Highlights from Recent Literature

1 Analytical

1.1 Single-Molecule Detection of Thionine on Aggregated Gold Nanoparticles by Surface Enhanced Raman Scattering

The authors report observations of single-mol. detection of thionine and its dynamic interactions on aggregated Au nanoparticle clusters using surface enhanced Raman scattering (SERS). C Ruan, W Wang and B Gu from the Oak Ridge Institute for Science and Education, Oak Ridge, USA, *Journal of Raman Spectroscopy*, 2007, **38(5)**, 568. Spectral intensities are independent of the size of Au nanoparticles studied (from 17 to 80 nm) at thionine concentration <10-12 M or at single-mol. concentration levels. Raman line separations and, in particular, spectral fluctuations and blinking were also observed, suggesting temporal changes in single mol. motion and/or arrangements of thionine on Au nanoparticle surfaces. In contrast, by using dispersed Au nanoparticles, only ensemble SERS spectra could be observed at relatively high concentrations (> 10-8 M thionine), and spectral intensities varied with the size of Au nanoparticles.

2 Catalysis

2.1 Catalytic Reduction of Nitrogen Monoxide by Propene in the Presence of Excess Oxygen over Gold Based Ceria Catalyst

The catalytic reduction of nitrogen monoxide by propene in the presence of excess oxygen over gold based ceria catalyst was studied. L Nguyen, C Potvin, G Djega-Mariadassou, L Delannoy, Laurent; C Louis from the Laboratoire de Reactivite de Surface, Universite Pierre et Marie Curie, Paris, France, *Topics in Catalysis* 2007, **42/43**, 91. Adsorption and temperature programmed desorption of NO/O_2 on Au/CeO_2 reveal that the catalyst adsorbs and desorbs NO over a large range of temperature A max. of 26% conversion of NOx was obtained around 210°C, with a selectivity of 50% to N_2.

2.2 Catalytic Effect of Gold Nanoparticles Self-Assembled in Multilayered Polyelectrolyte Films

Multilayer films composed of poly(L-arginine) (pArg) and mercaptoundecanoic acid (MUA) stabilized Au nanoparticles (Au-MUA NPs) were fabricated based on the electrostatic layer-by-layer self-assembly technique upon a Au electrode modified with a 1st layer of mercaptosuccinic acid (MSA). M Chirea, C Pereira, FSilva, Fernando from the Departamento de Quimica, Faculdade de Ciencias, Universidade do Porto, Oporto, Portugal, *Journal of Physical Chemistry C* 2007, **111(26)**, 9255. The formation of the pArg/Au-MUA NP self-assemblies as alternative multilayers was confirmed by UV-visible absorption spectroscopy and at. force microscopy while their electrochemical properties were studied using cyclic voltammetry, square wave voltammetry, and electrochemical impedance spectroscopy. Charge transport through the multilayer was studied experimentally by using the redox pair $[Fe(CN)_6]^{3-/4-}$. These new assemblies have a high permeability to the probe ions. The presence of the Au-MUA NPs greatly improves the condition and the electron-transfer ability of the film which exhibited new elec. properties characterized by a low impedance response and enhanced elec. current as more layers were added for both Au-MUA NP and pArg terminated multilayers. The behavior observed. is based on 2 cumulative contributions: electron transfer mediated by the Au-MUA NPs layers and ionic diffusion favored by the poly(L-arginine) layers due to the Donnan inclusion. The films obtained showed high conductive properties which represent very promising features for the construction of electrochemical sensors or nanoelectronic devices.

2.3 Nanocrystalline Cerium Oxide Produced by Supercritical Antisolvent Precipitation as a Support for High-Activity Gold Catalysts

Nanocrystalline CeO^2 was prepared by precipitation of a solution of the acetate using supercrit. CO_2 as an antisolvent. Z Tang, J Edwards, J Bartley, S Taylor, A Carley, A Herzing, C Kiely, G Hutchings from the School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK, *Journal of Catalysis* 2007, **249(2)**, 208. It was demonstrated that gold supported on this material is very active for the oxidation of CO at ambient temperature, particularly in comparison with CeO_2 prepared in a conventional manner by thermal decomposition of the acetate. Comparing the catalytic performance for CO oxidation with the most active catalysts in the current literature confirms the high activity of these new materials. They are considerably more active than previous Au/CeO_2 catalysts. The catalyst activity was found to be dependent on the precipitation conditions, which in turn was found to influence the dispersion of gold on the support, as evidenced by detailed microscopy and spectroscopy characterization. The most active fresh catalyst exhibited highly dispersed gold and showed no evidence of the existence of Au nanocrystals using detailed STEM anal. Following reaction with CO/O_2, subtle microstructural changes were apparent, although the morphology of the nanocrystalline CeO_2 support was unchanged; in particular, the Au, which was previously uniformly dispersed, showed signs of beginning to agglomerate into sub-5 nm particles. The stability and origin of the catalytic activity are discussed.

