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HIGHLIGHTS FROM RECENT LITERATURE

Highlights from recent literature

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Each issue of *Gold Bulletin* contains key highlights from the research and patent literature. Authors who publish high quality work in other journals are invited to send a copy of their publication to the Editor for inclusion in the next issue.

Nanotechnology

Visualization of latent fingermarks by nanotechnology: reversed development on paper—a remedy to the variation in sweat composition

A team at the Hebrew University of Jerusalem has developed a new procedure in which "negative" fingermarks are developed on paper by the application of gold nanoparticles that are capped by a bifunctional ligand. The head of this molecule is an acylpyridazine group, which can bind to cellulose. The tail is made of hydrocarbon chains with a sulfur-containing group at the end, which binds to gold and attaches the molecule to the surface of the gold nanoparticles. Treatment with a developer containing silver, which turns the areas with gold on them to black, results in a negative image of the fingerprint. This approach may contribute to the successful recovery of latent fingermarks by law enforcement agencies (Angew Chem Int Ed, DOI: 10.1002/anie.201205259).

The direct writing and focusing of nanoparticles generated by an electrical discharge

In this paper, the authors demonstrate a new method for direct writing of nanoparticles at ambient air pressure. An electrical discharge was used to generate gold nanoparticles of the order of 10 nm diameter, which were then transported and "focused" by an electric field in air, through the process of electric field-assisted diffusion, as opposed to normal ballistic focusing since the mean free path in air is very short. This process is novel and allows for practical normal atmospheric pressure-focused deposition of nanoparticles (Journal of Nanoparticle Research, vol. 14, no. 11 (2012), p. 1220, DOI: 10.1007/s11051-012-1220-y).

Temperature dependence of the surface plasmon resonance in gold nanoparticles

The temperature dependences of energy and width of the surface plasmon resonance were studied for gold nanoparticles with sizes 20–55 nm in a silica host matrix in the temperature range 17–915 °C. The increase of temperature leads to appreciable red shift and broadening of the surface plasmon resonance in Au nanoparticles. The thermal expansion was shown to be the main mechanism responsible for the temperature-induced red shift (Surf Sci, http://dx.doi.org/10.1016/j.susc.2012.10.019).

Bilayered Raman-intense gold nanostructures with hidden tags for high-resolution bioimaging

Conventional surface-enhanced Raman spectroscopy (SERS) probes reportedly suffer from limited brightness and poor reproducibility and stability making them unsuitable for routine in vivo applications. The authors demonstrate a novel class of layered SERS probes in which individual nanostructures host electromagnetic hot spots, thus increasing brightness by more than 2 orders magnitude compared to conventional individual nanostructures (Adv Mater, DOI: 10.1002/adma.201203415).

Optical response of plasmonic relief meta-surfaces

A team from Southampton University, UK has reported on the functionality of continuously metallic meta-surfaces for

optical magnetic reflection, perfect absorption, and active photonic switching/sensing. They used gold surfaces patterned with arrays of sub-wavelength surface features to couple incident light into localized plasmon modes, thereby modifying the intensity and phase of reflected light in effect changing the color of gold into a range of other colors (J Optic, vol. 14, no. 11, DOI:10.1088/2040-8978/14/11/114002).

Light-triggered biocatalysis using thermophilic enzyme–gold nanoparticle complexes

According to a multidisciplinary team at Rice University, the use of plasmonic nanoparticle complexes for biomedical applications such as imaging, gene therapy, and cancer treatment is a rapidly emerging field expected to significantly improve conventional medical practices. In contrast, the use of these types of nanoparticles to noninvasively trigger biochemical pathways has been largely unexplored. In this paper, they report the light-induced activation of the thermophilic enzyme *Aeropyrum pernix* glucokinase, a key enzyme for the decomposition of glucose via the glycolysis pathway, increasing its rate of reaction 60 % with light by conjugating the enzyme onto Au nanorods. The observed increase in enzyme activity corresponded to a local temperature increase within a calcium alginate encapsulate of 20 °C when compared to the bulk medium maintained at standard, non-thermophilic temperatures. The encapsulated nanocomplexes were reusable and stable for several days, making them potentially useful in industrial applications. This approach could significantly improve how biochemical pathways are controlled for in vitro and, quite possibly, in vivo use (ACS Nano, Article ASAP, DOI: 10.1021/nn3048445, publication date (web): December 13, 2012).

