

# Highlights from recent literature

## 1 Analytical

### 1.1 Smart surface of gold nanoparticles fabricated by combination of raft and click chemistry

A simple efficient post-modification route to the fabrication of hybrid gold nanoparticles with poly(N-isopropylacrylamide) based on click chemistry is described. T Zhang, Z Zheng, X Ding, Y Peng, Yuxing from the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Peop. Rep. China, *Macromolecular Rapid Communications* 2008, **29(21)**, 1716. The polymer was prepared by reversible addition fragmentation chain transfer radical polymn. (RAFT). The polymer was immobilized onto gold nanoparticles with grafting densities of 5.8 chains/nm<sup>2</sup> by a click reaction. The hybrid gold nanoparticles showed a temperature responsive phenomenon as the temperature changed between 20 and 45°C

### 1.2 Determination of gold by electrothermal atomic absorption spectrometry after single drop microextraction

Due to the importance of gold and their extremely low levels various matrixes, highly sensitive and rapid methods required for its trace and ultratrace detection S Nazari from the Department of Chemistry, Faculty of Science, Tarbiat Moallem University of Sabzevar, Iran, *Analytical Chemistry (Rajkot, India)* 2008, **7(5)**, 301. In trace element analysis, preconcentration and separation methods enhance the sensitivity and precision of the detection. In this work a high sensitive method is described for extraction and detection of gold in aqueous samples by liquid phase microextraction combined with a graphite furnace at. absorption spectrometry.

For obtaining higher sensitivity we applied method of "single drop microextraction" for detection of trace amts. of gold. In this method Au is reacted with 2-mercaptoaniline, the complex formed was then extd. into micro drop of 1,2-dichloroethane. After extraction, the microdrop was retracted and directly transferred into a graphite tube modified by [Pd(c)+Pd(i)]. The detection limit was calcd. to be 0.8 .mu.g/L (abs. value of 0.3 ng) based on 3.sigma.b. The RSD for 5 replicate analysis of 10 .mu.g/L Au was 6.5%. The calibration curve was linear in the range of 0.8 to 40 .mu.g/L with a sensitivity of 0.25 .mu.g/L.

## 2 Catalysis

### 2.1 Highly selective oxidation of benzyl alcohol to benzaldehyde catalyzed by bimetallic gold-copper catalyst

Vapor-phase oxidation of benzyl alcohol with air to benzaldehyde with high selectivity was carried out using Au-Cu/SiO<sub>2</sub> catalysts. C Della Pina; E Falletta, M Rossi from the Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita degli Studi di Milano, Milan, 20133, Italy, *Journal of Catalysis* 2008, **260(2)**, 384. Under optimum conditions, the benzaldehyde yield reached 98%.

### 2.2 Preparation of supported mono- and bimetallic nanoclusters of gold, nickel, and palladium by metal-vapor synthesis and their catalytic activity in hydrogenation of 1-hexene and hydrodechlorination of chlorobenzene

Using metal-vapor synthesis mono- and bimetallic nanoparticles of gold, nickel and palladium grafted on various supports were synthesized. Nanocompounds catalytic activity was investigated using hexene-1 hydration and chlorobenzene hydrodechlorination reactions. V Spiridonov, A Vasil'kov, V Podshibikhin, A Serdan, A Naumkin, G Lisichkin from the MGU im. M. V. Lomonosova, Moscow, Russia, *Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya*, 2007, **50(8)**, 108. Nanocompound chlorobenzene hydrodechlorination catalytic activity was proved to deplete amongst Pd > Ni .apprx. Au/Ni.

### 2.3 Aerobic oxidation of amines to imines catalyzed by bulk gold powder and by alumina-supported gold

Both bulk gold powder (.apprx.50 .mu.m particle size) and alumina-supported gold (50-150 nm) are highly active catalysts for the aerobic oxidative dehydrogenation of amines (CH-NH) to imines (C=N) under the mild conditions of 1 atm O<sub>2</sub> and 100°C. B Zhu, M Lazar, B Trewyn, R Angelici from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, USA, *Journal of Catalysis*, 2008, **260(1)**, 1. Reactions using the 5% Au/Al<sub>2</sub>O<sub>3</sub> catalyst make efficient use of the gold metal and offer a practical synthesis of imines from amines. These studies add to the growing list of reactions that are catalyzed by bulk gold metal.

### 2.4 Comparison of nanosized gold-based and copper-based catalysts for the low-temperature water-gas shift reaction

In this paper the catalytic performances for the low-temperature water gas shift reaction of Au/TiO<sub>2</sub> type A (from World Gold Council), Au/CeO<sub>2</sub> (developed at UPV-CSIC), CuO/Al<sub>2</sub>O<sub>3</sub> (from BASF), and CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (from REB Research & Consulting) have been compared. D Mendes, H Garcia, V Silva, A Mendes, L Madeira, LEPAE, Chemical Engineering Department, Faculty of Engineering, University

of Porto, Oporto, Portugal. *Industrial & Engineering Chemistry Research*, 2009, **48(1)**, 430. The catalysts were characterized by different techniques such as Raman spectroscopy, BET surface area measurements, temperature-programmed reduction, and high-resolution transmission electron microscopy, which gave addnl. information on the redox properties and textural and morphol. structure of the investigated samples.

The performances of these catalysts were evaluated in a wide range of operating conditions in a micro packed-bed reactor. It was observed that the presence of reaction products in the feed ( $\text{CO}_2$  and  $\text{H}_2$ ), as well as  $\text{CO}$  and  $\text{H}_2\text{O}$  feed concns., have significant effects on the catalytic performances. With a typical reformat feed the  $\text{Au/CeO}_2$  catalyst reveals the highest  $\text{CO}$  conversion at the lowest temperature investigated ( $150^\circ\text{C}$ ). However, while in the long tests performed the  $\text{CuO/ZnO/Al}_2\text{O}_3$  catalyst showed a good stability for the entire range of temps. tested ( $150\text{-}300^\circ\text{C}$ ), the  $\text{Au/CeO}_2$  sample clearly showed two distinct behaviors: a progressive deactivation at lower temps. and a good stability at higher ones. The selection of the best catalytic system is therefore clearly dependent upon the range of temps. used.

