

Highlights from recent literature

1 Analytical

1.1 3 D Characterization of gold nanoparticles supported on heavy metal oxide catalysts by HAADF-stem electron tomography

Living on the edge: Three-dimensional reconstructions from electron tomog. data recorded from Au Ce_{0.50}Tb_{0.12}Zr_{0.38}O_{2-x} catalysts show that gold nanoparticles are preferentially located on stepped facets and nanocrystal boundaries. J Gonzalez, J Hernandez, M Lopez-Haro, E del Rio; J Delgado, A Hungria, S Trasobares, S Bernal, P Midgley, J Calvino from the Departamento de Ciencia de los Materiales e Ingenieria Metalurgica y Quimica Inorganica, Facultad de Ciencias, Universidad de Cadiz, Spain, *Angewandte Chemie*, International Edition 2009, **48(29)**, 5313. An epitaxial relationship between the metal and support plays a key role in the structural stabilization of the gold nanoparticles.

2 Catalysis

2.1 Biomass into chemicals: One pot-base free oxidative esterification of 5-hydroxymethyl-2-furfural into 2,5-dimethylfuroate with gold on nano particulated ceria

Di-Me 2,5-furandicarboxylate (DMF) is a valuable biomass derived that can replace oil dependent PET polymers. 5-Hydroxymethyl-2-furfural (HMF) has been selectively converted into DMF (99 mol% yield) under mild conditions (65-130°C, 10 bar O₂) in the absence of any base, by using gold nanoparticles on nanoparticulated ceria. O Casanova, S Iborra, A Corma, Instituto de Tecnologia Quimica (UPV-CSIC), Universitat Politecnica de Valencia, Valencia, Spain. *Journal of Catalysis*, 2009, **265(1)**, 109. The catalyst can be reused several times without any loss of activity or selectivity. The absence of metal leaching has been checked by the three-phase test. A full reaction scheme has been established and it has been found that the rate-limiting step of the reaction is the alc. oxidation into aldehyde. After this, the reaction proceeds via aldehyde conversion into hemiacetal and further oxidation into the corresponding ester. Additionally, the effect of temperature, substrate-to-catalyst ratio, alcohol and

water has been studied in an attempt to explain the catalytic behavior of the Au-CeO₂.

2.2 Gold supported on hydroxyapatite as a versatile multifunctional catalyst for the direct tandem synthesis of imines and oximes

Two birds with one auric stone: The title system acts as a highly efficient heterogeneous catalyst for the one-pot tandem synthesis of imines or oximes from alcohols and the corresponding amines under mild conditions. H Sun, FZ Su, J Ni, Y Cao, HY He, KN Fan, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai, Peop. Rep. China, *Angewandte Chemie*, International Edition, 2009, **48(24)**, 4390.

2.3 Robust gold-decorated silica-titania pebbles for low-temperature CO catalytic oxidation

A deposition-pptn. (DP) process was used to synthesize SiO₂/TiO₂ core-shell pebbles decorated with nano-cryst. Au suitable for low-temperature catalytic CO oxidation S Lim, N Phonthammachai, Z Zhong, J Teo, T White from the School of Materials Science and Engineering, Nanyang Technological University, Singapore, *Langmuir*, 2009, **25(16)**, 9480. Micro-structure, phase content, crystallog., and catalytic activity were correlated with pH (3-8), aging time (15, 30, 60 min), and heat treatment used for Au crystn. (200-400.degree.). A homogeneous metal distribution, high Au load (3.7-4.4 wt. percent), and superior interfacial adhesion between Au and TiO₂ were obtained when the support pebbles were prepd. at 600.degree., a temperature lower than that required for the anatase-to-rutile transformation. Nucleation and growth of {111} faceted Au was favored at mid-pH (6.4-8); smaller crystals (<7.5 nm) were obtained at short aging times (.ltoreq.60 min) and low growth temps. (.ltoreq.300.degree.). Catalytic activity was optimized by homogeneously dispersing Au nano-crystals (3 nm) at pH 6.4 and 30-min aging time. These robust materials may offer superior activity and lifetimes when deployed in fluidized bed catalytic cracking units.

2.4 Shape and size controlled .alpha.-Fe₂O₃ nanoparticles as supports for gold-catalysts: Synthesis and influence of support shape and size on catalytic performance