The quest for shape control: a history of gold nanorod synthesis

The development of facile seeded growth syntheses for anisotropic gold nanoparticles (particularly gold nanorods) has spurred an interest in their optical properties and applications. The development of the first seeded growth synthesis for gold nanorods in 2001 was a transformative event, providing the first simple, convenient wet chemistry route to these nanomaterials. Over the past decade, the original seeded growth procedure has been the subject of further modifications that have continuously expanded researchers' access to anisotropic gold nanoparticles. Recent modifications to the synthesis have improved synthetic control over gold nanorod aspect ratio, increased synthesis up to the gram scale, and provided the opportunity to tightly control the absolute dimensions of AuNRs. Despite these advances, the mechanism of gold nanorod growth in this synthesis remains poorly understood. Recent investigations into gold nanorod growth mechanisms have revealed the process to be unexpectedly complex, suggesting that many different reagents interact synergistically to promote shape control, and that growth of the AuNR core may proceed by complex processes, such as stochastic nanorod growth. Nevertheless, the advent of new in situ characterization techniques promises to shortly reveal new insights into gold nanorod core growth and may inform further significant modifications, improving the efficiency and versatility of seeded growth synthesis. In this review, Samuel Lohse and Catherine Murphy from the University of Illinois recount the history of the seeded growth synthesis for gold nanorods and examine the impact of recent advances in this synthesis and current investigations into the mechanism of gold nanorod growth. See Lohse & Murphy, Chem Mater, Article ASAP, DOI: 10.1021/cm303708p, February 2013.

A plasmonic DNAzyme strategy for point-of-care genetic detection of infectious pathogens

Signal amplification from DNAzymes was combined with gold nanoparticles to give a simple and sensitive colorimetric assay for various genetic targets. The authors, based at the University of Toronto, report that the assay has 50 pM sensitivity without the need for purification steps and can detect multiple targets in parallel. This was applied to rapidly detect gonorrhea, syphilis, malaria, and hepatitis B infections. See Zagorovsky & Chan, Angewandte Chemie, Early View, DOI: 10.1002/anie.201208715, February 2013

A comparison study of gold nanohexapods, nanorods, and nanocages for photothermal cancer treatment

Gold nanohexapods represent a novel class of optically tunable nanostructures consisting of an octahedral core and six arms grown on its vertices. By controlling the length of the arms, their localized surface plasmon resonance peaks could be tuned from the visible to the near-infrared region for deep penetration of light into soft tissues. Here, a team led by Younan Xia in Missouri have compared the in vitro and in vivo capabilities of Au nanohexapods as photothermal transducers for theranostic applications by benchmarking against those of Au nanorods and nanocages. While all these Au nanostructures could absorb and convert near-infrared light into heat, Au nanohexapods exhibited the highest cellular uptake and the lowest cytotoxicity in vitro for both the as-prepared and PEGylated nanostructures. In vivo pharmacokinetic studies showed that the PEGylated Au nanohexapods had significant blood circulation and tumor accumulation in a mouse breast cancer model. Following photothermal treatment, substantial heat was produced in situ and the tumor metabolism was greatly reduced for all these Au nanostructures, as determined with ^{18}F-flourodeoxyglucose

positron emission tomography/computed tomography. Combined together, they conclude that Au nanohexapods are promising candidates for cancer theranostics in terms of both photothermal destruction and contrast-enhanced diagnosis. See Wang et al., ACS Nano, Article ASAP, DOI: 10.1021/nn304332s, February 2013.