2.4 Catalytic Activity of Gold Nanoparticles Incorporated into Modified Zeolites

Gold catalysts modified by Fe and Ni and supported on different zeolite matrixes have been studied by TEM, TPR, and catalytic testing. E Smolentseva, N Bogdanchikova, A Simakov, A. Pestryakov, M.Farias, A Tompos, A. V Gurin, Ensenada, Mexico, *Journal of Nanoscience and Nanotechnology* 2007, **7(6)**, 1882. The presence of a metal oxide additive allows stabilizing small gold particles, particularly in the case of Fe. The shape of light-off curves shows two temperature regions of the catalyst activity, a low-temperature range below 250° and a high-temperature range above 300° This situation is explained considering the existence of at least two types of catalytically active sites of gold assigned to gold clusters and gold nanoparticles, resp., while the ionic state of gold (Au3+) remains inactive. It is shown that interaction of gold with Fe promoter leads to activation of catalysts at low temperature due to a change of electronic state and redox properties of gold. NiO additive cause a similar, but less pronounced effect.

2.4 Bimetallic Gold/Palladium Catalysts for the Selective Liquid Phase Oxidation of Glycerol

A methodology for preparation of single phase bimetallic Au-Pd catalysts on activated carbon (AC) was developed and used to obtain Au/Pd catalysts at different at. ratio. A Villa, Alberto;C Campione, L Prati from the Dipartimento di Chimica Inorganica Metallorganica e Analitica e Centro CNR, Universita degli Studi di Milano, Milan, Italy, *Catalysis Letters* 2007, **115(3-4)**, 133. The bimetallic catalysts were tested in the liq. phase oxidation on glycerol in water using oxygen as oxidant and compared with monometallic Au and Pd catalysts. A strong synergistic effect is present in a large range of Au/Pd compn. ratio, being maximized for Au90-Pd10 composition. The Au-rich catalysts showed increased durability compared to Pd-rich alloy.

2.5 Gold Based Catalysts on Ceria and Ceria-Alumina for WGS Reaction (WGS Gold Catalysts)

Gold catalysts supported on ceria-alumina have been studied in WGS reaction. D Andreeva, I Ivanov, L Ilieva, J Sobczak, G Avdeev, K Petrov,from the Institute of Catalysis, BAS, Sofia, 1113, Bulgaria, *Topics in Catalysis*, 2007, **44(1-2)**, 173. A high and stable activity was established for the catalysts supported on ceria-alumina, prepared by mechanochemical activation in comparison to the corresponding samples, where ceria-alumina support was prepared by coprecipitation The catalysts were characterized by means of XRD, TPR, Raman and XPS spectroscopy. A correlation between WGS activity and the redox activity was found. On the basis of the results obtained a model of the reaction mechanism and of active sites was proposed.

2.6 Sol Derived Gold-Palladium Bimetallic Nanoparticles On TiO_2: Structure and Catalytic Activity In CO Oxidation

Bimetallic AuPd catalysts were prepared by deposition of bimetallic aq. sols formed in different ways: (i) co-reduction of the precursor Au and Pd ions by Na-citrate/tannic acid mixture, (ii) reduction of Au(III) ions onto preformed Pd sol, and (iii) reduction of Pd(II) ions onto a preformed Au sol. A Beck, A Horvath, Z Schay, G Stefler, Z Koppany, Zs.I Sajo, O Geszti, L Guczi, L. from the Institute of Isotopes of the Hungarian Academy of Sciences, Budapest, Hungary. *Topics in Catalysis* 2007, **44(1-2)**, 115. The Au/TiO_2 and Pd/TiO_2 samples as refs. were prepared from their resp. sols. The structure of the samples was characterized by XRF, XRD, XPS, TEM and CO chemisorption both in the as-prepared state and after calcination and reduction The catalytic activities of the calcined/reduced catalysts in the CO oxidation were compared. The presence of bimetallic crystalline phases was evidenced in all three samples both in the as prepared and calcined/reduced states, however, various extents of Pd surface enrichment were detected The catalytic activity of the bimetallic samples regardless of the preparation method, is about the same as that of the mixt. of the monometallic samples. No significant synergism is suggested in the present bimetallic samples.

2.7 Role of Cationic Gold in Supported CO Oxidation Catalysts

A review; CO oxidation catalyzed by supported gold has emerged as a vigorous research field in the preceding few years, driven by the recognition that this unreactive metal, when highly dispersed, is remarkably active and selective as a catalyst, offering good prospects for application. J Fierro-Gonzalez, J Guzman, B Gates, Departamento de Ingenieria Quimica, Instituto Tecnologico de Celaya,Celaya, 38010, Mexico, *Topics in Catalysis* 2007, **44(1-2)**, 103. It also offers good opportunities for fundamental understanding, because some of the reactants converted by supported gold are small mols. that are informative probes of the catalyst surface. Thus, CO oxidation has been used extensively to characterize supported gold catalysts. Nonetheless, no consensus has yet emerged regarding the catalytically active species, and it seems likely that catalytic activity is not restricted to a single kind of species. In the following review, we focused specifically on one class of catalytically active gold species for CO oxidation, cationic gold. The review includes summaries of (a) evidence of gold in various oxidation states in supported CO oxidation catalysts, including theoretical and experimentally results, esp. spectroscopic evidence of functioning catalysts; (b) evidence demonstrating that cationic gold plays a role in the catalytic sites in supported catalysts that contain both zerovalent and cationic gold; and (c) evidence that cationic gold plays such a role in supported catalysts that lack detectable zerovalent gold.

