanoparticles yields monodisperse alloy nanoparticles.

8.8 Preparation of Gold Nanoparticles with Narrow Size Distributions and Well Defined Shapes

The tailoring of size and shape of gold nanoparticles with nanosecond laser pulses was studied. The technique is based on the size- and shape-dependent surface plasmon resonance frequencies of metal nanoparticles. F Hubenthal, C Hendrich, H Ouacha, D Blazquez; F Traeger from the Institut fuer Physik and Center for Interdisciplinary Nanostructure Science and Technology – CINSaT, Universitaet Kassel, Kassel, 34132, Germany, *International Journal of Modern Physics B: Condensed Matter Physics, Statistical Physics, Applied Physics* 2005, **19(15, 16 & 17, Pt. 1)**, 2604. In the authors' recent experiments gold nanoparticles were prepared by deposition of atoms on dielec. substrates followed by diffusion and nucleation. This usually results in ensembles of oblate nanoparticles with a broad size and shape distribution. Irradiating the gold particles during growth with nanosecond laser pulses makes it possible to produce nanoparticles with a predetd. axial ratio independent of size. For example, irradiating gold

nanoparticles with a photon energy of 1.65 eV during growth stabilizes an axial ratio of $a/b = 0.14$, a being the short axis and b the long axis of the ellipsoidal nanoparticles. Furthermore, post-growth irradiation permits tailoring the average size of the nanoparticles by laser-induced surface diffusion and evaporation of atoms. In principle, it is possible to eliminate all particles of undesired sizes by choosing the appropriate photon energies. Narrowing of the width of the surface plasmon resonance from initially 0.52 eV (half width at half maximum) to 0.2 eV is possible by a single laser frequency. Combining both methods, i.e. laser irradiation during and after growth, finally results in a narrow size and shape distribution of the particles.

8.9 Mechanisms Controlling Crystal Habits of Gold and Silver Colloids

Examples of Au and Ag anisotropic colloids, such as prisms and rods, have appeared in the literature for many years. C. Lofton, W. Sigmund, from the Mater. Sci. Eng. Dep., Univ. Florida, Gainesville, FL, USA, *Advanced Functional Materials* 2005, **15(7)**, 1197. In most cases, the morphologies of these thermodynamically unfavorable particles were explained by the particular reaction environment in which they were synthesized. The mechanisms used to explain the growth generally fall into two categories, one in which chemisorbed molecules regulate the growth of specific crystal faces kinetically, and the other where micelle-forming surfactants physically direct the shape of the particle. This paper raises questions about the growth of anisotropic metal colloids that the current mechanisms cannot adequately address, specifically, the formation of multiple shapes in a single homogeneous reaction and the appearance of similar structures in very different synthesis schemes. Probably any growth mechanism should primarily take into consideration nucleation and kinetics, and not only thermodynamic or physical considerations. The authors suggest an alternative mechanism where the presence and orientation of twin planes in these face-centered cubic metals direct the shape of the growing particles. This explanation follows that used for Ag halide crystals, and has the advantage of explaining particle growth in many synthesis methods. In this mechanism, twin planes generate reentrant grooves, favorable sites for the attachment of adatoms. Shape and structural data are presented for Au and Ag particles synthesized using several different techniques to support this new model. Triangular prisms probably contain a single twin plane which directs that growth of the initial seed in two dimensions, but limits the final size of the prism. Hexagonal platelets probably contain two parallel twin planes that allow the fast growing edges to regenerate one another, allowing large sizes and aspect ratios to form. Rods and wires have a 5-fold symmetry, which may only allow growth in one dimension. It is expected that a superior mechanistic understanding will permit shape-selective synthesis schemes to be developed.