### 2.5 Gold-nano particles supported on Na-Y and H-Y types zeolites: activity and thermal stability for co oxidation reaction

Gold nano particles (GNP) were deposited on Na-Y and H-Y zeolite substrates using chloroauric acid ( $\text{HAuCl}_4$ ) solution. The synthesized catalysts were then characterized and the catalytic activity toward  $\text{CO}$  oxidation reaction was investigated using a tubular fix bed micro reactor under atm. pressure. S Jafari, H Asilian Mahabady, H Kazemian from the Department of Occupational and Environmental Health, Medical Faculty, Tarbiat Modares University, Tehran, Iran, *Catalysis Letters*, 2009, **128(1-2)**, 57.

It was found that  $\text{CO}$  conversion of 100% and 5% can be achieved at  $20^\circ\text{C}$  on  $\text{Au/Na-Y}$  and  $\text{Au/H-Y}$  fresh catalysts, resp. Thermal stability of catalysts was also investigated by treating the catalysts at  $400^\circ\text{C}$  for 4 h. After thermal stability test, activity tests of the catalysts at  $20^\circ\text{C}$  were shown that  $\text{CO}$  conversion of  $\text{Au/Na-Y}$  catalyst was decreased to 65% whereas the activity of the  $\text{Au/H-Y}$  at  $20^\circ\text{C}$  was increased up to 15%. Characterization tests were revealed that the structures of the zeolitic supports remained unchanged after thermal pretreatment.

### 2.6 Gold-film-catalyzed hydrosilylation of alkynes by microwave-assisted, continuous-flow organic synthesis (Macos)

Thin gold films on the surface of glass capillaries have proven to be highly active catalysts for the rapid hydrosilylation of alkynes that are flowed through the reactor while being heated by microwave irradiation. G Shore, M Organ from the Department of Chemistry, York University, Toronto, ON, M3J 1P3, Canada, *Chemistry – A European Journal*, 2008, **14(31)**,

9641. The films are able to be reused at least five times with no loss of activity and with no detectable levels of gold showing up in the hydrosilylated products.

### 2.7 Synthesis of porous .alpha.- $\text{Fe}_2\text{O}_3$ nanorods as catalyst support and a novel method to deposit small gold colloids on them

Two novel methods, one for prepn. of porous .alpha.- $\text{Fe}_2\text{O}_3$  nanorod catalyst support and another for the deposition of Au particles on the catalyst support with high efficiency and high dispersion, are reported. Z Zhong, J Teo, M Lin, J Ho from the Institute of Chemical Engineering and Sciences, Singapore, *Topics in Catalysis*, 2008, **49(3-4)**, 216. In the former,  $\text{FeO(OH)}$  nanorods were first prepared by a mild hydrothermal prepn. using tetraethylammonium hydroxide (TEAOH) as the structure director. The  $\text{FeO(OH)}$  product was then converted to porous .alpha.- $\text{Fe}_2\text{O}_3$  nanorods via calcination at  $300^\circ\text{C}$ . During this calcination, pores with a size distribution in the range of 1-5 nm were generated by removal of TEAOH mols. By employing the Au colloid-based and sonication-assisted method, in which lysine was used as the capping agent and sonication was employed to facilitate the deposition of the Au particles, it was possible to deposit very small Au particles (2-5 nm) into these pores. This method is rapid as the reaction/deposition is completed within 1 min. The prepared  $\text{Au/alpha-Fe}_2\text{O}_3$ -nanorod catalyst exhibited much higher catalytic activity than the  $\text{Au/com. alpha-Fe}_2\text{O}_3$  (Fluka) catalyst.

### 2.8 CO oxidation catalyzed by gold supported on MgO: spectroscopic identification of carbonate-like species bonded to gold during catalyst deactivation

MgO-supported gold prepared by adsorption of  $\text{Au}(\text{CH}_3)_2$  (acac) (acac is acetylacetonate) on partially dehydroxylated MgO was activated for  $\text{CO}$  oxidation catalysis by treatment in flowing helium at 473 K. X-ray absorption spectra showed that the activation involved reduction of the gold and formation of clusters (with an av. diam.  $<10 \text{ \AA}$ ) in which the gold was essentially zerovalent. Y Hao, M Mihaylov, E Ivanova, K Hadjiivanov, H Knoezinger, B Gates from the Department of Chemical Engineering and Materials Science, University of California, Davis, CA, 95616, USA, *Journal of Catalysis*, 2009, **261(2)**, 137.

During  $\text{CO}$  oxidation catalysis in a batch reactor, at least some of the gold was oxidized, as evidenced by the appearance of an Au .delta. + - $\text{CO}$  band at  $2151 \text{ cm}^{-1}$  in the IR (IR) spectrum. During operation in a flow reactor, the catalyst underwent deactivation, accumulating species such as carbonate and bicarbonate on its surface, as indicated by IR spectra. The accumulation of such species on the MgO support took place only during the initial period of operation of the catalyst, whereas the accumulation of such species on the gold continued throughout the operation, consistent with the inference that these species blocked catalytically

active sites on the gold. The catalyst was reactivated by decomposition of these species by treatment in helium at 473 K. After three activation-deactivation cycles, the average diameter of the supported gold clusters had increased to about 30 Å, and the catalytic activity increased. Thus, the results provide a resolution of the sep. effects on the catalytic activity of gold aggregation and accumulation of species such as carbonates and bicarbonates.