2.8 Preservation of the Activity of Supported Gold Catalysts for CO Oxidation

A review; procedures leading to the preservation of activity of supported gold catalysts for CO oxidation are reviewed. F Moreau, G C Bond,Institute for Materials Research, University of Salford, Salford, Greater Manchester, UK, *Topics*

in Catalysis 2007, **44(1-2)**, 95. The inclusion of iron as $Fe(OH)_3$ in prepg. catalysts using tin oxide, ceria and zirconia as supports gives better activity and much improved stability with time-onstream. In the case of Au/Fe-SnO_2 (0.5-0.9% Au), the effect is maximal with approximately 4% Fe. The stability of catalysts based on ceria as support is also much better when small amts. of either iron or lanthanum during preparation of the support by thermal decomposition of nitrates. Au/SnO_2 catalysts often suffer initial deactivation followed by an increase in activity with time-onstream; a period of refrigeration (7d) induces an excellent stability at high conversion.

2.9 Progress Towards the Commercial Application of Gold Catalysts

A review; now that gold catalysis is a valuable and exciting new field of catalysis as a whole, the exploitation of gold catalysts for com. applications is being pursued. C W Corti, R J Holliday, D T Thompson, World Gold Council, London, UK, *Topics in Catalysis* 2007, **44(1-2)**, 331. This is being assisted by new work on preparation and utilization methods to increase their durability during use. Other factors, including a substantial increase in investment in gold catalysis R&D, need to be considered before widespread application will occur. We show that new opportunities for com. exploitation can be monitored via patent mapping, followed by careful examn. of key patents.

2.10 Kinetics of the Water Formation in the Propene Epoxidation Over Gold-Titania Catalysts

The kinetics of the hydrogen oxidation were detected for a no. of different gold catalysts supported on titania, silica, and silicalite-1. A T Nijhuis, B M Weckhuysen, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands, *Preprints – American Chemical Society, Division of Petroleum Chemistry* 2007, **52(2)**, 292. A dual site Langmuir-Hinshelwood kinetic model was able to describe the reaction well. The kinetic parameters are independent of the support. Water was found to be strongly limiting the hydrogen oxidation rate.

3 Chemistry

3.1 Oxidation of Elemental Gold in Alcohol Solutions

Gold is designated as the noblest metal because of its chemical inertness. It is known to dissolve in cyanide solutions in the presence of air or H_2O_2 or in halogen-containing solutions, aqua regia being the most famous example. Herein, the authors report a unique thiol, esp. 4-pyridinethiol (4-PS), assisted dissolution of Au in alc. solutions M T Raeisaenen, M Kemell, M R T Leskelae, Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Finland, *Inorganic Chemistry (Washington, DC, United States)* 2007, **46(8)**, 3251. Although dissolution was found to be very selective for pyridinethiols, such a phenomenon is astonishing since thiols are commonly used as etch resists for Au and even 4-PS is extensively used as a surface modifier for Au. To gain further understanding of the dissolution process, the influence of the reaction conditions was extensively studied. On the basis of the obtained results, a mechanism for the dissolution reaction is proposed. Fascinatingly, by tuning of the reaction conditions, this phenomenon can be applied in selective preparation of self-supporting nanometer-thick Au foils.

3.2 The Adsorption of Gold on Activated Carbon from Thiosulfate-Ammoniacal Solutions

The adsorption of gold on activated carbon in ammoniacal thiosulfate solution was studied. P Navarro; C Vargas; M Alonso; F J Alguacil, Departamento de Ingenieria Metalurgica, Universidad de Santiago de Chile, Chile, *Gold Bulletin (London, United Kingdom)* 2006, **39(3)**, 93. The variables affecting the adsorption of gold on the carbon included temperature and concentrations of ammonium hydroxide, thiosulfate and those of accompanying cations and anions. The apparent activation energy for the adsorption process was estd. to be 19.4 kJ/mol, and indicates that the gold adsorption is film diffusion-controlled. The initial adsorption rate was high when compared to that of the overall adsorption process.