8.10 Investigating the Effects of Some Capping Agents Upon Gold Nanocrystals Stability, Size and Surface Plasmon Resonance

Preparation of gold nanocrystals with different capping agents is reported. 1-Dodecanethiol, dodecylamine, tri-n-octylphosphine (TOP), and tri-n-octylphosphine oxide (TOPO) were used as capping agents and the gold nanocrystals stability, size, and surface plasmon resonance (SPR) were investigated. H. Asadollahi, M. Shirvani, M. Nooshirvani, R. Noorafkan, A. Nabipoor from the Department of Semiconductor, Laser Research Center, Atomic Energy Organization of Iran, Tehran, Iran, *Journal of Sciences, Islamic Republic of Iran* 2005, **16(4)**, 351

8.11 Synthesis and Size Regulation of Gold Nanoparticles by Controlled Thermolysis of Ammonium Gold(I) Thiolate in the Absence or Presence of Amines

Controlled thermolysis of a gold(I) complex with no use of solvent was investigated as a novel synthetic method for the preparation of gold nanoparticles. M. Nakamoto, Y. Kashiwagi, M. Yamamoto from the Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka, Japan, *Inorganica Chimica Acta* 2005, **358(14)**, 4229. Precursors, ammonium gold(I) thiolate $[\text{RNMe}_3][\text{Au}(\text{SC}_{12}\text{H}_{25})_2]$ ($\text{R} = \text{C}_8\text{H}_{17}$, $\text{C}_{12}\text{H}_{25}$, and $\text{C}_{14}\text{H}_{29}$) and $[(\text{C}_{18}\text{H}_{37})_2\text{NMe}_2][\text{Au}(\text{SC}_{12}\text{H}_{25})_2]$, were prepared and the thermolysis of those precursors was conducted at 180°C for 5 h under an N_2 atmosphere, providing spherical gold nanoparticles stabilized by alkyl groups derived from the precursor, gold(I) complex. In spite of the thermolysis process, the average diameter of gold nanoparticles deriving from $[\text{C}_{12}\text{H}_{25}\text{NMe}_3][\text{Au}(\text{SC}_{12}\text{H}_{25})_2]$ was 22 nm, but the size distribution ranges from 11 to 76 nm. For the purpose of the size regulation of the gold nanoparticles, equimolar primary, secondary, or tertiary alkylamines are added as stabilizer and mild reductant to the controlled thermolysis of gold(I) complex at lower temperature of 165°C for 5 h. The gold nanoparticles obtained by the controlled thermolysis in the presence of stearylamine are well regulated and almost monodispersed nanoparticles with average diameter of 7.5 nm. Such size regulation resulted from the inhibition of the growth of gold nuclei by transforming reaction from ammonium and thiolate moieties to neutral tertiary amine, thiol and sulfide, which function as stabilizer for gold nanoparticles.

8.12 Gold Nanoparticles Prepared using Polyethylenimine adsorbed onto Montmorillonite

Polyethylenimine-modified montmorillonite (N-MMT) was used to prepare Au nanoparticles, where the montmorillonite (MMT) acted as a solid support to retain the conformation of polyethylenimine (PEI), and the amino groups of PEI were used simultaneously to both complex and reduce the Au ions. C. Chen, P. Kuo from the Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan,

Journal of Colloid and Interface Science 2006, **293(1)**, 101. From the results of x-ray diffraction, the reduction of Au ions occurs primarily on the MMT surface. In the presence of MMT, the formation of a flattened configuration on the clay instead of stretched-out ethylenimine segments of PEI gave smaller Au particles. With a higher acidification ratio, the recharging of the MMT surface with pos. NH_4^+ ionic sites of PEI is likely to prevent the flocculation of clay and thus facilitate the reduction of Au. The rate of Au reduction with N-MMT is faster at low pH values, this being in contrast to the usual trend observed for the reduction of Au ions. The use of PEI adsorbed onto MMT is able to act simultaneously as both a protective template and as a reducing agent, thereby greatly simplifying the process for preparing Au nanoparticles.