Synthesis of shape- and size-controlled .alpha.-Fe₂O₃ nano-particles was done using an amino acid-assisted hydrothermal method. Products were

characterized by transmission electron microscopy and x-ray diffraction. G Wang, W Li, K Jia, B Spliethoff, F Schueth, A Lu, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116012, Peop. Rep. China, *Applied Catalysis, A: General*, 2009, **364(1-2)**, 42. The type of amino acid significantly affected the shape and size of α - Fe_2O_3 nano-particles. Acidic amino acids typically led to formation of α - Fe_2O_3 nano-particles with spindle shape; however, rhombohedral-shaped α - Fe_2O_3 nano-particles were formed when basic amino acids were used. When colloidal Au nano-particles were deposited on the α - Fe_2O_3 nano-particle surface, Au/ α - Fe_2O_3 catalysts displayed substantial differences in catalytic activity for CO oxidation with differently-shaped α - Fe_2O_3 nano-particle supports. Generally, spindle-shaped Au/ α - Fe_2O_3 had higher catalytic activity than catalysts based on rhombohedral Fe_2O_3 . Under catalytic test conditions with a spindle-shaped Au/ α - Fe_2O_3 catalyst, large hematite crystals induced higher catalytic activity than smaller crystals; for rhombohedral Au/ α - Fe_2O_3 catalysts, medium-sized α - Fe_2O_3 nano-crystals exhibited high catalytic activity for CO oxidation.

2.5 Selective oxidation of methanol to hydrogen over gold catalysts promoted by alkaline-earth-metal and lanthanum oxides

A series of alumina-supported gold catalysts was investigated for the CO-free production of hydrogen by partial oxidation of methanol. The addn. of alk. earth metal oxide promoters resulted in a significant improvement of the catalytic performance. B Hereijgers, B Weckhuysen, Inorganic Chemistry and Catalysis Group, Debye Institute for NanoMaterials Science, Utrecht University, Utrecht, Netherlands. *ChemSusChem*, 2009, **2(8)**, 743. The methanol conversion was $\approx 85\%$ with all studied catalyst materials, however, the selectivity for hydrogen increased from 15% to 51% when going from the unpromoted to a BaO-promoted catalyst. The formation of the undesired byproducts CO, methane, and di-Me ether was considerably reduced as well. The observed trend in catalyst performance follows the trend in increasing basicity of the studied promoter elements, indicating a chem. effect of the promoter material. Superior catalytic performance, in terms of H_2 and CO selectivity, was obtained with a Au/ La_2O_3 catalyst. At 300.degree. the hydrogen selectivity reached 80% with only 2% CO formation, and the catalyst displayed a stable performance over at least 24 h onstream. Furthermore, the formation of CO was found to be independent of the oxygen

concentration in the feed. The com. lanthanum oxide used in this study had a low sp. surface area, which led to the formation of relative large gold particles. Therefore, the catalytic activity could be enhanced by decreasing the gold particle size through deposition on lanthanum oxide supported on high-surface-area alumina.

2.6 N-Formylation of amines via the aerobic oxidation of methanol over supported gold nanoparticles

Gold nanoparticles supported on NiO catalyze the one-pot N-formylation of amines with methanol and mol. oxygen to produce formamides at a selectivity of 90%. T Ishida, M Haruta from the Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo, Japan, *ChemSusChem*, 2009, **2(6)**, 538. This process generates Me formate in situ, followed by reaction with amines.

2.7 Catalytic activity of gold nanocluster catalyst protected by poly(N-vinyl-2-pyrrolidone)

A review. H Sakurai, T Tsukuda from the Research Center for Molecular Scale Nanoscience, Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki, Japan, *Yuki Gosei Kagaku Kyokaiishi*, 2009, **67(5)**, 517. Gold (Au) clusters smaller than 2 nm and stabilized by poly(N-vinyl-2-pyrrolidone) (Au:PVP) show higher activity for aerobic oxidation such as alc. oxidation, α -hydroxylation of benzylic ketones, and homocoupling of boronates as well as for non-oxidative (formal Lewis acidic) reactions including intramol. hydroalkoxylation/amination of non-activated alkenes. Physical measurements revealed that the catalytically active gold clusters are neg. charged by electron donation from PVP and the catalytic activity is enhanced with increasing neg. charge on the gold core. Partial electron transfer from the anionic gold clusters of Au:PVP into the LUMO (π^*) of O_2 generates superoxide-like or peroxide-like species and the Lewis acidic center, both of which play an important role in the above catalytic activity.

2.8 Engine exhaust catalysts containing palladium-gold

An emission control catalyst that exhibits improved CO and HC reduction performance includes a supported platinum-based catalyst, and a supported palladium-gold catalyst. The two catalysts are coated onto different layers, zones, or monoliths of the substrate for the emission control catalyst such that

the platinum-based catalyst encounters the exhaust stream before the palladium-gold catalyst. Zeolite may be added to the emission control catalyst as a hydrocarbon absorbing component to boost the oxidation activity of the palladium-gold catalyst. The inventors have enabled the use of supported catalysts comprising palladium and gold species as emission control catalysts by overcoming the problem which they have discovered through tests that HC species present in the exhaust inhibit the oxidation activity of such catalysts. Publication number: US2009214396 (A1) Publication date: 27th Aug 2009, Inventor(s): KL Furdala T Truex. With the present invention, such HC inhibition effects are reduced sufficiently by exposing the exhaust to the platinum-based catalyst before the palladium-gold catalyst and/or by adding a hydrocarbon absorbing material, so that the oxidation activity of the palladium-gold catalyst can be improved and the overall catalytic activity of the emission control catalyst can be boosted to effective levels. The inventors have confirmed through vehicle performance tests that the emission control catalysts according to embodiments of the present invention perform as well as platinum-palladium catalysts in reducing CO and HC emissions from a vehicle.