4 Electrochemistry

4.1 Electro-Oxidation of Altertoxin I (Atx-I) at Gold Electrodes Modified by Dodecanethiol Self-Assembled Monolayers

The adsorptive accumulation of ATX-I, a mycotoxin produced by the fungi the Alternaria alternate genus, onto polycrystalline M B Moressi; J J Calvente,; R Andreu, H Fernandez, M Zon, Departamento de Quimica, Universidad Nacional de Rio Cuarto, Rio Cuarto, Argentina, *Journal of Electroanalytical Chemistry* 2007, **605(2)**, 118. Au electrodes modified by a self-assembled monolayer (SAM) of 1-dodecanethiol (DDT) from unstirred solutions of the pure com. reagent in 20% acetone (Ac) + 80% pH 7 phosphate buffer solutions (PBS) was studied by cyclic (CV) and square wave voltammetries (SWV). The influence of different experimentally conditions on the adsorptive process was analyzed. The specific interaction of ATX-I with these modified Au electrodes was adequately described by a Freundlich adsorption isotherm. Electrochemical impedance spectroscopy (EIS) measurements were used to assess the state of the adsorbed thiol mols., demonstrating that optimum conditions for anal. detection require the presence of defects in the monolayer, where analyte accumulation and charge transfer rate are enhanced with respect to well ordered monolayers. SWV was employed to generate the calibration curves. For a signal-to-noise ratio of 3:1, a detection limit of 4 .times. 10-8 mol dm-3 (14 ppb) was calcd. at a frequency (f) of 40 Hz.

5 Electronics and Sensors

5.1 In Situ Infrared Study of the Adsorption and Surface Acid-Base Properties of the Anions of Dicarboxylic Acids at Gold Single Crystal and Thin-Film Electrodes

The adsorption of malonic and succinic acids and their anions at Au electrodes was studied by in situ IR spectroscopy by combining external and internal reflection expts. performed, resp., with Au single crystal and sputtered Au thin-film electrodes deposited on Si substrates. J M Delgado; A Berna; J M Orts; A Rodes, J M Feliu, Departamento de Quimica Fisica e Instituto Universitario de Electroquimica, Universidad de Alicante, Spain, *Journal of Physical Chemistry C* 2007, **111(27)**, 9943. The in situ IR spectra obtained in solutions with pH = 1 confirmed the potential-dependent specific adsorption of bimalonate anions in a bidentate configuration irresp. of the crystallog. orientation of the Au electrodes. The high signal-to-noise ratio assocd. with the surface-enhanced IR absorption (SEIRA effect) in the case of the Au thin-film electrodes allows the observation of the carbonyl band for adsorbed bimalonate together with addnl. bands between 2000 and 3000 cm-1 that can be tentatively assigned to the formation of H bonds between neighbour bimalonate anions. The intensities of all these bands characteristic of adsorbed bimalonate decrease with increasing solution pH for which adsorbed malonate anions predominate. The analysis of the intensities of the .nu.as(OCO) and .nu.(CO) bands for the uncoordinated carboxylate/carboxylic group of the adsorbed malonate/bimalonate and succinate/bisuccinate systems allows the estn. of the pKa value for their surface acid-base equil. The obtained values, around 4.8 for adsorbed malonic acid anions and around 5.3 for adsorbed succinic acid anions, are below those of the corresponding solution equilibrium. The decrease of pKa_2 upon adsorption of bimalonate/malonate anions is lower than for adsorbed bioxalate/oxalate anions and higher than for the bisuccinate/succinate system. This behavior is related to the effect of the distance between the uncoordinated carboxylic group and the electrode surface on the electrostatic interaction of the former with the pos. charged surface.

5.2 Ab Initio Study of Electronic and Structural Properties of Gold Nanowires with Light-Element Impurities

Electronic, bonding, and structural properties of monoat. Au wires containing impurities of at. H and C were studied by the projector augmented-wave method within the generalized gradient approxn. N V Skorodumova; S I Simak; A E Kochetov; B Johansson, Condensed Matter Theory Group, Department of Physics, Uppsala University, Sweden., *Physical Review B: Condensed Matter and Materials Physics* 2007, **75(23)**, 235440/1. Light impurities cause significant charge redistribution in monoat. Au wires altering bonding and affecting the wire structural properties. Light impurities can drastically promote the parity oscillations of conductance occurring already in pure Au wires, thus demonstrating how the electronic and structural characteristics of nanowires can be tuned by appropriate doping.

6 Medical and Dental

6.1 Drug and Gene Delivery Using Gold Nanoparticles

A review. G Han; P Ghosh; R De, Mrinmoy; M Vincent, Department of Chemistry, University of Massachusetts, USA, *NanoBiotechnology* 2007, **3(1)**, 40. Monolayer-functionalized gold nanoparticles provide attractive vehicles for pharmaceutical delivery applications as a result of their size and the unique properties and release mechanisms imparted by their monolayer. This review provides examples of recent advances in the field of drug and gene delivery using gold nanoparticles.