9 Refining

9.1 Choosing the Concentration Technology for Sulfide Gold-Bearing Ores of Nonferrous Metals

The basic technology schemes of accompanying gold production from sulfide complex ores of Ural region are observed V Bocharov, V Ignatkina, from the MISiS (Tekhnol. Univ.), Moscow, Russia, *Gornyi Zhurnal* 2005, **(1)**, 46. It is mentioned, that the most high degree of gold extraction can be achieved using combined gravitation-flotation schemes of ore concentration, in combination with hydrometallurgical processing. The dependence of gold and copper extraction into combined concentration as a function of the amount of pyrite sulfur is discussed.

9.2 Commercial Application of and Improvement on Gold Extraction by Carbon Fiber Cathode Electrolysis Process

The technology of extraction of Au by using C fibers as cathode was used in plant production for years. B Yang, from the Yuerya Gold Mine, Kuancheng, Peop. Rep. China, *Youse Jinshu, Yelian Bufen* 2003, **(4)**, 35. The application, improvement process, characteristics, and prospect of this technology were discussed in detail based on the plant practice.

9.3 Structural Effect of Monoamide Compounds on the Extraction of Gold

The solvent extraction of Au(III) in a HCl solution with N,N-di-n-octylacetamide (DOAA), N,N-di-n-octylbutyramide (DOBA) and N,N-di-n-octylhexanamide (DOHA) has been studied. H Narita, M Tanaka, K Morisaku, T Yaita, S Suzuki, Y Isomae, T Abe, from the Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki, Japan, *Solvent Extraction Research and Development, Japan* 2005, **12**, 123. The dependence of the distribution ratios for Au(III) on the concentration of HCl, hydrogen ions and extractant are similar for the three

systems. The distribution ratios for Au(III) increase with increasing HCl concentration. The slopes obtained from the dependence of the hydrogen ion concentration 0.5-3.0 M and extractant concentration 0.01-0.2 M were ≈ 1 and ≈ 2 , resp. The extd. complexes formed in all the systems are similar under these conditions. The magnitude of the distribution ratios falls in the order DOAA \gg DOHA \approx DOBA. This order is not consistent with the hydrophobicity order of the extd. complex and charge d. of the amide oxygen atom. Therefore, the steric effect of the alkyl chain attached to the amide carbonyl carbon atom seems to be the detg. factor in these extraction systems. The shortest side chain of DOAA could not hinder the coordination of the amide oxygen atom with Au(III).

9.4 Roasting and Cyanide Leaching Process Study on As, Sb and C Content Refractory Gold Concentrate

The roasting and cyanide leaching process for extg. Au from Zhenyuan As-bearing and Sb-bearing carbonous concentration was presented. C Yuan, Y Wang, from the Beijing General Research Institute of Mining + Metallurgy, Beijing, Peop. Rep. China, *Youse Jinshu, Yelian Bufen* 2003, **(3)**, 32. The Au extraction recovery from As-bearing and Sb-bearing carbonous concentration by the cyanide leaching process is $<10\%$, and it can be raised to 73.2% by roasting-cyanidization process. The Au recovery can be improved further to 90.4% by Sb removal with Na_2S , followed by roasting and cyanide leaching process. The Sb concs. can be sold as a byproduct.

9.5 A Method for Leaching or Dissolving Gold from Ores or Precious Metal Scrap

The hydrometallurgical leaching of native gold from gold-bearing ores or the dissolution of gold metal during the recycling of electronic and precious metal scrap is performed every day using hazardous chems. such as sodium cyanide or aqua regia. N Geoffroy, F Cardarelli, from the Department of Mining, Metals, and Materials Engineering, McGill University, Montreal, Canada, *JOM* 2005, **57(8)**, 47. These chems. represent health and safety risks for workers and a serious threat for the environment. However, even if several other reagents are known to dissolve gold at the lab. scale, none of these are used industrially. Hot mixts. of hydrochloric acid with strong oxidizing compounds are known to generate in-situ nascent chlorine which is capable of dissolving gold efficiently. In this study, the authors investigated the capability of a hot mixture of hydrochloric acid and ground manganese (IV) oxide to dissolve gold metal either under atm. or pressurized conditions. The best result was obtained under a pressure of 639 kPa at 90°C with a dissolution rate of 0.250 g-cm⁻²h⁻² and it was compared to that reported in the literature for other industrial reagents.