Enhancement of dye-sensitized photocurrents by gold nanoparticles: effects of plasmon coupling

Plasmonic metal nanoparticles are known to work as light-harvesting antennae and to enhance photocurrents of photovoltaic cells and reaction rates of photocatalysts. The effects are expected to increase the energy conversion efficiency and to reduce the thickness of a light-absorbing layer and costs for materials. In this work, a team of Japanese researchers examined the plasmonic enhancement of dye-sensitized photocurrents by Au nanoparticle ensembles with different particle densities to study the effects of interparticle plasmon coupling on the photocurrent enhancement. The coupling effects allow enhancement in a longer wavelength region. The optimum particle size for the enhancement by coupled nanoparticles is 100 nm, whereas that for isolated nanoparticles is 40 nm because the plasmon coupling effect is more significant for larger nanoparticles. Theoretical calculations reproduce those results. See Kawawaki et al., J Phys Chem C, Article ASAP, DOI: 10.1021/jp3120836, January 2013

Biomimetic, synthetic HDL nanostructures for lymphoma

New therapies that challenge existing paradigms are needed for the treatment of cancer. A multidisciplinary team led by Shad Thaxton report (see Yang et al., PNAS, 2013, vol. 110, no. 7, pp. 2511–2516) a nanoparticle-enabled therapeutic approach to B cell lymphoma using synthetic high-density lipoprotein nanoparticles (HDL-NPs). HDL-NPs are synthesized using a gold nanoparticle template to control conjugate size and ensure a spherical shape. Like natural HDLs, biomimetic HDL-NPs target scavenger receptor type B-1, a high-affinity HDL receptor expressed by lymphoma cells. Functionally, compared with natural HDL, the gold NP template enables differential manipulation of cellular cholesterol flux in lymphoma cells, promoting cellular cholesterol efflux and limiting cholesterol delivery. This combination of scavenger receptor type B-1 binding and relative cholesterol starvation selectively induces apoptosis. HDL-NP treatment of mice bearing B cell lymphoma xenografts selectively inhibits B cell lymphoma growth. As such, HDL-NPs are biofunctional therapeutic agents, whose mechanism of action is enabled by the presence of a synthetic nanotemplate. HDL-NPs are active in B cell lymphomas and, potentially, other malignancies or diseases of pathologic cholesterol accumulation.

Use of functionalized gold nanoparticles to assay uranium

French researchers report the use of particular functionalized gold nanoparticles to determine the presence and/or assay the amount of uranium in a solution. After the functionalized gold nanoparticles have been placed in the solution, the assay may especially be carried out by spectrophotometry. The invention also relates to a kit that can be used for uranium assays in situ in the field. See WO2013017784 (A1).

Electronics

Giant stretchability of thin gold films on rough elastomeric substrates

Stretching metallic conductors to large deformations while maintaining a low and constant electrical resistance is one of the main challenges in stretchable electronics technologies. Here, the authors report the conservation of conductivity for deformations of up to 100 % in 80 and 500 nm thick gold films deposited on rough polydimethylsiloxane substrates. By combining the roughness effect with prestretching of the substrate during deposition, a fine-scale random wrinkling morphology develops and the stretchability was enhanced even further. The stretchability was also improved by increasing the thickness of the film. A high number of large deformation cycles were accommodated without electrical failure (Acta Materialia, http://dx.doi.org/10.1016/j.actamat.2012.10.001)

Gold- and palladium-induced embrittlement phenomenon in microbumps with Au/Pd(P)/Ni(P) metallization pads

In this study (J Electron Mater, December 2012, vol. 41, issue 12, pp. 3266–3275), the microstructural evolution of Sn-3Ag-0.5Cu/Au/Pd(P)/Ni(P) microbumps during isothermal aging was examined. The results of this study show that appropriate deposition of Au/Pd(P)/Ni(P) is very important for the thermal/mechanical reliability of microbumps.

Development and evaluation of direct deposition of Au/Pd(P) bilayers over Cu pads in soldering applications

The thermal reliability of Sn-3Ag-0.5Cu/Au/Pd(P)/Cu solder joints was evaluated in this study (J Electron Mater, December 2012, vol. 41, issue 12, pp. 3276–3283). After reflow and subsequent solid-state aging (180 °C), the reaction product species at the interface included Cu_6Sn_5 [or $(Cu,Pd)_6Sn_5$] and Cu_3Sn, and their growth was strongly dependent on the Pd(P) thickness, $\delta_{Pd(P)}$. The findings suggest that direct deposition of Au/Pd(P) bilayers over the Cu pads can effectively modify the mechanical reliability of solder joints

Metallurgy

Grain growth inhibition in thin nanocrystalline Au films by grain boundary diffusion and oxidation of Ti

The authors studied grain growth in thin nanocrystalline Au films. Stabilization of an Au layer could be attributed to thermal grain boundary grooves on the Au surface filled with Ti oxide. The grooves exhibited an elongated morphology characterized by a low apparent dihedral angle value, atypical for thermal grain boundary grooves in pure metals. The authors demonstrated that grooves with this morphology are very efficient in pinning grain boundary motion and developed a quantitative model of grain boundary grooving coupled with grain boundary interdiffusion in thin bilayer films (Acta Materialia, vol. 61, issue 2, January 2013, pp. 529–539, DOI: org/10.1016/j.actamat.2012.09.076).