## 2.9 Genesis of a cerium oxide supported gold catalyst for CO oxidation: transformation of mononuclear gold complexes into clusters as characterized by X-ray absorption spectroscopy

CeO<sub>2</sub>-supported mononuclear gold species synthesized from Au(CH<sub>3</sub>)<sub>2</sub>(acac) catalyzed CO oxidation at 353 K, with a turnover frequency of 6.5 times. 10<sup>-3</sup> mols. of CO (Au atom s)<sup>-1</sup> at CO and O<sub>2</sub> partial pressures of 1.0 and 0.5 kPa, resp. V Aguilar-Guerrero, R Lobo-Lapidus, B Gates from Department of Chemical Engineering and Materials Science, University of California, Davis, CA, 95616, USA, *Journal of Physical Chemistry C* 2009, **113(8)**, 3259. As the catalyst functioned in a flow reactor, the activity increased markedly so that within about 10 h the conversion of CO had increased from about 1% to almost 100%. Activated catalyst samples were characterized by X-ray absorption spectroscopy and found to incorporate clusters of gold, which increased in size, undergoing reduction, with increasing time of operation. The X-ray absorption near-edge structure spectrum of the catalyst used for the longest period was indistinguishable from that characterizing gold foil. Extended X-ray absorption fine structure data characterizing the catalyst after the longest period of operation indicated the presence of clusters of approx. 30 Au atoms each, on av. The evidence that the catalytic activity increased as the clusters grew is contrasted with earlier reports pointing to increasing activity of supported gold clusters as they were made smaller in a cluster size range largely exceeding ours.

## 2.10 How gold deposition affects anatase performance in the photocatalytic oxidation of cyclohexane

Gold deposition on Hombikat UV100 was found to neg. affect the activity of this anatase catalyst in selective photooxidation of cyclohexane. J Carneiro, C Yang, J Moma, J Moulijn, G Mul, Catalysis Engineering, DelftChemTech, Delft University of Technology, Delft, 2628 BL, Netherlands, *Catalysis Letters* (2009), **129(1-2)**, 12. By ammonia TPD and DRIFT spectroscopy it was detd. that the Au deposition procedure leads to a significant decrease in OH-group d. (mol m<sup>-2</sup>BET) on Hombikat, suggesting that the amt. of surface OH-groups, rather than the presence or absence of Au, is detg. the catalytic performance. The importance of surface OH-groups was demonstrated by comparing the performance of Hombikat (with and without Au deposition)

to surface propoxylated TiO<sub>2</sub>, synthesized by a sol-gel method from titanium isopropoxide. The effect of the deposition recipe of noble metals on the surface compn. of TiO<sub>2</sub> should thus be taken into account in evaluating and explaining photocatalytic performance of TiO<sub>2</sub> modified by noble metals (Au), in particular in non-aqueous phase reactions.

## 2.11 Low-temperature preferential oxidation of CO in a hydrogen rich stream (Prox) over Au/TiO<sub>2</sub>: thermodynamic study and effect of gold-colloid Ph adjustment time on catalytic activity

By simulating CO and H<sub>2</sub> oxidns. at thermodyn. equil. and studying the catalytic oxidns. over Au/TiO<sub>2</sub>, preferential oxidation of CO in a H<sub>2</sub> rich stream (PROX) was investigated. W Yu, W Lee, C Yang, B Wan, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, *Journal of the Chinese Institute of Chemical Engineers* 2007, **38(2)**, 151. During the simulation, at least two cases under different gaseous feeds, H<sub>2</sub>/CO/O<sub>2</sub>/N<sub>2</sub> = 50/1/0.5/48.5 or 50/1/1/48 (vol.%) were examined under the assumption of an ideal gas and one atm. pressure in the reactor. It was found that the addition of 1% O<sub>2</sub> (the latter case) effectively reduced CO concentration to less than 100 ppm in the temperature range between 0 and 90°C. This range narrowed to between 0 and 50°C with the addition of 3% H<sub>2</sub>O and 15% CO<sub>2</sub> in the feed.

The thermodynamic study suggests that 1% CO in a H<sub>2</sub> rich system can be decreased to below 100 ppm within those low temperature ranges, if there is no substantial adsorptions onto the catalyst surface and the reactions rapidly reach equil. During the catalysis reaction study, a well-pH adjusted Au/TiO<sub>2</sub> catalyst was found very active for PROX. CO conversions at the reactor outlet were close to those at equil. Au/TiO<sub>2</sub> used in this work was prepared via deposition-pptn. (DP) method. The influence of gold colloid pH (at 6) adjustment time on gold loading, gold particle size and chloride residue on TiO<sub>2</sub> surface was detected by at. absorption (AA), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). A pH adjustment time of at least 6 h for the prepn. of gold colloids at room temperature was demonstrated to be essential for the high catalytic activity of Au/TiO<sub>2</sub>. This was attributed to the smaller gold particle and the less chloride residue on the catalyst surface.

## 3 Chemistry

### 3.1 Solubility switch of gold nanoparticles through hydrogen bond association

Gold nanoparticles (AuNPs) coated with hexafluoroisopropanol moieties were prepared, and their surface was changed through simple hydrogen bond assocn. with various amines, which allow orientation of the soly. of these AuNPs in detd. organic solvents. D Vuluga, J Legros, B Crousse, D Bonnet-

Delpon Laboratoire BioCIS-CNRS, Faculte de Pharmacie, Univ Paris Sud, Chatenay-Malabry, F-92296, France, *Chemical Communications* (Cambridge, United Kingdom) 2008, **40**, 4954

### 3.2 Influence of oxygen vacancies on the properties of ceria-supported gold

The adsorption of CO on nanosized gold particles deposited on a cerium oxide substrate is strongly influenced by the roughness and concentration of oxygen vacancies of the CeO<sub>x</sub> substrate surface. Literature showed that Au nucleates at step edges on oxidized samples. C Weststrate, R Westerstrom, E Lundgren, A Mikkelsen, J Andersen, A Resta, Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Lund, S-221 00, Sweden, *Journal of Physical Chemistry C* 2009, **113(2)**, 724. For oxidized samples the Au dispersion is dependent on the surface roughness. A rough CeO<sub>2</sub> surface has a higher step d., which results in a Au higher particle d. with a smaller av. diam. Other studies showed that Au nucleates on oxygen vacancies on reduced CeO<sub>x</sub> substrates. Small Au particles adsorbed on oxygen vacancies exhibit a significantly higher Au 4f binding energy than Au particles on oxidized CeO<sub>2</sub>. Relatively less CO adsorbs on small Au particles on a reduced substrate, with a significantly lower adsorption energy than on Au on an oxidized substrate. For larger particles the influence of oxygen vacancies in the substrate is negligible.