2.9 Propene epoxidation with dioxygen catalyzed by gold clusters

Gold clusters (<2.0 nm), but not gold nanoparticles, deposited on alkaline-treated titanosilicalite-1 allow O₂ and H₂O to react to give hydroperoxides (-OOH). H Jiahui, A Tomoki, F Jérémy, F Tadairo, T Takashi, H Masatake Haruta, *Angewandte Chemie*, **48**, 42, 7862. These transfer to neighboring Ti sites to form Ti-OOH (see scheme), which is responsible for propene epoxidation to give propene epoxide (PO). Gold catalysis: benzanellation versus alkylidenecyclopentenone synthesis. A series of different furan-yn-ols were prepared by a three-step sequence. Their reaction with Gagosz's catalyst Ph₃PAuNTf₂ depends strongly on the substitution pattern of the substrate and the quality of the leaving group. SK Hashmi, M Wölfle, *Tetrahedron*, **65(44)**, 9021. Benzofurans, alkylidenecyclopentenones or Meyer-Schuster type products can be obtained. Improving the leaving group quality leads to the preferred formation of benzofurans.

3 Chemistry

3.1 The effect of aniline concentration in the ligand exchange reaction with citrate-stabilized gold nanoparticles

Sodium citrate reduction of hydrogen tetrachloroaurate is one of the most efficient routes in the synthesis of gold nanoparticles. However, a major limitation of this method is that it results only in citrate-stabilized Au nanoparticles, and exchange reactions of the citrate for another stabilizer must be undertaken in cases where other surface functionalities are desired. These exchange reactions can be studied by using a variety of techniques. J Newman, W MacCrehan, Analytical Chemistry Division, National Institute of Standards and Technology, Gaithersburg, MD, USA, *Langmuir* 2009, **25(16)**, 8993. Two techniques used for anal. are (1) UV-visible spectroscopy, which takes advantage of the plasmon resonance of Au nanoparticles (2) liq. chromatog. to examine a residual exchanger in the supernatant liq. at equil. Exchange of the citrate on the surface of Au nanoparticles with aniline was studied in which different concns. of aniline are added. While the equil. plasmon resonance band spectra were similar for high and low concentrations of added aniline, the spectra as a function of time differed markedly. Surprisingly, increasing the concentration of added aniline slowed the evolution of a second red-shifted band. TEM imaging showed that the addn. of neither high nor low concns. of aniline caused a significant difference in particle size, and the appearance of the large second band was most likely due to an oligomeric aniline species surrounding the particles. As aniline is known to undergo polymn. under a variety of conditions, it is postulated that aniline polymn. is a competitive event to the ligand exchange process, and increasing the aniline concentration increases the likelihood of polymn. kinetically competing with association of the aniline species interacting with the Au nanoparticle surface. This behavior was further supported by liq. chromatog. data, which demonstrated that the aniline exchanged at .apprx.4% of the initial amt. of citrate present in the synthetic mixt.

3.2 Gold nanoparticles under gas pressure

The influence of CO mol. adsorption on the thermodynamically favored at-scale structures of Au nanoparticles is studied theor. K McKenna, Department of Physics and Astronomy, London Centre for Nanotechnology, University College London, London, WC1E 6BT, UK, *Physical Chemistry Chemical Physics*, 2009, **11(21)**, 4145. Nanoparticle

free energies are calcd. using an embedded atom model potential in conjunction with a simple statistical mechanics model allowing nanoparticles contg. up to 10,000 atoms (7 nm diam.) to be simulated. The sequence of high stability morphologies with increasing no. of atoms is modified from (decahedral .fwdarw. icosahedral .fwdarw. Marks-decahedral .fwdarw. truncated octahedral) in vacuum to (octahedral.fwdarw. Marks-decahedral .fwdarw. truncated octahedral) under gas pressure. As well as being of fundamental interest, these effects are relevant to applications in gas sensing and heterogeneous catalysis.

4 Electrochemistry

4.1 Effects of linker molecules on the attachment and growth of gold nanoparticles on indium tin oxide surfaces

As a linker mol. to attach Au nanoparticles (AuNPs) on In Sn oxide (ITO) surfaces, cysteamine was examd. together with known 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminopropyltrimethoxysilane (APTMS). M Oyama, A Orimo, K Nouneh, Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, Japan, *Electrochimica Acta*, 2009, **54(22)**, 5042. Systematic comparisons of AuNPs' nanostructures formed on ITO were carried out after the room temperature treatment in an EtOH soln. of linker mols. followed by the attachment of AuNPs using (i) 1-step immersion into the 20-nm Au colloidal solution or (ii) 2-step immersion, i.e., a seed-mediated growth treatment. Consequently, in case (i), APTMS was most effective for denser and homogeneous attachment of AuNPs on ITO surfaces with keeping the dispersion. With the MPTMS or cysteamine linkers in case (i), AuNPs aggregated on the ITO surfaces, and the attached amt. of AuNPs were larger with the MPTMS linker. But in case (ii), nanostructural growth of AuNPs was possible with MPTMS or cysteamine using the seed-mediated growth, while the growth of AuNPs was significantly suppressed with the APTMS linker. Because quite different results were obtained between APTMS and cysteamine, the attachment and nanostructural growth of AuNPs on the org. linker layers cannot be simply governed by the functional groups, $-NH_2$, on the outer surfaces.