7 Metallurgy, Materials and Coatings

7.1 Homocysteine-Protected Gold-Coated Magnetic Nanoparticles: Synthesis and Characterization

An easy and simple 2-step reaction is employed to synthesize a new type of ligand-protected (homocysteine-protected) Au-coated Fe oxide nanoparticle (homocys-Au-Fe_3O_4). Fe_3O_4 nanoparticles are used as the central core to prep. homocys-Au-Fe_3O_4 in aq. state without precipitation and aggregation of nanoparticles. Fe_3O_4 nanoparticles are initially prepared and subsequently coated with Au layers under hot citrate reduction of $HAuCl_4$. C K Lo; D Xiao; M M F Choi, Department of Chemistry, Hong Kong Baptist University, Peop. Rep. China, *Journal of Materials Chemistry 2007*, 17(23), 2418. The citrate monolayer of the nanoparticles is then ready for place-exchange with homocysteine mols. to produce the well dispersed homocys-Au-Fe_3O_4 nanoparticles. These homocys-Au-Fe_3O_4 nanoparticles were fully characterized by XPS, visible absorption spectroscopy, magnetic susceptibility measurements, FTIR spectroscopy, TGA, at. absorption spectroscopy, energy dispersive x-ray spectroscopy, x-ray powder diffraction, SEM, TEM and high-resolution TEM. The homocys-Au-Fe_3O_4 nanoparticles show good paramagnetic properties and are coated with ultra-thin layers of Au atoms (.approximately 0.5 nm) having an average diameter of .approximately12 nm. These magnetic nanoparticles are well dispersed in H_2O and stable at physiol. pH without precipitation The visible absorption spectrum of homocys-Au-Fe_3O_4 can be altered by pH. These nanoparticles are aggregated in an acidic environment but dissociated at high pH conditions in a reversible manner. This article provided important insights into the design of new H_2O-sol. magnetic nanoparticles for biomedical, analytical and catalytic applications.

8 Nanotechnology

8.1 Evolution of Size and Shape in the Colloidal Crystallization of Gold Nanoparticles

The addition of dodecanethiol to a solution of oleylamine-stabilized Au nanoparticles in $CHCl_3$ leads to aggregation of nanoparticles and formation of colloidal crystals. O C Compton, F E Osterloh, Department of Chemistry, University of California, Davis, USA, *Journal of the American Chemical Society*, 2007, **129(25)**, 7793. Based on results from dynamic light scattering and SEM the authors identify three different growth mechanisms: direct nanoparticle aggregation, cluster aggregation, and heterogeneous aggregation. These mechanisms produce amorphous, single-crystalline, polycrystalline, and core-shell type clusters. In the latter, Au nanoparticles encapsulate an impurity nucleus. All crystalline structures exhibit fcc. or icosahedral packing and are terminated by (100) and (111) planes, which leads to truncated tetrahedral, octahedral, and icosahedral shapes. Importantly, most clusters in this system grow by aggregation of 60-80 nm structurally nonrigid clusters that form in the 1st 60 s of the expt. The aggregation mechanism is discussed in terms of classical and other nucleation theories.

8.2 Directional Assembly of Polyaniline Functionalized Gold Nanoparticles

Polyaniline encapsulated and functionalized self-assembled gold nanoparticles were synthesized using an interfacial polymn. approach. K Mallick; M J Witcomb; M S Scurrell, Molecular Sciences Institute, University of the Witwatersrand, S. Africa, *Journal of Physics: Condensed Matter* 2007, **19(19)**, 196225/1. The polyaniline and gold nanoparticles were formed at the aq. and org. interface and a directional growth of the self-assembled gold nanoparticles was observed. The resultant composite material was characterized by different techniques. IR, Raman and UV-visible (UV-vis) spectra provided information on the chemical structure of the polymer. UV-vis spectrum also indicated the functionalization of the gold nanoparticles by the polymer. TEM images showed the morphology of the polymer and the metal particles.

8.3 Gold Nanoparticles from Oxonium Precursor: Synthesis in the Presence of Primary Amine and Characterization

A convenient method of the synthesis of gold NPs with low polydispersity is described. Triphosphinogold oxonium salt $[O(AuPPh_3)3]BF_4$ in the presence of amine and dioxygen is a versatile gold atom source in mesitylene. P Uznanski; C Amiens; B Chaudret; E Bryszewska, Centre for Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland, *Polish Journal of Chemistry* 2006, **80(11)**, 1845. The amine takes part in the reduction of gold(I) atom precursor. Therefore in a 1/1 Au(I)/hexadecylamine stoichiometry, "naked" gold nanoparticles are produced which ppt. within some minutes from the solution and form a gold mirror. Only an excess of amine enables the synthesis of ligand-protected nanoparticles which furthermore display a great tendency to self-organize. Solvent effect on the course of the reaction is discussed.