## 4 Electrochemistry

### 4.1 Interrogation of surfaces for the quantification of adsorbed species on electrodes: oxygen on gold and platinum in neutral media

The authors introduce a new in situ electrochemistry technique based on the scanning electrochemistry microscope (SECM) operating in a transient feedback mode for the detection and direct quantification of adsorbed species on the surface of electrodes. J Rodriguez-Lopez, M; Alpuche-Aviles, A Bard, Center for Electrochemistry, Department of Chemistry and Biochemistry, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, USA, *Journal of the American Chemical Society* 2008, **130(50)**, 16985. A SECM tip generates a titrant from a reversible redox mediator that reacts chemistry with an electrogenerated or chemistry adsorbed species at a substrate of about the same size as the tip, which is positioned at a short distance from it (.apprx.1 .mu.m). The reaction between the titrant and the adsorbate provides a transient pos. feedback loop until the adsorbate is consumed completely.

The sensing mechanism is provided by the contrast between pos. and neg. feedback, which allows a direct quantification of the charge neutralized at the substrate. The proposed technique allows quantification of the adsorbed species generated at the substrate at a given potential

under open circuit conditions, a feature not attainable with conventional electrochemistry methods. Also, the feedback mode allows the tip to be both the titrant generator and detector, simplifying notably the exptl. setup. The surface interrogation technique the authors introduce was tested for the quantification of electrogenerated oxides (adsorbed oxygen species) on gold and platinum electrodes at neutral pH in phosphate and TRIS buffers and with two different mediator systems. Good agreement is found with cyclic voltammetry at the substrate and with previous results in the literature, but the authors also find evidence for the formation of incipient oxides which are not revealed by conventional voltammetry. The mode of operation of the technique is supported by digital simulations, which show good agreement with the exptl. results.

### 4.2 Fabrication of gold nanoprism thin films and their applications in designing high activity electrocatalysts

A simple, 1-step wet chemistry method was developed for fabrication of closely packed Au nanoprism thin films (Au-PFs for short) on the In Sn oxide (ITO) coated glass substrates. W Li, H Ma, J Zhang, X Liu, X Feng, Key Laboratory for Colloid and Interface Chemistry of State Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, Peop. Rep. China, *Journal of Physical Chemistry C* 2009, **113(5)**, 1738. Most Au prisms have micrometer-scale edge length and nanometer-scale thickness (herein defined as nanoprism according to the thickness).

They are single cryst., whose basal surfaces are atomically flat {111} planes and lateral surfaces are {110} planes. The Au-PFs were further used as the substrate electrodes to construct bimetallic and trimetallic Au-based catalysts. A tiny amt. of Pt or Pd, the equiv. of a monolayer, was deposited onto the Au nanoprism thin film electrodes (Au-PFEs for short) by the underpotential deposition (UPD) of a Cu at. layer on the Au surfaces, followed by redox replacement of the UPD Cu with a Pt or Pd monolayer. Once after surface modification with a Pt monolayer, Au-PFEs exhibited greatly enhanced catalytic activity toward the electrooxidation of MeOH and much better poison resistance than com. Pt-based catalysts. The as-prepared bimetallic Au-Pt and trimetallic Au-Pd-Pt catalysts are expected to act as the promising electrocatalysts for the MeOH oxidation

### 4.3 Synthesis, characterization, luminescence, and electrochemistry of the tetranuclear gold(I) amidinate clusters, precursors to CO oxidation catalysts: Au<sub>4</sub>[(ArNC(H)NAr)]<sub>4</sub>, Au<sub>4</sub>[(PhNC(Ph)NPh)]<sub>4</sub> and Au<sub>4</sub>[(PhNC(CH<sub>3</sub>)NPh)]<sub>4</sub>

A review of the chemistry of the tetranuclear Au(I) amidinate complexes is presented. Tetranuclear Au(I) amidinate clusters are produced by the reaction of the Na salt of a amidine ligand with the Au precursor Au(THT)Cl in a (1:1) stoichiometry.



H Abdou, A Mohamed, J Fackler, Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A and M University, College Station, TX, USA, *Journal of the Chinese Chemical Society* (Taipei, Taiwan) 2007, **54(5)**, 1107. The structures of the tetranuclear  $Au_4[ArNC(H)NAr]_4$ , Ar = C<sub>6</sub>H<sub>4</sub>-4-OMe, C<sub>6</sub>H<sub>3</sub>-3,5-Cl, C<sub>6</sub>H<sub>4</sub>-4-Me, C<sub>6</sub>H<sub>4</sub>-3-CF<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>, C<sub>10</sub>H<sub>7</sub> and the tetranuclear  $Au_4[PhNC(Ph)NPh]_4$  and  $Au_4[PhNCMeNPh]_4$  were characterized by x-ray crystallog. The av. Au...Au distance between adjacent Au(I) atoms is .apprx.3.0 .ANG., typical of compds. having an aurophilic interaction. The four Au atoms are located at the corner of a rhomboid with the amidinate ligands bridged above and below the near plane of the four Au(I) atoms.