4.2 Size-dependent electrochemical properties of gold nanorods

Electrochem. properties of Au electrodes sequentially modified by self-assembled 1,6-hexanedithiol (1,6HDT) and Au nanorods (AuNRs) were studied by cyclic voltammetry, square-wave voltammetry, and electrochem. impedance spectroscopy, using $[Fe(CN)_6]^{3-/4-}$ as redox probes. M Chirea, A Cruz, C Pereira, AF Silva, CIQ-UP L4 Faculdade de Ciencias, Universidade do Porto, Oporto, Portugal, *Journal of Physical Chemistry C*, 2009, **113(30)**, 13077. The nanorods stabilized by cetyltrimethylammonium bromide (CTAB) with aspect ratios of 2.20, 2.80, and 3.77 were grown by a seed-mediated procedure and chem. bonded to the 1,6HDT-coated electrodes by a place exchange reaction at a 27.degree. soln. temperature Topog. tapping mode at. force microscopy measurements revealed an end bonding of the 2.20 aspect ratio rods and a side surface bonding of the 2.80 and 2.77 aspect ratio rods. Analysis of the electrochemical responses as a function of the sizes and surface orientations of the rods revealed that the electron transfer is faster at electrodes modified with smaller and vertically aligned nanorods than those modified with larger and randomly attached nanorods (side surface bonding). A progressive increase in the charge transfer resistance RCT from bilayers composed of 1,6HDT and 2.20 aspect ratio rods to bilayers composed of 1,6HDT and rods of 2.80 or 3.77 aspect ratios is described by a tunneling parameter of $\beta = 1.07$ per thiol chain unit. This behavior suggests that the electron transfer kinetics is controlled by coherent electron tunneling across the 1,6HDT monolayer. The several orders of magnitude changes of the apparent charge transfer resistance upon nanorod adsorption suggest a charging of the rods by the redox probes in soln. and electron transfer across them. The electron transfer proceeds via a 3-step process: charging of the rods by the redox probes in solution, electron transport across the rods, and electron tunneling across the 1,6HDT-SAM toward the underlying Au substrates.

5 Electronics and sensors

5.1 Understanding the electronic properties of molecule/metal junctions: The case study of thiols on gold

In this work, the author reviews his recent results on the electronic properties of thiolate/metal interface. Work function change, mol. level alignment and

interfacial state formation of the methylthiolate/Au(111) and dimethyl-disulfide/Au(111) interfaces are investigated by UPS and XPS. V De Renzi, INFM Center for nanoStructures and bioSystem at Surfaces and Dipartimento di Fisica, Universita di Modena e Reggio Emilia, Modena, Italy, *Surface Sciencem*, 2009, **603**(10-12), 1518. A complete picture of the electronic properties of both the dimethyl-disulfide (DMDS) weakly-adsorbed and the methylthiolate (MT) chemisorbed phases is obtained by direct quant. comparison between the expt. and theory. The modifications of the electronic properties of the DMDS thin film, induced by a MT buffer layer are also discussed. Moreover, the cysteine/Au(111) system is investigated as an example of interface formed by mols. with large intrinsic dipole moment. Finally, surface inhomogeneity and its influence on the interface electronic properties is briefly discussed, in light of the important concept of local work function.

5.2 Investigation of gold nanoparticle inks for low-temperature lead-free packaging technology

Gold nanoparticle inks were investigated as a potential candidate for lead-free packaging applications. Inks consisted of surfactant-passivated nanoparticles dissolved in a solvent. T Bakhishev, V Subramanian, Department of Electrical Engineering and Computer Science, University of California, Berkeley, CA, USA, *Journal of Electronic Materials*, Published online: 18th August 2009. Optimized gold inks are able to sinter at temperatures as low as 120°C and achieve conductivities of up to 70% of bulk. Once sintered, the metallic structure reverts to bulk-like properties and approaches bulk reliability and performance. Thus nanoparticle-based solders would operate at much lower homologous temperatures as compared with alloy-based solders. Nanoparticle inks under investigation were sintered at 180°C. The resulting material exhibited a resistivity of 5 $\mu\Omega$ cm, which is significantly lower than those of Pb-Sn and Sn-Ag-Cu. Electromigration studies were carried out and time to failure was investigated as a function of temperature. Electromigration activation energy was calculated through Black's equation to be 0.52 eV, which is consistent with surface/grain boundary diffusion. These studies suggest that nanoparticle-ink-based films show excellent robustness, due to their irreversible conversion to bulk-like materials. Nanoparticle inks are thus promising candidates for next-generation lead-free solders.