8.4 Wet Chemical Synthesis of Gold Nanoparticles Using Silver Seeds: A shape Control from Nanorods to Hollow Spherical Nanoparticles

A seed-mediated method was employed here for CTAB-assisted gold nanoparticle growth. 3-4 Nm silver aq. colloid was stabilized by sodium citrate and used as seed solution to initial gold particle growth. Z-C Xu; C-M Shen; C-W Xiao; T-Z Yang, H-R Zhang, J-Q Li; H-L Li; H-J Gao, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing, Peoples Republic of China, *Nanotechnology* 2007, **18(11),** 115608/1. The concentration of seed solution was calcd. based on its relationship with silver atom concentration and seed particle statistical mean vol. It was found that there is a max. seed concentration of 8.57 .times. 10-12 M (.approximately 25 .mu.l 0.343 .times. 10-8 M seed solution added) in 10 mL 2.5 .times. 10-4 M $HAuCl_4$ growth solution for growth of rodlike particles. Below this seed amt., the aspect ratio of nanorods could be controlled by varying the silver seed amt., i.e. nanorods with aspect ratio .approximately 18.9 were obtained when the seed concentration in the growth solution was 0.343 .times. 10-12 M by adding 1 .mu.l 0.343 .times. 10-8 M silver seed solution and nanorods with aspect ratio .approximately9.69 were obtained when the seed concentration in the growth solution was 1.715 .times. 10-12 M by adding 5 .mu.l 0.343 .times. 10-8 M silver seed solution. As the seed concentration in the growth solution was more than 8.58 .times. 10-12 M (25 .mu. l 0.343 .times. 10-8 M silver seed solution was added), there were no rodlike particles formed but spherical ones instead. These spheres were further studied by TEM and found to all be hollow structures. It was suggested that there were probably two different nucleation processes for growth of nanorods and spheres. For hollow spheres, the reaction between Ag seeds and Au ions formed hollow structures based on the Ag particle template effect. Then further growth of Au on these hollow structures produced hollow gold nanospheres. For nanorods, due to the very low concentration of silver seed (molar ratio of Ag seed: Au = 3.426 .times. 10-8), the growth process here probably was started by silver-induced Au nucleation, in which reduction of gold ions by silver resulted in small gold clusters. These gold clusters further grew up into nanoparticles and nanorods in the presence of CTAB.

9 Refining

9.1 Gold and Cyanides. Part 1

A review on recovery of gold via leaching mineral raw materials (gold ores and ore concs.) by means of cyanidation. Grudev, Stoyan, MGU "Sv. Ivan Rilski", Bulg., Minno Delo i Geologiya 2006, 61(2), 38. The formation of a very stable Au(CN)2-complex with the cyanide ion is shown. The assocd.

dissolution of other metals and metal sulfides during the leaching and the formation of solutions with a quite complex compn. including different cyanide compounds is discussed. The toxicity of those compounds towards different organisms was presented as well as the need for detoxification of the wastewater after the gold extn. If properly applied, the cyanidation is indicated to carry a relatively small risk for the environment and its inhabitants.

9.2 Gold and cyanides. Part 2

A review on the methods of detoxification of cyanides in spent solutions from leaching of gold-bearing ores. S Grudev, MGU "Sv. Ivan Rilski", Bulgaria, Minno Delo i Geologiya (2006), 61(3), 21-24. A brief discussion on the application of cyanide-free techniques of gold leaching is given.

9.3 Extraction of Gold(III), Palladium(II), and Platinum(IV) by 1-[[2-92,3-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole from Hydrochloric Acid Solutions

Solvent extn. was studied for gold(3+), palladium(2+), and platinum(4+) by propiconazole (1) from 3M hydrochloric acid solutions R A Khisamutdinov; Y I Murinov; O V Shitikova, Inst. of Organic Chemical, Sci. Center of Ufa, Russ. Acad. of Sci., Ufa, Russia, *Zhurnal Neorganicheskoi Khimii* 2007, **52(6)**, 1041. The extn. scheme includes protonation of 1 and then coordination to a metal according to anion-exchange mechanism. Concentration and thermodn. consts. of the extn. were calcd. Commonly used for plant protection, 1 is presently recommended for the cojoint extn. of noble metals.

9.4 Method for Processing of Gold Ores

M N Zlobin; V V Novikov; V V Rudakov; V K Sovmen; S I Zel'berg; M Z Kazimirov, E A Kompaneytsev, PA ZAO "Polyus", Russia, Patent Number 2304024, C1, August 2007, describe a method for processing of gold ores is proposed. SUBSTANCE: method involves complete (non-selective) mining of ore; staged grinding of ore in grinders; sepg. ground ore into size grades; seperating off-grade part and mining waste from ground graded ore using lump-by-lump X-ray spectroscopic separation process and small-portion X-ray spectroscopic sorting-out process; performing addnl. grinding combined with screening of concentrated ore part in grinders in closed cycle after addnl. size sepn. into at least two grades; performing addnl. extn. of useful component from refuses of small-portion X-ray spectroscopic coarse-grain products sorting process by providing vibration concentration; thereafter, discharging refuses into dump waste product; directing vibration concentration product for additional grinding in closed cycle; additional extg. useful component from refuses of small-portion X-ray spectroscopic small-grain products sorting process by performing double sequential vibration concentration process; thereafter, discharging these refuses into dump waste product; subjecting concd. product of this stage of small-portion X-ray spectroscopic sorting process and vibration concentration process after carrying-out of above operations, corresponding to main processes, to air sepn. procedure, said concd. product being preliminarily fractionated.

