Gold Bull (2012) 45:241–245
DOI 10.1007/s13404-012-0074-5

HIGHLIGHTS FROM RECENT LITERATURE

# Highlights from recent literature

Published online: 20 November 2012


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.

## CATALYSIS

### Atomic origins of the high catalytic activity of nanoporous gold

The authors explain that the catalytic performance of nanoparticulate gold (NPG) strongly depends on size and support and catalytic activity usually cannot be observed at characteristic sizes larger than 5 nm. In this paper, the authors report atomic insights of the NPG catalysis, characterized by spherical aberration-corrected transmission electron microscopy (TEM) and environmental TEM. A high density of atomic steps and kinks is observed on the curved surfaces of NPG, comparable to 3–5 nm nanoparticles, which are stabilized by hyperboloid-like gold ligaments. In situ TEM observations provide evidence that the surface defects are active sites for the catalytic oxidation of CO and residual Ag stabilizes the atomic steps by suppressing {111} faceting kinetics (Nature Materials doi:10.1038/nmat3391).

### Activation and deactivation of Au–Cu/SBA-15 catalyst for preferential oxidation of CO in $H_2$-rich gas

This work aimed to develop an efficient Au/CuO/SBA-15 catalyst for preferential oxidation (PROX) of CO in a $H_2$-rich gas and obtain a clear structure–property relationship of the catalyst. Although this catalyst is extremely active for the PROX reaction at room temperature and superior to the Au/SBA-15 and CuO/SBA-15 catalysts, it deactivates easily. Clear experimental evidence showed that CuO was reduced to $Cu_2O$ and Cu in the reductive reaction gas mixture, and the Cu further combined/dissolved into the Au particles during the reaction. The alloying of Au and Cu not only decreased the catalytic activity of the Au particles but also reduced the ability of CuO to activate molecular oxygen. Fortunately, this alloying process could be reversed via a simple calcination in air to activate the catalyst (ACS Catal. 2012, 2 (3), pp 360–369).

### Graphene oxide: an ideal support for gold nanocatalysts

Via ab initio calculations, the authors predict that compared with pristine graphene, graphene oxide (GO) is a much better candidate for support of gold nanocatalysts in terms of activity and feasibility. Using $Au_8$ clusters supported on GO as model catalysts, the researchers show that the reaction barrier of the catalyzed CO oxidation can be greatly reduced from around 3.0 to 0.2 eV without the need of defects or strain in the underlying support (J. Phys. Chem. C, DOI: 10.1021/jp3053218).

### NOx purification catalyst

This invention relates to a catalyst able to exhibit an NOx purification performance at a low temperature and/or in an oxidizing atmosphere. The catalyst is composed of particles having an average particle size of 0.2 to 100 nm, with specific reference to gold atoms and iron atoms in a state of close proximity (see WO2012108060 (A1)).

### Solvent-free liquid-phase oxidation of 1-hexene using supported gold catalysts

The authors report the solvent-free oxidation of 1-hexene with air by using supported gold catalysts with a catalytic

amount of tert-butyl hydroperoxide as initiator. It is reported that gold supported on graphite is an effective catalyst for such oxidations and that graphite was the preferred support. Preparation of catalysts using modified sol immobilisation was found to be effective, particularly when the PVA stabiliser was removed by a solvent treatment prior to the reaction. (ChemCatChem. doi:10.1002/cctc.201200273)

**Gold nanoparticle-catalyzed formation of nitrogen-containing compounds—from mechanistic understanding to synthetic exploitation**

This review (ChemCatChem, 4: 1021. doi:10.1002/cctc.201290026) covers synthetic and mechanistic details of reactions including those of amines, along with imine and amide syntheses. Research in this emerging field has boomed in recent years. The benefits of gold-supported catalysis for these reactions include the absence of deactivation by N-adsorption, high activities and selectivities, and opportunities for tandem or one-pot reactions with simple catalyst recovery.