9.6 Coal-Oil Assisted Flotation for the Gold Recovery

A new approach coal-oil slurry assisted gold flotation was used to recover gold particles. S Sen, A Seyrankaya, Y Cilingir, from the Mining Engineering Department, Division of Mineral Processing, Dokuz Eylul University, Bornova, Izmir, Turkey, *Minerals Engineering* 2005, **18(11)**, 1086. The coal-oil-gold agglomeration process considers the preferential wetting of coal and gold particles. The method takes advantage of the greater hydrophobicity and oleophilicity of coal and gold compared to that of most gangue materials. Unlike the previous studies on coal-oil-gold agglomeration, this method uses a small amount of coal and agglomerating agents. Some experiments were conducted on synthetic gold ore samples to reveal the reaction of the coal-oil slurry assisted gold flotation process against the size and no. of gold particles in the feed. There is no significant difference in process gold recoveries for feeds assaying different Au particles. Although there was a slight decrease in coarse gold particles, the process seems to be effective for the recovery of gold grains as coarse as 300 μm . The decrease in the finest size $<53 \mu\text{m}$ is considered to be the decrease in collision efficiency between the agglomerates and finest gold particles. The effect of changing the coal quantity for const. ore and oil amts. was also investigated. The process gives similar results for both artificial and natural ore samples. The best results have been obtained by using a 30:1 coal-oil ratio.

9.7 Biotreatment of Flotation and Gravitational Concentrates of Gold-Bearing Pyrite-Arsenopyrite Ores

Bioleaching of flotation and gravitational concs. of pyrite-arsenopyrite ores were studying on lab. and pilot facilities. 95% Arsenopyrite was oxidized during 90 h in continuous process of bioleaching of flotation concentration containing 5.1% As. P Pustoshilov, A Belyi, Y Gurevich, J Kitapbaeva, from the Inst. Biofiz., RAN, Russia, *Tsvetnye Metally (Moscow, Russian Federation)* 2005, **(3)**, 20. Biooxidation of arsenopyrite in gravitational concentration (14.9% As) was in 130-140 h. Fluctuations of ratio of oxidized As in solid to solubilized As were observed in lab. and pilot experiments. Concentration of As equal 8-12 g/l did not decrease in the bioleaching rate. At the experimental-industrial process of bioleaching, opening of Au was 89-91%.

9.8 Gold Leaching by Thiosulphate Solutions: A Critical Review on Copper(II)-Thiosulfate-Oxygen Interactions

A review. The reported reaction rates for the reduction of copper(II) by thiosulfate and oxidation of gold by copper(II) are reviewed, and the results are quantified. G Senanayake, from the A.J. Parker Cooperative Research Centre for Hydrometallurgy, Department of Mineral Science and Extractive Metallurgy, Murdoch University, Perth, 6150, Australia, *Minerals Engineering* 2005, **18(10)**, 995. The production of sulfate and trithionate during oxygenation can

be rationalized according to three stoichiometric relationships corresponding to the [oxygen]/[thiosulfate] consumption ratios of 0.67/1, 1/1 and 1/2. These three ratios represent the formation of 100% trithionate, 1:1 mixture of trithionate and sulfate, and 100% sulfate, resp. The detrimental effect of excess aeration/oxygenation on gold extraction can be related to the formation of disulfite ion and its assocn. with copper(II)-ammonia complex ions, and subsequent disproportionation. However, controlled aeration minimizes copper(II) reduction and maintains a higher rate of gold oxidation. It also lowers thiosulfate oxidation by favoring

9.9 Recovery of Gold Concentrate from Copper Ore Elution Residue Method

Au concentration is recovered from an elution residue containing S and Au and produced by wet refining of Cu pure ore. N Nagase, M Imamura, K Ando, from the Sumitomo Metal Mining Co., Ltd., Japan, Patent number JP2006057133, A2,2/3/2006. The elution residue is supplied to centrifugal sep'n, while being heated to the degree sufficient to melt the simple S, and the Au concentration and simple S are obtained. The heating is conducted in a nonoxidizing atm. at 110-150°C. Separation of Au concentration and simple S can be conducted with high Au recovery ratio.