9.5 Recovery of Gold from Ammonia-Thiosulfate Media with Amberlite Ira-410

Adsorption and elution of gold in thiosulfate-ammonia media were studied at lab. level using the Amberlite IRA-410 ion exchange resin. Tests were carried out in a stirred reactor, maintaining a const. temperature (25°) with a solution vol./resin mass ratio of 833.3 mL/g during 3 h. Departamento de Ingenieria Metalurgica, Universidad de Santiago, Chile, *Revista de Metalurgia (Madrid, Spain)* 2006, **42(5)**, 354. The variables tested were pH (9-11), thiosulfate concentration (0-0.5 M), ammonia concentration (0-0.5 M), and selectivity in the presence of cupric ion. The obtained results indicated that gold adsorption was quick, the presence of thiosulfate decreased strongly the adsorption, and the presence of ammonia did not have a major affect on the adsorption. Copper was in a certain measurement a competitor of gold, but its highest neg. effect was that it acted as a catalyst of the oxidizing reaction of thiosulfate (S2O2-3) to tetrathionate (S4O2-6) and trithionate (S3O2-6), which could cause a partial elution of gold during the load stage. Also, the behavior of ClO-4, SO2-3, and ClO- as eluents was studied in both gold and copper elution. These tests were also carried out in a stirred reactor at a constant temperature (25°) with an aqueous solution vol./resin mass ratio of 200 mL/g for 3 h. The results demonstrated that copper was eluted more quickly than gold in all the cases.

9.6 Method for Treating and Circularly Utilizing Oxynitride in Smelting of Gold

The title method comprises the steps of: (1) adding gold slurry and water to a high-pressure kettle, sealing the kettle, stirring, opening the oxygen-supply valve to introduce oxygen till the oxygen content at the vent reaches 99.9%, closing the oxygen-supply valve and vent, adding nitric acid by an injector till the liq./solid ratio is (4-6):1 while heating the kettle and introducing oxygen, reacting at 70-90°C and 0.2-0.3MPa for 4-6h, slowly discharging the tail gas after lixiviation, washing the tail gas by a column containing 20% base; and (2) adding purified gold slurry and water to the high-pressure kettle, sealing the kettle, stirring, opening the oxygen-supply valve to introduce oxygen till the oxygen content at the vent reaches 99.9%, closing the oxygen-supply valve and vent, adding 8-12% hydrochloric acid by an injector, adding 6-9% nitric acid by an injector till the liq./solid ratio is (4-6):1 while heating the kettle and introducing oxygen, reacting at 70-90°C and 0.2-0.3MPa for 4-6h, slowly discharging the tail gas after lixiviation, and washing the tail gas by a column containing 20% base. D Wang; C Gong; D Dong; S Jin, PA Changchun Gold Research Institute, Peop. Rep. China, Patent number, CN101029357, A, September 2007. The method has the advantages of circular utilization of NOx, low addn. of nitric acid, low cost, and little pollution.

9.7 Method for Fast Extracting Gold and Silver Through Optimized Wet Method

The title method comprises the steps of: (1) adding 14-25 vol.% clear aqua regia containing gold to an acidproof reaction kettle at 16-26°C, aerating, and stirring; (2) adding anhyd. sodium sulfite (1.25-1.6 wt. times gold in aqua regia) while stirring till no black ppt. appears, standing to ppt. for 0.5-1 h, and filtering, (3) washing with boiled water 3-5 times, adding nitric acid till the liq. level excess the gold soil, and heating to dissolve and remove impurities, and (4) washing with water 3-5 times, and drying at 100-200°C. Y Zhang; R Zhang, Ruiqiang, PA Peop. Rep. China. Patent Number CN101029354, A September 2007. The method has the advantages of high speed, high recovery rate (99.99%), significant reaction termination, simple operation, low cost, no toxic raw material, high safety, little pollution, and high gold purity (compliant of 1# gold std.).