5.3 Gold helix photonic metamaterial as broadband circular polarizer

The authors investigated propagation of light through a uniaxial photonic metamaterial composed of three-dimensional gold helices arranged on a two-dimensional square lattice. J Gansel, *Science*, 2009 **325**, 1513. These nanostructures are fabricated via an approach based on direct laser writing into a positive-tone photoresist followed by electrochemical deposition of gold. For propagation of light along the helix axis, the structure blocks the circular polarization with the same handedness as the helices, whereas it transmits the other, for a frequency range exceeding one octave. The structure is scalable to other frequency ranges and can be used as a compact broadband circular polarizer.

5.4 Cross-interaction between Au/Sn and Cu/Sn interfacial reactions

The cross-interaction between Sn/Cu and Sn/Au interfacial reactions in an Au/Sn/Cu sandwich structure was studied. Y Yen, H Tseng, K Zeng, S Wang, C Liu, *Journal of Electronic Materials* **38**, 11. Field-emission electron probe microanalysis (FE-EPMA) revealed that the Cu content in the three Au-Sn phases (AuSn , AuSn_2 , and AuSn_4) was very low, less than 1 at.%. This means that Cu from the opposite Cu foil did not participate in the interfacial reaction at the Sn/Au interface. On the opposite Sn/Cu side, Au-substituted $(\text{Cu,Au})_6\text{Sn}_5$ formed within the initial 1 min of reflow. With prolonged reflow, the Au content in the Au-substituted $(\text{Cu,Au})_6\text{Sn}_5$ increased and it transformed into a Cu-substituted $(\text{Au,Cu})\text{Sn}$ phase with 25 at.% Cu after 1 min of reflow at 250°C. The x-ray diffraction (XRD) pattern confirmed the phase transformation of Au-substituted $(\text{Cu,Au})_6\text{Sn}_5$ to Cu-substituted $(\text{Au,Cu})\text{Sn}$ phase. In addition, there was greater Au consumption in the Au/Sn/Cu sandwich joint structure than in the single Au/Sn reaction case, due to some of the Au participating in the opposite Sn/Cu interfacial reaction.

6 Medical and dental

6.1 Gold nanoparticles in nanomedicine: preparations, imaging, diagnostics, therapies and toxicity

This critical review provides an overall survey of the basic concepts and up-to-date literature results concerning the very promising use of gold nanoparticles (AuNPs) for medicinal applications. E Boisselier, D Astruc, Didie, Institut des Sciences Moleculaires, UMR CNRS Universite Bordeaux I,

Talence, France, *Chemical Society Reviews*, 2009, **38(6)**, 1759. It includes AuNP synthesis, assembly and conjugation with biol. and biocompatible ligands, plasmon-based labeling and imaging, optical and electrochem. sensing, diagnostics, therapy (drug vectorization and DNA/gene delivery) for various diseases, in particular cancer (also Alzheimer, HIV, hepatitis, tuberculosis, arthritis, diabetes) and the essential in vitro and in vivo toxicity. It will interest the medicine, chemistry, spectroscopy, biochemical, biophysics and nanoscience communities (211 refs.).

7 Metallurgy, materials and coatings

7.1 Surface observation for seed-mediated growth attachment of gold nanoparticles on a glassy carbon substrate

A seed-mediated growth method for surface modification was applied to the attachment of gold nanoparticles (AuNPs) to glassy carbon (GC) surfaces. M Oyama, S Yamaguchi, J Zhang, Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo, Kyoto, Japan, *Analytical Sciences*, 2009, **25(2)**, 249. By simply immersing a GC plate at first into a seed soln. contg. 4 nm Au nano-seed particles and then into a growth soln. contg. HAuCl_4 , ascorbic acid and cetyltrimethylammonium bromide, AuNPs could be successfully attached to the GC surface via the growth of nanoparticles. A possible control of the size and d. of AuNPs on GC was examd. by observing surface images with a field-emission scanning electron microscope (FE-SEM) after several preps. with different immersion times. Compared with previous results on the growth of AuNPs on indium tin oxide (ITO) surfaces, it was characteristic that the AuNPs attached to GC surfaces exhibited smaller size and higher d. as well as a flatter and non-crystal-like morphol. In addn., for performing the dense attachment of regular nano-sized AuNPs on GC surfaces, immersion for 2 h into the growth soln. was sufficient. Longer immersion for 24 h caused an irregular growth of bold Au micro-crystals, while 24 h was necessary in the case of AuNPs on ITO surfaces. Shorter seeding and growth times were found to be effective for a sparse attachment of smaller Au nanoparticles whose size was ca. 20 nm. It was clarified that the seed-mediated growth method for surface modification was valid for fabricating a nanointerface composed of AuNPs on GC surfaces.