9.10 Method for Recovering Gold, Silver and Copper from Slags

The invention relates to a process for recovering gold, silver and copper from slags resulting from the melting process of the dore alloy obtained by the electrolysis of gold-silver containing cyanhydric eluates. R Radulescu, P Georgescu, G Filip, N Tomus, C Muntean, B Ioan from the Institutul de Cercetari si Proiectari Pentru Metale Rare si Radioactive, Romania, Patent No. RO 120079, B1, 30/08/2005. The silver and the copper are solubilized, by leaching, in nitric acid. The silver from the solution is selectively pptd. as silver chloride and then it is reduced by sugar in alk. environment to metallic silver. The copper from the nitrate solution is recovered by concentration on iron swarf. The gold is leached by wet chlorination, purified by ion exchange and reduced by means of hydroquinone to pure gold.

9.11 Increasing gold demand. New industrial applications

A review. The industrial demand for Au has remained relatively static over the past decade and is a small proportion of total Au demand. C Corti, R Holliday, from the Coregold Technology Consultancy & World Gold Council UK, *Transactions of the Institutions of Mining and Metallurgy, Section B: Applied Earth Science* 2005, **114(2)**, B115. Current applications are briefly reviewed and the prospects for future growth discussed. Substantial growth in demand will come only from the development of new applications for gold. The prospects for new applications based on emerging science and technology are reviewed with particular emphasis on gold catalysis, an exciting new sector for which com.

prospects appear promising. The work of the World Gold Council and others to encourage exploitation of the technology is highlighted in the context of future demand prospects.

9.12 Method and Device for Recovering Gold from Aqueous Solution Containing Cyanide

The method includes separating aqueous solution containing Au and cyanide using reverse osmosis membrane into a concentrated solution and a permeation liquid, and electrolyzing the concentrated solution to recover Au. T Tahara, H Kokubo, H Abe, T Shimofusa, from the Asahi Pretec Corp., Japan, Patent number JP 2006037194, A2, 09/02/2006. Optionally, the permeation liquid is again separated using reverse osmosis membrane into a concentrated solution and a permeation liquid, and the concentrated solution is electrolyzed to recover Au. The permeation liquid is used as plating process water. The device is also claimed.

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

A review. 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. C Anderson, E Dahlgren, H Huang, P Miranda, D Stacey, M Jeffrey, I Chandra, from the The Center for Advanced Mineral and Metallurgical Processing, Montana Technology, Butte, MT, 59701, USA, *Treatment of Gold Ores, Proceedings of the International Symposium on the Treatment of Gold Ore, Calgary, AB, Canada*, Aug. 21-24, 2005, 145. 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 pregrabbing 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 concentration application, a chalcopyrite gold concentration application, a pregrabbing gold ore application, and a cyanide consuming gold ore application will be delineated in this paper.

9.14 Cleaner Gold, Diamonds and more

A review. The range of applications is broadening and the importance of gravity as a recovery method is growing. E Lewis-Gray, *Mining Magazine* 2005, **192(4)**, 22. The past 20 years have seen major changes in gravity sepn. after stagnation for much of the 20th century. More recently, changes in the gold sector have started to refocus from batch concentration to continuous gravity concentration. Newer continuous sepn. devices, such as the InLine Pressure

Jig (IPJ), Falcon C and Kelsey Jig, are changing flowsheets and testwork protocols. Continuous sepn. devices have also allowed sulfide and gold carrier recovery, which is likely to have far larger application than the traditional focus on the recovery of free gold. Continuous concentration also provides for the application of gravity devices in a pre-concentration step, which can substantially reduce both capital and operating costs of the treatment plant. There are new industry testwork protocols to support the search for continuous gravity device recovery. Grade recovery testwork programs (see table 1) are now frequently used instead of, or in conjunction with, the standard GRG test for batch centrifugal concentrator recovery. Results from testwork provide a continuum of outcome and indicate the optimum mass pull recovery point and its grade relation on the grade recovery curve for the particular application.