9.8 The Effect of Sulphur Species on Thiosulphate Leaching of Gold

Thiosulfate is a metastable anion that tends to readily undergo chemical decomposition in aq. solutions The presence of tetrathionate, trithionate, and sulfide is unavoidable in the ammoniacal thiosulfate system, as they are products of thiosulfate decomposition D Feng, J S J van Deventer, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Australia, *Minerals Engineering* 2007, **20(3)**, 273. Thiosulfate decomposition is of great importance in the thiosulfate leaching of gold. The effect of three typical sulfur species tetrathionate, trithionate, and sulfide on thiosulfate leaching has been investigated in both pure gold and ore systems. The gold dissolution increased at low concentrations of the sulfur species, but decreased at high concentrations The presence of these sulfur species significantly reduced thiosulfate decomposition, and this beneficial effect became more prominent at high levels of the species. The Eh-pH diagram for the Au-N-S-H_2O system indicated that the sulfide ion could form HS- to complex gold, enhancing gold leaching. Tetrathionate, trithionate, and sulfide would convert to thiosulfate with some elemental sulfur being formed via oxidation or reduction routes. The presence of the sulfur species shifted the thiosulfate decomposition reactions, and hence stabilized thiosulfate. Raman spectra demonstrated that the gold surfaces were readily passivated in the presence of the sulfur species, and the passivation tended to be more severe at higher levels of the species

9.9 Evaluation of Kinetic and Diffusion Phenomena in Cyanide Leaching of Crushed and Run-of-mine Gold Ores

This paper compares the rates of pore diffusion and cyanide gold dissolution in coarse, porous gold oxide ore particles. S C Bouffard; D G Dixon, Barrick Technology Centre, Vancouver, Canada, *Hydrometallurgy* 2007, **86(1-2)**, 63. Several size fractions of a gold oxide ore from a Nevada heap leaching operation were leached individually in a well mixed solution of const. pH (10.5, 11, or 12), const. cyanide concentration (50, 200, or 500 ppm), and const. temperature (5, 22, or 40°C). Particles were coarse, ranging from - 1.7 mm (10 mesh) to 152 mm (6 in.). Leaching of -1.7 mm (10 mesh) particles was complete in 24 h. The leaching kinetics was not influenced by the pH or the dissolved gold concentration A model, which does not include the pore diffusion, as the latter was found to be extremely rapid in such small particles, predicts the conversion X as a function of time, cyanide concentration, and temperature. According to the data and the model, increasing temps. and increasing cyanide concentrations were found to increase the leaching kinetics. Leaching of larger particles was much slower than -1.7 mm (10 mesh) fines, requiring as many as 85 days to reach near complete gold extn. from particles 102 mm (4 in.) to 152 mm (6 in.) in size. In a static cyanide heap leach operation, this time period is very comparable to the time of irrigation of the uppermost lift. According to the diffusion/reaction model developed for the coarse particles, the advance of cyanide and oxygen into the pores of these particles was found to be slower than in the -1.7 mm (10 mesh) particles, but still was much faster than the gold dissolution reaction itself. The outward diffusion of dissolved gold was also found to be very rapid. The precise measurements of the gold dissolution kinetics of coarse particles made in this study dispels, in part, the well-accepted hypothesis that solute diffusion rates control gold heap leaching of crushed and run-of-mine ores. The kinetic model that we have developed for coarse ore leaching in well mixed environments could also predict accurately the gold extn. in large columns. This evidence attests to the slowness of the dissolution of gold in coarse particles, unfortunately leaving crushing alone as the most effective option to shorten the leach cycle.

10 General

10.1 The Colours of Nanometric Gold

A set of broad-range NIR-vis-UV optical absorption spectra, measured for selected Au-cluster thiolate compounds (GCTs, containing .approximately 20 to 300 Au atoms), is consistently displayed and then analyzed within the dielec.-functions approach. R B Wyrwas; M M Alvarez; J T Khoury; R C Price; T G Schaaff; R L Whetten, School of Chemistry & Biochemistry, Georgia Institute of Technology, *USA, European Physical Journal D: Atomic, Molecular, Optical and Plasma Physics* 2007, **43(1-3)**, 91. The size-evolution toward 'bulk' (Au diameter >3-nm) optical response is thereby clearly demonstrated. The emergence of apparent energy gaps, Eon, for onset of optical absorption, as well as other fine-structure, is consistent with that of a well-quantized metallic electronic structure for the compounds' cores: the onset-band location Eon and intensity are attributed semiclassically to a circulation-frequency resonance of the Fermi-level electrons. With decreasing cluster-size, an increasing fraction

of the integrated (sum-rule) intensity is missing' from the < 4 eV region. This might be explained by the outermost layer consisting of Au(I)thiolate complexes.

10.2 Inorganic Replication of Human Hair and In Situ Preparation of Gold Nanoparticles

The structure of hair was replicated via a sol-gel processing using human hair as the template. S-X Liu; J-H He, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, Peoples Republic of China, *Wuji Cailiao Xuebao* 2006, **21(6)**, 1313. When using Na silicate and TEOS as the precursor, the cell structure of hair cuticle was not well replicated. When using tetra-Bu titanate as the precursor, however, TiO_2 microtubes were obtained, with nanopores in their wall and nanoporous platelets on their outer surfaces, which were derived from cuticle cells on hair surfaces. The nanopores in the microtubes acted as an effective nanoreactor for in situ synthesis of Au nanoparticles. The microchannels, nanopores and noble metal nanoparticles may provide a unique combination that would be attractive in such applications as catalysis, adsorption, and separation.