The angles at Au...Au in the cyclic units are 70-116°. The tetranuclear Au(I) amidinate clusters each show different luminescence behavior. The tetranuclear clusters  $Au_4[ArNC(H)NAr]_4$ , Ar = C<sub>6</sub>H<sub>4</sub>-4-OMe, Ar = C<sub>6</sub>H<sub>4</sub>-3-CF<sub>3</sub>, Ar = C<sub>6</sub>H<sub>4</sub>-4-Me and Ar = C<sub>6</sub>H<sub>3</sub>-3,5-Cl are the 1st tetranuclear Au(I) cluster species from Group 11 elements that show fluorescence at room temperature. The tetranuclear naphthyl deriv. Ar = C<sub>10</sub>H<sub>7</sub> is luminescent only at 77 K. The pentafluorophenyl deriv. Ar = C<sub>6</sub>F<sub>5</sub> does not show any photoluminescence in the solid state nor in the solution. The lifetimes of the naphthyl and trifluoromethylphenyl complexes are in the millisecond range indicating phosphorescent processes. Electrochemistry and chemistry oxidation studies of the tetranuclear Au(I) amidinate clusters are presented. The tetranuclear complexes  $Au_4[ArNC(H)NAr]_4$ , Ar = C<sub>6</sub>H<sub>4</sub>-4-OMe, Ar = C<sub>6</sub>H<sub>4</sub>-4-Me, and Ar = C<sub>6</sub>H<sub>3</sub>-3,5-Cl, show three reversible waves at 0.75, 0.95, 1.09 V vs. Ag/AgCl at a scan rate of 500 mV/s in 0.1M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> at a Pt working electrode in CH<sub>2</sub>Cl<sub>2</sub>. Three reversible waves at 0.87, 1.19, 1.42 V vs. Ag/AgCl at a scan rate of 100 mV/s are also observed for the tetranuclear complex  $Au_4[PhNC(Ph)NPh]_4$  in CH<sub>2</sub>Cl<sub>2</sub>. The pentafluorophenyl amidinate deriv.,  $Au_4[ArNC(H)NAr]_4$ , Ar = C<sub>6</sub>F<sub>5</sub> shows no oxidation wave <1.8 V. Recently  $Au_4[ArNC(H)NAr]_4$  is a very effective catalyst precursor for room temperature CO oxidation.

## 5 Electronics and sensors

### 5.1 Use of ultra-thin organic silane films for the improvement of gold adhesion to the silicon dioxide wafers for (Bio)sensor applications

A mono-functional silane reagent, 3-mercaptopropyltrimethoxysilane (MPS) was used to modify the surface of silicon wafers. M Ben Ali, F Bessueille, J Chovelon, A Abdelghani, N Jaffrezic-Renault, M Maaref, C Martelet, Institut Supérieur des Sciences, Appliquées et de Technologies, Sousse, Tunisia, *Materials Science & Engineering, C: Biomimetic and Supramolecular Systems*, 2008, **28(5-6)**, 628. The structure of the SAMs formed with the MPS was investigated by contact angle measurements, ellipsometry, AFM, and XPS.

The deposition of a metallic gold layer via ultra-high vacuum (UHV) evapn. reveals good adhesion properties on Au/MPS/SiO<sub>2</sub>/Si structure. The chemisorption between the SAM and the gold evapd. layer is confirmed by adhesion tests and optimum curing treatment is found 1 h at 100°C. This very simple methodol., avoiding the usage of Cr and other metals as undercoating layers and could be proposed further for (bio)sensors applications.

## 6 Medical and dental

### 6.1 PEGylated gold nanoparticle vehicles for targeted delivery of anti-cancer drug

There has been great interest in the development of nanoscopic therapeutic systems to improve drug delivery to target cancer cells, and the usefulness of a variety of nanoscale colloidal particles such as liposomes, polymeric micelles, silica nanoparticles, and gold nanoparticles (AuNP<sub>5</sub>) has been investigated. C Park, J Lee, H. Kim H Park, C Kim, Department of Polymer Science and Engineering, Inha University, Incheon, S. Korea, *PMSE Preprints* 2008, **99**, 531. The authors presented the use of a novel AuNP carrier as a therapeutic vehicle. The authors developed a novel AuNP, which is covered with CDs, PEG, and targeting antibody, to evaluate the capability as a carrier for a hydrophobic anticancer drug without chemistry modification of drug mols. The synergistic effect of AuNP carriers with 3-lapachone, which is a cancer selective anticancer agent, was evaluated. Since a variety of hydrophobic drugs can be easily encapsulated into the hydrophobic pocket of cyclodextrins, the multifunctional AuNP carriers described here can serve as a versatile nanoplatform for the delivery of anticancer drugs.

## 7 Metallurgy, materials and coatings

### 7.1 Highly stable localized plasmon transducers obtained by thermal embedding of gold island films on glass

Strongly bound and highly stable gold island films on glass are obtained by a simple, one-step prepn. procedure based on high-temperature annealing and partial embedding of gold nanostructures evapd. on glass, providing stable and effective localized plasmon transducers. T Karakouz, A Tesler, T Bendikov, A Vaskevich, I Rubinstein, Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100, Israel, *Advanced Materials (Weinheim, Germany)* 2008, **20(20)**, 3893.

### 7.2 Effects of gold nanoparticles on the fabrication of red colored high refractive index lead glass

Red colored gold ruby glass used for decorations in ancient times was actually gold nanotechnol. at work by the addition of gold particles into molten lead glass. P Dararutana,

J Dutchanephet, P Chetanachan, P Wathanakul, N Sirikulrat, The Royal Thai Army Chemical Department, Bangkok, Thailand *Advanced Materials Research (Zuerich, Switzerland)* (2008), **55-57**(Smart Materials), 601. Most of high refractive index glasses are based on lead-bearing silicate glass. High refractive index lead glasses (HRLG) made from local sands and lead oxide were successfully fabricated both in lab. and larger scales. In this study, gold metal was doped into the lead glass mixts. Morphol. of the prepared lead glass was observed using SEM and compared with that of the red colored Ancient Thai Glass (ATG). It was found that the fabricated red colored HRLG yielded similar color and clarity to the red colored ATG. From electron micrographs, the presence of gold in lead glass was in the form of nanoparticles. The optical properties of the glasses were also examined.

## 8 Nanotechnology

### 8.1 First observation of dynamic shape changes of a gold nanoparticle catalyst under reaction gas environment by transmission electron microscopy

The surface structure of catalytic gold nanoparticles was observed dynamically during CO oxidation using an environmental-cell transmission electron microscope (E-cell TEM) system. In the developed system, the gold catalyst specimen can be set under the reaction gas condition by sepg. it from the vacuum using ultra-thin carbon films. K Ueda, T Kawasaki, H Hasegawa, T Tanji, M Ichihashi, Department of Electrical Engineering and Computer Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan, *Surface and Interface Analysis* 2008, **40(13)**, 1725. We have developed a method capable of yielding for carbon films 8-nm thick, capable of withstanding a gas pressure of 2 atm. In situ observations using the above system indicated marked changes in the surface shape of the gold nanoparticle catalyst during the reaction.