Diffusion mechanism in the gold–copper system

A study of interdiffusion has been conducted in the Au-Cu system, which has complete solid solution in the higher temperature range and ordered phases in the lower temperature range. Initial experiments were conducted at higher temperatures, where atoms can diffuse randomly. Higher values of interdiffusion coefficients were found in the range of 40–50 at % Cu. This trend was explained with the help of thermodynamic factor and possible concentration of vacancies (J Mater Sci Mater Electron, December 2012, vol. 23, issue 12, pp. 2152–2156).

18-karat gray gold

The Swiss group Cendres & Metaux describes an alloy of 18-karat white gold comprising by weight at least 75 % gold between 13 and 23 % Cr and between 2 and 12 % of Pd and at least one element selected from Fe, Ru, Pt, Co, Ga, Ge, Mn, and Ni. The alloy is characterized by a yellowness index less than 10, thus presenting a white color comparable to that of gold rhodium. The alloy also has a good polishing making it particularly attractive for applications in jewelry and watches. The invention also relates to a timepiece, jewelry, or a writing instrument, comprising at least one component made of said alloy. See EP2546371 (A1).

Catalysis

Small gold clusters formed in solution give reaction turnover numbers of 10^7 at room temperature

According to a team from Instituto de Tecnología Química in Spain (Science, 2012, vol. 338, no. 6113, pp. 1452–1455, DOI: 10.1126/science.1227813), very small gold clusters (three to ten atoms) formed from conventional gold salts and complexes can catalyze various organic reactions at room temperature, even when present at concentrations of parts per billion. Absorption and emission ultraviolet–visible spectroscopy and matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry revealed that, for example, the ester-assisted hydration of alkynes began only when clusters of three to five gold atoms were formed. The turnover numbers and turnover frequencies associated with these catalyzed reactions can be as high as 10^7 and 10^5 per hour, respectively. Indeed, these results may open the door for future industrial applications beyond fine chemicals, which are typically produced in smaller scale.

Air purification by gold catalysts supported on PET nonwoven fabric

A new filter-type Au/ZrO_2 catalyst was fabricated by using poly (ethylene terephthalate) (PET) nonwoven fabric as a support according to a team of Japanese researchers led by Masatake Haruta (Appl Catal B Environ, 2013, http://dx.doi.org/10.1016/j.apcatb.2012.12.018). Owing to its flexibility, thinness, lightness, and easy handling, this form of a catalyst is advantageous in practical use for air purification over the existing catalyst forms such as pellets and honeycombs. Zirconium oxide fine particles were first deposited on PET nonwoven fabric in the presence of 3-methacryloxypropyltrimethoxysilane to form a thin layer like a fish scale and then gold nanoparticles (NPs) were deposited on ZrO_2 fine particles by deposition–precipitation method. The catalyst was active enough at room temperature and oxidized 1,000 ppm CO and removed 140 ppm HCHO in air. The catalytic activity of Au/ZrO_2 supported on PET nonwoven fabric was also measured under similar conditions to those for practical air purification in offices and houses for the oxidation of 0.5 ppm HCHO and high HCHO conversion (close to 100 %) was maintained up to 136 h.