9.15 Mechanisms of Gold Recovery from Aqueous Solutions using a Novel Tannin Gel Adsorbent Synthesized From Natural Condensed Tannin

We report a novel recovery system for gold (Au), which is one of the precious metals contained in electronic scrap, utilizing tannin gel particles. T Ogata, Y Nakano, from the Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Technology, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan, *Water Research* 2005, **39(18)**, 4281. Tannin gel particles were prepared by a process of crosslinking of condensed tannin (wattle tannin), which is a ubiquitous and inexpensive natural material having many hydroxyl groups. The adsorption mechanism of gold onto tannin gel particles was elucidated: the adsorption of gold takes place through the reduction of trivalent gold ions to metallic gold on the surface of tannin gel particles, which is accompanied by the simultaneous oxidization of the hydroxyl groups of tannin gel. Addnl., the adsorption capacity of gold was found to be extremely high, 8000 mg-Au/g-dry gel. The outstanding characteristics of tannin gel particles for gold offers the possibility of efficient recovery of other precious metals.

9.16 A Comparative Analysis of Gold-Rich Plant Material using Various Analytical Methods

During 2003 a field demonstration of gold phytoextraction technology was conducted in Brazil. C Anderson, F Moreno, F Geurts, C Wreesmann, M Ghomshei, J Meech, from the Institute of Natural Resources, Massey University, Palmerston North, N.Z., *Microchemical Journal* 2005, **81(1)**, 81. As there is no com. available biogeochem. standard ref. material with an elevated concentration of gold, the trial biomass was analyzed for its gold content using five analysis methods, at five labs., to confirm the concentration of gold in the harvested plant material. Nitric and hydrochloric acid digest followed by ICP-OES solution analysis of a dore bead prepared through fire assay of vegetative material was considered the benchmark analysis method to which the other results were

compared. The gold concns. reported by the five labs. varied widely. Flame at. absorption analysis of a solution prepared through the digest of plant ash by aqua regia proved the most accurate analysis method relative to fire assay. Gold concns. reported by a New Zealand com. lab. using ICP-MS and a standard biol. materials digestion procedure were affected by the digestion method used. X-ray fluorescence results were affected by synthetic stds. that were prepared specifically for this study. Alternatively, matrix effects may not were fully cor. for using XRF. Analysis of metal-rich biomass is becoming more common due to the popularity of studies that use plants to absorb heavy metals. The results of the comparative study emphasize that due care and consideration must be given to the selection of the analysis method chosen to analyze such plant material. The results also highlight the need for standard ref. materials that are suitably enriched in metals, such that these may be of use to phytoextraction studies.

10 General

10.1 Manufacture of Pigment Dispersant-Protected Silver Core-Gold Shell Fine Particles without Washing

The manufacturing method includes reduction of Au ions at the interlayers between H₂O-incompatible org. solvent dispersions containing H₂O-insol. polymer pigment dispersant-protected Ag fine particles and Au ion-containing aqueous solutions and deposition of Au on Ag surfaces. Y Tsutsui, from the Mitsuboshi Belting Ltd., Japan, Patent No. JP 2006052238, A2, 23/2/2006. The fine particles manufactured by the method are useful for pigments for plastics and coatings. Thus, Ag-Au core-shell fine particles protected with a CO₂H and amine-containing polyester dispersant (Solsperse) manufactured from a Ag PhMe solution and a chloroauric acid aqueous solution showed good dispersibility in acetone and Bu lactate.