**Nanoscale gold intercalated into mesoporous silica as a highly active and robust catalyst**

The authors report how stable gold/mesoporous silica nanocomposites (with Au nanoparticles intercalated in the walls of mesoporous silica) were successfully synthesized by the hydrothermal method and applied as catalysts. The intercalated systems demonstrated high activity, were robust, and readily reusable. This approach to imparting stability to nanoscale materials may be much more broadly applicable and expand the types of environments in which they can be utilized. See Nanotechnology Volume 23 Number 29, 2012, doi:10.1088/0957-4484/23/29/294010.

**Gold-catalyzed direct arylation**

Biaryls (two directly connected aromatic rings, $Ar^1$–$Ar^2$) are common motifs in pharmaceuticals, agrochemicals and organic materials. Current methods for establishing the $Ar^1$–$Ar^2$ bond are dominated by the cross-coupling of aryl halides ($Ar^1$–X) with aryl metallics ($Ar^2$–M). The authors report that, in the presence of 1 to 2 mol% of a gold catalyst and a mild oxidant, a wide range of arenes ($Ar^1$–H) undergo site-selective arylation by arylsilanes ($Ar^2$–$SiMe_3$) to generate biaryls ($Ar^1$–$Ar^2$), with little or no homocoupling ($Ar^1$–$Ar^1$/$Ar^2$–$Ar^2$). Catalysis proceeded at room temperature and tolerated a broad range of functional groups, including those incompatible with cross-coupling. These features expedite biaryl preparation, as demonstrated by synthesis of the nonsteroidal anti-inflammatory diflunisal. See Science 28 September 2012: Vol. 337 no. 6102 pp. 1644–1648, DOI: 10.1126/science.1225709.

NANOTECHNOLOGY

**Three-dimensional orientation-unlimited polarization encryption by a single optically configured vectorial beam**

The interplay between light polarization and matter is the basis of many fundamental physical processes and applications. However, the electromagnetic wave nature of light in free space sets a fundamental limit on the three-dimensional polarization orientation of a light beam. Although a high numerical aperture objective can be used to bend the wavefront of a radially polarized beam to generate the longitudinal polarization state in the focal volume, the arbitrary three-dimensional polarization orientation of a beam has not been achieved yet. In this work, the authors present a novel technique for generating arbitrary three-dimensional polarization orientation by a single optically configured vectorial beam. As a result, by applying this technique to gold nanorods, orientation-unlimited polarization encryption with ultra-security is demonstrated. (Nature Communications Volume: 3, Article number: 998 doi:10.1038/ncomms2006).

**Engineering plasmonic gold nanostructures and metamaterials for biosensing and nanomedicine**

This review (Advanced Materials, Volume 24, Issue 38, pages 5153–5165, October 2, 2012, DOI: 10.1002/adma.201200622) describes progress in the development of plasmonic Au nanostructures (p-AuNSs) or metamaterials geared towards a broad range of biological and biomedical applications. Due to their tunable and versatile plasmonic properties, such artificially engineered p-AuNSs and materials have the potential to push biosensor sensitivity towards the single-molecule detection limit, enabling new bioimaging modalities and new analytical techniques and tools capable of single-molecule detection, analysis and manipulation and to revolutionize the diagnosis and treatment of many diseases, including cancers. This report summarizes and highlights recent major advances in the emerging field of bio application-oriented engineering of p-AuNSs and hybrids, focusing on design considerations and ways to carry them out. A brief overview of the optical properties of p-AuNSs is introduced, and then, the importance of plasmonic engineering and future promising research directions and challenges in the field are discussed.

**Light-driven plasmonic color filters by overlaying photoresponsive liquid crystals on gold annular aperture arrays**

Light-driven plasmonic color filters have been demonstrated by integrating gold annular aperture arrays with photoresponsive liquid crystals (LCs). Upon photoirradiation, a nematic–isotropic phase transition of the LCs arises from the *trans–cis* photoisomerization of photochromic LCs. As a result, the effective refractive index experienced by the impinging light changes, modulating the transmission intensity. (Adv. Mater. 24: OP131–OP135. doi:10.1002/adma.201104440).