### 8.2 Photochemical strategies for the synthesis of gold nanoparticles from Au(III) and Au(I) using photoinduced free radical generation

A comprehensive study of the ketone-photoinduced formation of gold nanoparticles (AuNPs) from gold ions in aqueous and micellar solution has been carried out. L Marin, K McGilvray, J Scaiano, Instituto de Tecnologia Quimica CSIC-UPV, Universidad Politecnica de Valencia, Valencia, 46022, Spain, *Journal of the American Chemical Society*, 2008, **130(49)**, 16572. Ketones are good photosensitizers for nanoparticle synthesis not because of the energy they can absorb or deliver but rather because of the reducing free radicals they can generate; thus, efficient nanoparticle generation requires a careful selection of substrates and exptl. conditions to ensure that free-radical generation occurs

with high quantum efficiency and that gold ion precursors do not cause UV screening of the org. photosensitizers. A key consideration in achieving AuNP synthesis with short exposure times is minimizing excited-state quenching by gold ions; this can be achieved by temporal or spatial segregation or a combination of the two.

Temporal segregation can be accomplished by using unimol. precursors, such as benzoin, that yield ketyl radicals from triplet precursors with lifetimes of a few nanoseconds. Spatial segregation can be achieved by using self-assembled structures such as micelles. In this case, the process can be assisted by selecting ketones with n, $\pi$ \* triplet states and by adding good hydrophobic hydrogen donors such as 1,4-cyclohexadiene. Systems involving bimol. reactions of ketones are catalytic in that the ketone is recovered at the end of the reductive process. Rate const. have been detd. for the quenching of excited triplets and for the scavenging of ketyl radicals by Au(I) and Au(III); in general, these values are within an order of magnitude of the rate const. for diffusion control. This article provides a paradigm for the photochemistry prodn. of nanoparticles of gold and other metal ions that highlights ten aspects that must be considered in order to design successful photochemistry systems for nanoparticle generation.

### 8.3 Synthesis and conductance measurement of periodic arrays of gold nanoparticles

We report a formation method and an elec. characterization of aligned arrays of Au nanoparticles (.apprx.20-40 nm). Y Kakefuda, K Narita, T Komeda, S Yoshimoto, S Hasegawa, IMRAM, Tohoku University, Sendai, 980-0877, Japan, *Applied Physics Letters* 2008, **93(16)**, 163103/1. We synthesized the structure by immersing a substrate vertically into a solvent with nanoparticle and letting the solvent evap. The periodicity of the arrays has been controlled in 10-40 .mu.m range by tuning the evapn. rate of solvent. The resistivity shows a drastic decrease (.apprx.10<sup>-4</sup>) when annealed at .apprx.170°C. While it is considerably due to a breakdown of ligands surrounding the Au particles, the large change in cond. should be used for sensors to examine the interface mols. between Au nanoparticles. (c) 2008 American Institute of Physics.

### 8.4 Influence of substrate morphology on the growth of gold nanoparticles

We have simulated the vacuum deposition and subsequent growth of gold nanoparticles on various substrates in order to explore the effects that substrate morphol. has on the resultant morphol. of gold nanoparticles. G Grochola, I Snook, S Russo, School of Applied Sciences, RMIT University, Melbourne, 3001, Australia, *Journal of Chemical Physics* (2008), **129(15)**, 154708/1. The substrates and conditions explored included, the three low index faces, namely, (111), (100), and (110) for both fcc and bcc cryst. substrate structures, including various substrate lattice const. and

temps. Firstly, we cataloged the major nanoparticle morphologies produced overall.

While some substrates were found to produce a mixt. of the main nanoparticle morphologies we were successful in identifying certain substrates and temperature conditions for which only 1h, Dh, or certain fcc cryst. nanoparticles can be grown almost exclusively. The substrate characteristics, temperature conditions, and governing growth dynamics are analyzed. We shed light on the balance between substrate influences and vacuum growth tendencies. From observations we can speculate that a substrate alters both the free energy stability of gold nanoparticles and/or the free energy barriers to transformation between certain morphologies. As such we find that substrates are an effective tool in templating the selective growth of desired nanoparticles or surface nanostructures. (c) 2008 American Institute of Physics.

### 8.5 Curvature-directed assembly of gold nanocubes, nanobranched, and nanospheres

Gold nanocubes, nanobranched, and nanospheres were prepared in high yields by using a seeded growth method in the presence of cationic surfactants. X Kou, Z Sun, Z Yang, H Chen, J Wang, Jianfang, Department of Physics, The Chinese University of Hong Kong, Peop. Rep. China, *Langmuir* 2009, **25(3)**, 1692. The resulting Au nanostructures are encapsulated with a surfactant bilayer and pos. charged. The nanocubes are single-crystal and enclosed with low-index facets. The nanobranched and nanospheres are multiply twinned. Each nanobranched possesses a varying no. of sharp tips which expose high-index facets. Glutathione was used to induce the assembly of the Au nanostructures, including both monocomponent (nanocubes and nanobranched) and bicomponent (nanocube-nanosphere and nanobranched-nanosphere) systems. The assembly occurred predominantly at the vertices of the nanocubes and sharp tips of the nanobranched. This curvature-directed assembly can be attributed to the preferential bonding of glutathione to the highly curved sites of the Au nanostructures. The fact that the curvature-directed assembly occurs for both the single-crystal nanocubes and multiply twinned nanobranched strongly suggests that the preferential bonding of glutathione to the curved sites is due to the less ordered surfactant bilayer at the curved sites than on the flat surfaces.