8 Nanotechnology

8.1 Preparation of gold microparticles using halide ions in bulk block copolymer phases via photoreduction

Gold microparticles were prepared from a gold salt in the solid bulk phase of a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer via a photoreduction process in the presence of halide ions. S Cha, K Kim, W Lee, J Lee, Department of Chemical and Biological Engineering, Seoul National University, Seoul, Shilim-9-Dong, Gwanak-Gu, S. Korea, *Journal of Solid State Chemistry*, 2009, **182(6)**, 1575. The shape and size of the gold microparticles were dependent on the type and amt. of halide ions as well as the type of cation used due to the combined effects of the adsorption power and oxidative dissolution ability of the additives on the gold surfaces. Gold nanorods were obtained when poly(ethylene oxide) was used instead of the block copolymer. Evidently the poly(propylene oxide) part in the block copolymer is essential for the formation of gold microparticles, even though the degree of the direct interaction between the blocks and gold salt is not significant.

8.2 One-step synthesis and characterization of gold-hollow pbSX hybrid nanoparticles

Syntheses of hollow hybrid nanostructures of PbS_x -Au of .apprx.10 nm are presented using a 1-step reaction under mild exptl. conditions. J Yang, J Peng, Q Zhang, F Peng, H Wang, H Yu, Department of Chemical Engineering, South China University of Technology, Guangzhou, 510640, Peop. Rep. China, *Angewandte Chemie, International Edition* 2009, **48(22)**, 3991. The redox reaction of Au precursors with PbS nanocrystals in the presence of dodecylamine leads to the hollow feature of hybrid nanostructures. These hybrid nanoparticles are characterized by transmission electron microscope (TEM), selected area electron diffraction (SAED), energy dispersive x-ray spectroscopy (EDS), and XPS. The resultant hybrid nanostructures are built by solid Au and hollow PbS_x (nonstoichiometric lead sulfide) nanoparticles.

8.3 Honey mediated green synthesis of gold nanoparticles

Bio-directed synthesis of nanoparticles is of interest to biologists, chemists and materials scientists. The biosynthesis of gold nanoparticles has been carried out by several groups of scientists by using plants, fungi and bacteria. D Philip, Department of Physics, Mar Ivanios College, Thiruvananthapuram,

India, *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, 2009, **73A**(4), 650. Now a greener synthesis of Au nanoparticles is reported by using natural honey as a reducing and capping agent. By adjusting the concns. of HAuCl_4 and honey in aq. solns., colloids having a larger propensity of either anisotropic or spherical nanocrystals could be obtained at room temperature. The nanoparticles obtained were characterized by UV-visible spectra, high-resoln. TEM and XRD. The spherical particles obtained had a diam. of .apprx.15 nm as shown by XRD patterns and TEM images. The high crystallinity with the fcc. phase is evidenced by bright circular spots in SAED pattern and clear lattice fringes in the high-resoln. TEM image. FTIR measurements were carried out to identify the possible biomols. responsible for capping and efficient stabilization of the Au nanoparticles synthesized using honey. The carboxylic acid group vibrations and amide I and II bands indicate the binding of protein with Au surfaces through the amine group rather than the carboxyl group.

8.4 A washing-free and amplification-free one-step homogeneous assay for protein detection using gold nanoparticle probes and dynamic light scattering

In this study, we developed a one-step, washing-free and amplification-free assay for protein analysis using gold nanoparticle probes (GNPs) and dynamic light scattering (DLS) technique. X Liu and Q Huo, *Journal of Immunological Methods*, 2009, **349**, 1, 38. The target protein concentration was determined by analyzing the level of GNP aggregation caused by antibody-antigen interactions using DLS. Two formats of assays were designed for mouse IgG detection. In the first format of assay, mouse IgG was directly mixed with GNPs conjugated to goat anti-mouse IgG. Due to the multiple binding sites of primary mouse IgG by the secondary antibody, mouse IgG caused nanoparticle aggregation. Mouse IgG can be detected at a concentration as low as 0.5 ng/mL and the dynamic range of this assay is between 0.5 and 50 ng/mL. A second format of assay developed in this study is a competitive assay conducted by using both mouse IgG and goat anti-mouse IgG conjugated GNPs. In this assay format, mouse IgG was detected within a dynamic range of 100 ng/mL to 10 $\mu\text{g/mL}$. The CV% of these assays is generally well within 10%. In conclusion, we demonstrated here that by using GNPs as a light scattering enhancer and selecting the proper assay formats, low cost, easy-to-conduct, and highly sensitive bioassays can be developed for protein detection and analysis.