Hydrodechlorination catalysis of Pd-on-Au nanoparticles varies with particle size

Trichloroethene (TCE), a common carcinogen and groundwater contaminant in industrialized nations, can be catalytically degraded by Au nanoparticles partially coated with Pd ("Pd-on-Au NPs"). In this work, a collaborative team led by Michael Wong at the Rice University synthesized Pd-on-Au NPs using 3, 7, and 10 nm Au NPs with Pd surface coverages between 0 and 150 % and studied how particle size and composition influenced their TCE hydrodechlorination activity. They observed volcano-shape dependence on both Au particle size and Pd surface coverage, with 7 nm Au NPs with Pd coverages of 60–70 % having maximum activity. Using extended X-ray absorption fine-structure spectroscopy,

the team found a strong correlation between catalytic activity and the presence of 2-D Pd ensembles (as small as two to three atoms). Aberration-corrected scanning transmission electron microscopy further confirmed the presence of Pd ensembles. The Pd dispersion and oxidation state generally changed from isolated, metallic Pd atoms to metallic 2-D Pd ensembles of varying sizes, and to partially oxidized 3-D Pd ensembles, as Pd surface coverage increased. These changes occurred at different surface coverages for different Au particle sizes. These findings highlight the importance of controlling particle size and surface coverage in bimetallic catalysts. See Pretzer et al., J Catal, vol. 298, February 2013, pp. 206–217

Heterogeneous, composite, carbonaceous catalyst system and methods that use catalytically active gold

Heterogeneous catalyst systems, methods of making these systems, and methods of using these systems, wherein catalytically active gold is deposited onto composite support media are described in patent US2013039836 (A1) by a team at 3M. The composite support media is formed by providing nanoporous material on at least a portion of the surfaces of carbonaceous host material. In representative embodiments, relatively fine, nanoporous guest particles are coated or otherwise provided on surfaces of relatively coarser activated carbon particles. Catalytically active gold may be deposited onto one or both of the guest or host materials either before or after the guest and host materials are combined to from the composite host material. PVD is the preferred catalyst system of depositing gold

Gold complexes

Gold(I) hydroxide complexes of the form Z-Au-OH and di-gold complexes of the form Z-Au-([mu]OH)-Au-Z where groups Z are two electron donors are described in patent US2013035322 (A1) by a team from the University of St Andrews. The groups Z may be carbenes, for example, nitrogen-containing heterocyclic carbenes, phosphines, or phosphites. The complexes can be used as catalysts, for example, in reactions such as hydration of nitriles, skeletal arrangement of enynes, alkoxycyclization of enynes, alkyne hydration, the Meyer–Shuster reaction, 3,3′ rearrangement of allylic acetates, cyclization of propargylic acetates, Beckman rearrangements, and hydroamination. The complexes can be used in medicine, for example, in the treatment of cancer.

Nanosized gold catalysts for CO oxidation and water gas shift reactions

Methods of making supported monolithic gold (Au) catalysts that can be used for generating a hydrogen-rich gas from gas mixtures containing carbon monoxide, hydrogen, and water via a water gas shift reaction, and for the removal of carbon monoxide from air at a low reaction temperature via its oxidation reaction, are described in EP2539069 (A1). It includes methods of making highly dispersed gold catalysts on washcoated monoliths and the stabilization of monolithic catalyst supports by the addition of a third metal oxide, such as zirconia (ZrO_2), lanthanum oxide (La_2O_3), or manganese oxide (Mn_xO_y). The catalyst supports and/or washcoats may include a variety of transition metal oxides such as alpha iron oxide ([alpha]-Fe_2O_3), cerium oxide (CeO_2), ZrO_2, gamma alumina ([gamma]-Al_2O_3), or their combinations.

Stability improvement of Au/Fe-La-Al_2O_3 catalyst via incorporating with a Fe_xO_y layer in CO oxidation process

Various amounts of α-Fe_2O_3 were incorporated into the parent Au/Fe-La-Al_2O_3 catalyst using post-adding iron nitrate precursor via the wetness impregnation method with water, ethanol, and acetone as the solvents, respectively. Though post-addition of iron oxides makes gold particle aggregation with less catalyst activity than the parent one in the CO oxidation reaction, the most striking thing is that the Fe-modified catalysts present better online stability according to Chinese researchers led by Caixia Qi at the Shandong Applied Research Center of Gold Nanotechnology (see Appl Catal B Environ, http://dx.doi.org/10.1016/j.apcatb.2013.01.056). At the same time, in situ thermal treatment can totally recover the activity of the spent Fe-modified catalysts but not the parent one. Water as a solvent performed better than ethanol and acetone; the corresponding catalysts exhibit the best catalytic performance with the most serious Au particle aggregation after post-addition of iron species