### 8.6 Preparation of gold nanoshell on core of carbon microspheres

This article reported a new method to synthesize Au nanoshell via carbon nanoparticle as the dielec. core. S Chen, C Wang, Key Laboratory of Molecular Engineering of Polymers (Ministry of Education), Department of Macromolecular Science, Fudan University, Shanghai, 200433, Peop. Rep. China, *Gaodeng Xuexiao Huaxue Xuebao* 2008, **29(6)**, 1090. The carbon nanoparticles were prepared through hydrothermal reaction of glucose and Au seeds. This carbon nanoparticles inherit reactive surfaces which facilitate the loading of Ag

nanoparticles, then the Ag nanoparticles act as the seeds for further reduction of chloroauric acid in the presence of cetyltrimethyl ammonium bromide (CTAB) and ascorbic acid to form a complete Au nanoshell on the surface of carbon nanoparticles (carbon nanoparticle as the core and Au layer as the shell). Successful forming of complete Au nanoshell was proved by transmission electron microscopy (TEM) and UV-Vis absorption spectra. The Au nanoshell shows a strong absorption in the range of near-IR (NIR). The exptl. results indicate that this method is a facile and effective way for the synthesis of Au nanoshell with NIR absorption properties.

### 8.7 Functionalized gold nanoparticles: synthesis, structure and colloid stability

A review. Gold nanoparticles and their arrays are some of the most studied nanomaterials, with promising applications in many fields such as electronics, optoelectronics, catalysis and biol. J Zhou, J Ralston, R Sedev, D Beattie, Ian Wark Research Institute, University of South Australia, Adelaide, SA5095, Australia, *Journal of Colloid and Interface Science* 2009, **331(2)**, 251. In order to protect bare gold nanoparticles from aggregation, to manipulate the optical, electronic and catalytic properties of the gold core, as well as to control interfacial properties, the gold nanoparticles are generally capped by an org. layer. Previous studies have revealed that many phenomena (e.g., wetting, friction and adhesion), are sensitive to the top few angstroms of a surface.

The interfacial properties of a gold surface derivatized with a self-assembled monolayer will thus be dictated by the functionalities present on the outer side of the monolayer. The synthesis, functionalization and surface structure of monolayer-protected gold nanoparticles have been intensively studied in recent times. In addition, the aggregation and dispersion of colloidal nanoparticles is one of the key issues related to their potential applications. The forces that govern the colloid stability of nanoparticle dispersions, and how to control them, have yet to be fully investigated. Here special attention has been paid to control of colloid stability using external stimuli. In this feature article, the following five areas are reviewed: synthesis and applications of nanostructured particles; formation and structure of self-assembled monolayer protected gold nanoparticles; colloid stability-DLVO and non-DLVO forces; photochemistry, photochromism and pyrimidine; and manipulation of colloid stability with external stimuli.

### 8.8 Advances and prospects of gold nanorods

A review. With the development of nanotechnol., many novel nanomaterials with unique properties such as magnetic, electronics, and photonics are increasingly being exploited. Gold nanorods, which are rod-shaped nanomaterials, show powerful potential in biol./biomedical fields, esp. photothermal therapy, biosensing, imaging, and gene delivery for the treatment of cancer. D Yang, D Cui, Department of Bio-Nano Science and Engineering, National

Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Institute of Micro and Nano Science and Technology, Shanghai Jiao Tong University, Shanghai, Peop. Rep. China, *Chemistry – An Asian Journal* 2008, **3(12)**, 2010. Many scientific groups have shown strong interests in gold nanorods and have attempted to push them towards possible clinical applications. However, owing to the quantum-size effects of nanomaterials, people have also raised some concerns about the potential toxicity hazards. Therefore, it is becoming urgent to study and exploit the biol. effects of gold nanorods for benefit in the near future.

## 9 Refining

### 9.1 New method of gold concentration and extraction from graphitic ores of the turgenevskoye deposit, primorye

The method of thiocarbamide solution usage for extraction and concentration of microscopic, fine, and ultrafine gold from carbonaceous rocks is suggested, which is more promising from the ecol. point of view than the cyanides usually used in gold mining. A Khanchuk, M Medkov, L Plyusnina, V Molchanov, Far East Geological Institute, Far East Division, Russian Academy of Sciences, Vladivostok, Russia, *Doklady Earth Sciences* 2008, **423(8)**, 1304. The methods of gold extraction from graphite ore presented may be also used successfully for creation of low-waste technol. for processing mineral resources.

### 9.2 Biogenic Sulfide for Cyanide Recycle and Copper Recovery in Gold-Copper Ore Processing

In the SART process (sulfidization-acidification-recycle-thickening), the cyanide associated with the copper cyanide complexes is released by NaHS dosing to ppt. copper and convert cyanide to HCN gas under weakly acidic conditions and allow it to be recycled back to the leach process as free cyanide. Copper is also recovered as a valuable, high-grade  $Cu_2S$  byproduct. Cyanide recycling allows the leach circuit to be operated at higher cyanide levels and maximize the leach efficiency and minimizing copper deportment to gold electrowinning. M Adams, R Lawrence, M Bratty, BioteQ Water (Australia) Pty Ltd., Guildford, WA, 6935, Australia, *Minerals Engineering* 2008, **21(6)**, 509.

The first com. plant is at Telfer in Western Australia. Biogenically produced hydrogen sulfide can be used to replace chemistry sulfide at significantly lower cost and with the added advantage of lowering the acid demand substantially. While the capital cost of a biogenic SART plant is higher than a cyanide detoxification plant, this will be more than offset by the revenues generated by copper recovery and savings realized by cyanide recycle which allows for a short pay-back time on the incremental capital. BioteQ is

currently working with Columbia Metals Corporation Ltd., Canada, to apply its sulfide generating and pptn. technol. in a SART circuit at both of Columbia's gold projects in Northern Mexico. Processing of ores from both mines has presented challenges resulting from cyanide-sol. copper. The BioteQ biogenic SART process technol., economics and com. status as well as environmental and operating outcomes are reviewed.