8.5 Microstructure changes in nanoparticulate gold films under different thermal atmospheres and the effects on bondability

Sintering in a furnace under different thermal atmospheres of air, nitrogen (N_2) or N_2 bubbled through formic acid (FA/N_2) was carried out for a spin-coated gold nanoparticle (NP) ink. Temperatures of 200, 250 and 290°C were applied for each atmosphere. J Seonhee J Jaewoo, Y Oh, Electro Material and Device (eMD) Center, Central R&D Institute, Samsung Electro-Mechanics Co. Ltd., 314 Maetan3-Dong, Yeongtong-Gu, Suwon, Gyunggi-Do South Korea, *Acta Materialia*, 2009, **57**, (18), 5613. The size of the NPs was measured by transmission electron microscopy and the decomposition temperatures of the solvent and the organic capping molecules of the ink were determined by thermo-gravimetric analysis. The changes in the microstructure of Au NP films after sintering were studied using the field emission scanning electron microscopy, X-ray diffractometry, atomic force microscopy and focused ion beam analysis. Organic residues remaining on the film were detected by Fourier transform infrared spectroscopy and sheet resistance was measured using a four point probe for the calculation of resistivity. Wire bonding tests on the Au film were performed for bondability. The Au NP films sintered under air showed neck growth as temperature increased, while the films sintered under N_2 showed grain growth, except for the film sintered at 290°C. Coalescence and grain growth as well as porosity were observed in the film sintered under FA/N_2 . The infrared absorption peaks of stretch and deformation were found as organic residues, with C-O stretch peak only being detected in the film sintered under FA/N_2 . All of the samples represented a preferred Au (111) orientation. The film sintered under N_2 showed good quality compared with those sintered under air or FA/N_2 and the resistivity was about twice the bulk value. Wire bonding tests were successful in all the films sintered under air, N_2 or FA/N_2 atmospheres.

8.6 Characterization and performance of nucleic acid nanoparticles combined with protamine and gold

Macromolecular nucleic acids such as DNA vaccines, siRNA, and splice-site switching oligomers (SSO) have vast chemotherapeutic potential. R DeLong, U Akhtar, M Sallee, B Parker, S Barber, J Zhang, M Craig, R Garrad, A Hickey, E Engstrom, *Biomaterials*, 2009, **30**, (32), 6451. Nanoparticulate biomaterials hold promise for DNA and RNA delivery when a means for binding is identified that retains

structure–function and provides stabilization by the nanoparticles. In order to provide these benefits of binding, we combined DNA and RNA with protamine – demonstrating association to gold microparticles by electrophoretic, gel shot, fluorescence, and dynamic laser light spectroscopy (DLLS). A pivotal finding in these studies is that the Au–protamine–DNA conjugates greatly stabilize the DNA; and DNA structure and vaccine activity are maintained even after exposure to physical, chemical, and temperature-accelerated degradation. Specifically, protamine formed nanoparticles when complexed to RNA. These complexes could be detected by gel shift and were probed by high throughput absorbance difference spectroscopy (HTADS). Biological activity of these RNA nanoparticles (RNPs) was demonstrated also by a human tumor cell splice-site switching assay and by siRNA delivery against B-Raf – a key cancer target. Finally, RNA:protamine particles inhibited growth of cultured human tumor cells and bacteria. These data provide new insights into DNA and RNA nanoparticles and prospects for their delivery and chemotherapeutic activity.

8.7 Demonstration of a spaser-based nanolaser

One of the most rapidly growing areas of physics and nanotechnology focuses on plasmonic effects on the nanometre scale, with possible applications ranging from sensing and biomedicine to imaging and information technology. However, the full development of nanoplasmonics is hindered by the lack of devices that can generate coherent plasmonic fields. MA Noginov, G Zhu, AM Belgrave, R Bakker, VM Shalaev, EE Narimanov, S Stout, E Herz, T Suteewong & U Wiesner, *Nature*, 2009, **460**, 1110. It has been proposed that in the same way as a laser generates stimulated emission of coherent photons, a ‘spaser’ could generate stimulated emission of surface plasmons (oscillations of free electrons in metallic nanostructures) in resonating metallic nanostructures adjacent to a gain medium. But attempts to realize a spaser face the challenge of absorption loss in metal, which is particularly strong at optical frequencies. The suggestion to compensate loss by optical gain in localized and propagating surface plasmons has been implemented recently and even allowed the amplification of propagating surface plasmons in open paths. Still, these experiments and the reported enhancement of the stimulated emission of dye molecules in the presence of metallic nanoparticles lack the feedback mechanism present in a spaser. Here we show that 44-nm-diameter nanoparticles with a gold core and dye-doped silica shell allow

us to completely overcome the loss of localized surface plasmons by gain and realize a spaser. And in accord with the notion that only surface plasmon resonances are capable of squeezing optical frequency oscillations into a nanoscopic cavity to enable a true nanolaser, we show that outcoupling of surface plasmon oscillations to photonic modes at a wavelength of 531nm makes our system the smallest nanolaser reported to date and to our knowledge the first operating at visible wavelengths. We anticipate that now it has been realized experimentally, the spaser will advance our fundamental understanding of nanoplasmonics and the development of practical applications.