**Solar cells: a solid-state plasmonic solar cell via metal nanoparticle self-assembly**

Incident light excites surface plasmon resonances in metal nanoparticles. Located at a $TiO_2$/hole conductor interface, gold (and silver) nanoparticles induce sustainable photocurrents upon excitation. In this paper (Advanced Materials, Volume 24, Issue 35, page 4729), a simple fabrication method for this plasmonic solar cell, based on metal nanoparticle self-assembly, is described.

**Facile deposition of gold nanoparticle thin films on semi-permeable cellulose substrate**

This study reports the facile method for the deposition of gold nanoparticle thin film onto a monoporous semi-permeable cellulose membrane through the diffusion of borohydride ions leading to the reduction of $AuCl_4^-$ ions. The synthesised gold nanoparticle thin film was deposited on one side of the membrane that was exposed to $AuCl_4^-$ ions while the other side containing a reducing agent remained clear. The gold nanoparticle thin film exhibited a broad surface plasmon resonance peak at 529 nm. Various characterization techniques were employed and all demonstrated the presence of gold thin film. The reported method represents a simplistic method for the deposition of gold nanoparticle thin films (Materials Letters, Volume 88, 1 December 2012, Pages 132–135 doi.org/10.1016/j.matlet.2012.08.043).

**Plasmonic-enhanced organic solar cells**

Organic bulk-heterojunction solar cells have several good characteristics, such as ease of fabrication and low-cost materials. However, the bottleneck in their adoption is their much lower efficiency as compared with their silicon counterparts. In previous work, the authors demonstrated that by appropriately inserting AuNPs in the OPV device, the efficiency can be increased by 30 % and that silanization of ITO positively impacts device performance, where they identified the field enhancement due to AuNPs as the main reason for the increase in the efficiency of the device. In this work, the authors further investigate the impact of self-assembly of the gold nanoparticles on the efficiency (Proc. SPIE 8471, Next Generation (Nano) Photonic and Cell Technologies for Solar Energy Conversion III, 84710D, October 12, 2012; doi:10.1117/12.930406).

ELECTRONICS

**Ag–Au–Pd ternary alloy-based bonding wire**

This invention by Japanese company Tanaka relates to a new alloy for bonding wire, the material used in semiconductor chip packaging (WO2012108082 A1). The aim is to improve the reliability at which a bonding wire for semiconductors that is used in high-temperature and high-humidity environments is bonded to an aluminum pad. The inventors propose a ternary alloy-based wire comprising 4–10 mass% of gold, 2–5 mass% of palladium, with the remainder constituted of silver.

**Electroplating hard gold plating solution and plating method using same**

Disclosed by Metalor Technologies is a plating solution which does not generate pinholes in a gold film even if the gold film has a thickness of less than 0.1 μm (EP2511400 A1). Partial plating is performed using an electrolytic hard gold plating solution containing gold cyanide and/or gold cyanide salt, water-soluble cobalt salt or water-soluble nickel salt, an electric conductive salt of organic acid, an aromatic sulfonic acid compound, a combination of one or more items selected from group consisting of carboxylic acids, oxycarboxylic acids, and the salts thereof, and a nitrogen-containing five-membered heterocyclic compound.

**Enhancement of high-TC superconducting thin film devices by nanoscale polishing**

The effects of mechanical nanoscale polishing on the superconducting parameters of $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films and bi-crystal grain boundary Josephson junctions were investigated by the authors. They prepared samples with additional gold nanocrystallites in the

YBCO film. As they were distributed throughout the whole YBCO film, they provided a low-resistance ohmic contact even if parts of the film were removed. Polishing was performed either before or after the patterning and did not change the properties of the grain boundary. However, nanopolishing reduces the film roughness in a significant way, which makes it an indispensable tool for the preparation of integrated superconducting circuits (Supercond. Sci. Technol. 25 115019 doi:10.1088/0953-2048/25/11/115019).