### 9.3 Experimental study on retreatment for recovery of gold and zinc from tailings

Flotation for recovery gold and zinc from the tailings of certain processed gold sulfide ores was carried out. J Lu, Zijin Design and Research Institute of Mining and Metallurgy, Shanghang, Fujian Province, Peop. Rep. China, *Youse Jinshu, Xuankuang Bufen*, 2007, **(1)**, 13-15, 8. By adopting the flowsheet of closed-cycle flotation of single-stage gold roughing, single-stage gold cleaning, three-stage gold scavenging, single-stage zinc roughing single-stage zinc cleaning and three-stage zinc scavenging, gold conc. contg. 27.25 g/t with recovery of 86.03% and zinc conc. contg. zinc 56.84% with recovery of 79.90% were obtained.

### 9.4 Leaching of gold and silver from crushed Au-Ag wastes

Au-Ag noble metal wastes represent a wide range of waste types and forms with various ballast elements and components. The thiourea process of gold and silver extraction from ores, concentrates or secondary raw materials consists of gold and silver leaching into the thiourea solution and the consequent precipitation of these metals from the solution J Ficeriova, P Balaz, E Dutkova, E Gock, Institute of Geotechnics of the SAS, Kosice, 043 53, Slovakia, *Open Chemical Engineering Journal* 2008, **2**, 6. Due to the non-toxic character of thiourea it is the perspective alternative to the up to now most frequently used cyanide method. The thiourea leaching of gold and silver from electronic waste, goldsmith's waste and ceramic waste using crushing as the pretreatment step was investigated. For electronic waste, it was possible to achieve 97% gold and 94% silver recovery within 120 min of thiourea leaching. Up to 98% of gold and 96% of silver were recovered from goldsmith's waste after 60 min of leaching. In the case of ceramic waste, we achieved up to 98% gold and 97% silver extraction efficiency after only 45 min of leaching. In comparison with the classical cyanide leaching, thiourea leaching acts faster and without a harmful.

### 9.5 Kinetic and equilibrium effects in gold ore cyanidation

Cyanide leaching of two West African gold ores was studied in multiple labs. to provide process-engineering data for plant design purposes. M Brittan, Gold Fields, International Development Projects, Englewood, CO, USA, *Minerals & Metallurgical Processing* 2008, **25(3)**, 117. Unusually slow



leach extraction kinetics were observed by using routine cyanide leach test procedures with pregnant solution monitoring. Carbon-in-leach testing, however, showed normal rapid kinetic behavior, with the same ultimate gold extractions being reached in much shorter elapsed times. Kinetic curves based on washed solids assays also exhibited more typical leaching characteristics. The results bore all the hallmarks of some equil. inhibition of the leaching. Ore gangue components were responsible for a weakly adsorbing gold-cyanide complex reaction product, thereby holding up sol. gold in the solid phase. The term preg-borrowing was coined to describe the reversible phenomenon and distinguish it from irreversible preg-robbing. The two ores investigated may represent an extreme form of a more general effect that in most instances might pass unnoticed. The effect can lead to misinterpretation of kinetic leach curve data and underestimation of calculated ore head grades.

### 9.6 Recovery of gold from hydrochloric acid by means of selective coagulation with persimmon extract

Gold was selectively pptd. from other metals with a solution of persimmon ext. which contains persimmon tannin, a kind of polyphenol. H Kawakita, R Yamauchi, D Parajuli, K Ohto, H Harada, K Inoue, Department of Applied Chemistry, Saga University, Saga, Japan, *Separation Science and Technology* 2008, **43(9-10)**, 2375. Quant. recovery of gold was achieved in the HCl concentration range  $<0.5 \text{ mol/dm}^3$ . X-ray diffraction analysis and a digital micrograph of the filtered cake indicated the formation of gold particle during the recovery process. High selectivity of the persimmon ext. is ascribed to the reduction of Au(III) to elemental form.

### 9.7 Experimental research on nitric acid oxidation extracting technique of gold concentrate

An exptl. research on nitric acid oxidation pretreatment of refractory gold conc. was carried out in Dongbeizhai gold mine. R He, Riying, Zijin Mining Group Co., Ltd., Shanghang, Fujian Province, 364200, Peop. Rep. China, *Huangjin* 2007, **28(5)**, 36. After nitric acid oxidation pretreatment, S, As, Fe and other non-ferrous metal was extd. into the lixivium, and could be precipitated with lime. The gold recovery rate of the oxidized residue could reach 95.56%.

## 10 General

### 10.1 Visual cocaine detection with gold nanoparticles and rationally engineered aptamer structures

A bioassay strategy is designed to detect small-mol. targets such as cocaine, potassium, and adenosine, based on gold nanoparticles and engineered DNA aptamers. J Zhang, L Wang, D Pan, S Song, F Boey, H Zhang, C Fan, Shanghai Institute of Applied Physics, Chinese Academy of Sciences,, Shanghai, 201800, Peop. Rep. China, *Small* 2008, **4(8)**, 1196. In this design, an aptamer is engineered to be two pieces of random, coil-like single-stranded DNA, which reassembles into the intact aptamer tertiary structure in the presence of the specific target. Au nanoparticles can effectively differentiate between these two states via their characteristic surface-plasmon resonance-based color change. Using this method, cocaine in the low-micromolar range is selectively detected within minutes. This strategy is also generic and applicable to the detection of several other small-mol. targets.

### 10.2 Transfer printing of 3D hierarchical gold structures using a sequentially imprinted polymer stamp

Complex three-dimensional (3D) hierarchical structures on polymeric materials are fabricated through a process referred to as sequential imprinting. F Zhang, H Low, Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 117602, Singapore, *Nanotechnology* 2008, **19(41)**, 415305/1-415305/5. In this work, the sequentially imprinted polystyrene film is used as a soft stamp to replicate hierarchical structures onto gold (Au) films, and the Au structures are then transferred to a substrate by transfer printing at an elevated temperature and pressure. Continuous and isolated 3D structures can be selectively fabricated with the assistance of thermo-mech. deformation of the polymer stamp. Hierarchical Au structures are achieved without the need for a corresponding three-dimensionally patterned mold.