8.8 Model for UV induced formation of gold nanoparticles in solid polymeric matrices

UV irradiation of polymeric PMMA films containing HAuCl₄ followed by annealing at 60–80°C forms gold nanoparticles directly within the bulk material. N Sapogova and N Bityurin, *Applied Surface Science*, 2009, **255**, (24), 9613. The kinetics of nanoparticle formation was traced by extinction spectra of nanocomposite film changes vs annealing time. We propose that UV irradiation causes HAuCl₄ dissociation and thus provides a polymeric matrix with atomic gold. The presence of an oversaturated solid solution of atomic gold in the polymeric matrix leads to Au nanoparticle formation during annealing. This process can be understood as a phase transition of the first order. In this paper we apply several common kinetic models of the phase transition for describing Au nanoparticle formation inside the solid polymer matrix. We compare predictions of these models with the experimental data and show that these models cannot describe the process. We propose that the stabilization effect of the matrix on the growing gold nanoparticles is important. The simplest model introducing some probability for the transition from growing nanoparticle to the non-growing, stabilized form is suggested. It is shown that this model satisfactorily describes the experimentally observed evolution of the extinction spectrum of Au nanoparticles forming in a polymer matrix.

8.9 Synthetically programmable dna binding domains in aggregates of DNA-functionalized gold nanoparticles

Nanoparticles that assemble into core/shell aggregate structures comprising thermally addressable, phase-separated DNA binding domains are designed. S Hurst, H Hill, R Macfarlane, J Wu, V Dravid, C Mirkin, *Small*, **5**, 19, 2156. Since the strength of the DNA binding in these domains differs,

these aggregate systems exhibit two distinct melting transitions upon dehybridization resulting from the stepwise disassociation of the entire structure. These materials are ideal for probing the structure-function relationship of DNA-linked nanoparticle aggregates.

8.10 Gold nanoparticle based surface-enhanced raman scattering spectroscopy of cancerous and normal nasopharyngeal tissues under near-infrared laser excitation

The capabilities of using gold nanoparticle based near-infrared surface-enhanced Raman scattering (SERS) to obtain biochemical information with high spatial resolution from human nasopharyngeal tissue were presented in this paper. S Feng, J Lin, M Cheng, Y Li, G Chen, Z Huang, Y Yu, R Chen, H Zeng, *Applied Spectroscopy* 2009, **63**, Issue 10, pages 268A, 1089 The gold nanoparticles used have a mean diameter of 43 nm with a standard deviation of 6 nm. The SERS bands of nasopharyngeal tissue were assigned to known molecular vibrations of nucleic acids, amino acids, proteins, and metabolites. We also observed the blinking phenomenon at the tissue level when measuring the nasopharyngeal tissue SERS spectra, most frequently in signal intensity but also occasionally in peak positions. This phenomenon is excitation light intensity dependent. This work demonstrated great potential for using SERS imaging for distinguishing cancerous and normal nasopharyngeal tissues on frozen sections without using any dye labeling or other chemical species as functionalized binding sites.

8.11 Electrocatalysis on gold nanostructures: Is the {1 1 0} facet more active than the {1 1 1} facet?

The anisotropic electrocatalytic properties of gold nanobelts and nanoplates enclosed by either {110} or {111} facets were studied. Different strategies were used to synthesize these materials. It was found that the {110} surface of gold does not necessarily show a higher electrocatalytic activity than the {111} surface. Y Chen, W Schuhmann and A Hassel, *Electrochemistry Communications* 2009, **11**, (10), 2036. The {110} surface of gold is more active than the {111} surface for glucose oxidation in both, neutral and alkaline media. However, for methanol oxidation in alkaline solution, the {110} surface shows a lower activity than the {111} surface, which is contrary to the general belief that {110} facet is the most active surface among the three basal planes. The possible mechanisms are discussed.

8.12 Gold and silver nanoparticles conjugated with heparin derivative possess anti-angiogenesis properties

Silver and gold nanoparticles display unique physical and biological properties that have been extensively studied for biological and medical applications. M Kemp, A Kumar, S Mousa, E Dyskin, M Yalcin, P Ajayan, R Linhardt, SA Mousa, *Nanotechnology*, 2009, **20**, (45), 5104. Typically, gold and silver nanoparticles are prepared by chemical reductants that utilize excess toxic reactants, which need to be removed for biological purposes. We utilized a clean method involving a single synthetic step to prepare metal nanoparticles for evaluating potential effects on angiogenesis modulation. These nanoparticles were prepared by reducing silver nitrate and gold chloride with diaminopyridinyl (DAP)-derivatized heparin (HP) polysaccharides. Both gold and silver nanoparticles reduced with DAPHP exhibited effective inhibition of basic fibroblast growth factor (FGF-2)-induced angiogenesis, with an enhanced anti-angiogenesis efficacy with the conjugation to DAPHP ($P < 0.01$) as compared to glucose conjugation. These results suggest that DAPHP-reduced silver nanoparticles and gold nanoparticles have potential in pathological angiogenesis accelerated disorders such as cancer and inflammatory diseases.