### High reliability gold-based solder alloys for microelectronics packaging for high-temperature applications

The performance of the Au–Ge eutectic solder alloy and the Au–Si eutectic solder alloy at 300 °C up to 500 h has been reported. Coarsening of the dispersed (Ge) phase as well as the dissolution of the hard (Ge) phase into the soft (Au) matrix is observed during thermal aging. Shear testing and nanoindentation confirmed the loss of strength of the Au–Ge bulk solder during thermal aging at 300 °C. However, a fraction of the lost strength was recovered during the final stages of thermal aging at 300 °C for 500 h. The coarsening effect was more pre-dominant in the Au–Si eutectic alloy. The pace at which the Au–Si eutectic alloy loses its strength during aging at 300 °C is significantly higher, when compared to Au–Ge eutectic alloy. Based on the present work's findings, it can be concluded that among the binary eutectic alloys, Au–Ge eutectic alloy is better suited for high-temperature applications. This paper was presented at 19th IEEE International Symposium on the Physical and Failure Analysis of Integrated Circuits (IPFA), 2–6 July 2012 DOI 10.1109/IPFA.2012.6306308.

## SENSORS

### Ultrasensitive detection of a protein by optical trapping in a photonic–plasmonic microcavity

Microcavity and whispering gallery mode biosensors derive their sensitivity from monitoring frequency shifts induced by protein binding at sites of highly confined field intensities, where field strengths can be further amplified by excitation of plasmon resonances in nanoparticle layers. The authors propose a mechanism based on optical trapping of a protein at the site of plasmonic field enhancements for achieving ultrasensitive detection in only microliter-scale sample volumes and in real-time. Using glass microspheres covered in gold nanoparticles, the German and US scientists managed to detect proteins at femtomole concentrations. They demonstrated femtomolar sensitivity corresponding to a few 1,000 s of macromolecules. Simulations based on Mie theory agreed well with the optical trapping concept at plasmonic 'hotspots' locations. (Journal of Biophotonics, Special Issue: Lab-on-a-Chip Based Diagnostics, Volume 5, Issue 8–9, pages 629–638, August 2012, DOI: 10.1002/jbio.201200040).

### Selective visual detection of TNT at the sub-zeptomole level

Highly sensitive and highly selective tests are important for the early detection of disease, the detection of environmental toxins, or for the detection of explosives at airports. Increased selectivity for the target analytes helps to avoid false-positive results. In the journal *Angewandte Chemie*, researchers have now introduced a specific detection method for the explosive TNT that can be used to detect even a single molecule. The visual detection of 2,4,6-trinitrotoluene and $Hg^{2+}$ at the sub-zeptomole level was demonstrated using a hybrid material of gold and silver (Angew. Chem. Int. Ed. doi:10.1002/anie.201203810).

### Colorimetric detection of mercury ions based on plasmonic nanoparticles

This online-first publication in *Advanced Materials* recent progress in the development of gold nanoparticle-based colorimetric assays for $Hg^{2+}$ is summarized, with a particular emphasis on examples of functionalized gold nanoparticle systems with oligonucleotides, oligopeptides, and functional molecules. Besides highlighting the current design principle for plasmonic nanoparticle-based colorimetric probes, the discussions on challenges and the prospect of next-generation probes for in-the-field applications are also presented (DOI 10.1002/smll.201200811).

### Nanoparticle cluster arrays for high-performance SERS through directed self-assembly on flat substrates and on optical fibers

The authors have demonstrated template-guided self-assembly of gold nanoparticles into ordered arrays of uniform clusters suitable for high-performance SERS on both flat (silicon or glass) chips and an optical fiber faucet. Excellent SERS performance, as evidenced by a high enhancement factor, $>10^8$ on flat chips and $>10^7$ for remote sensing, using SERS-enabled optical fibers was demonstrated. The best performing cluster arrays in both cases were achievable without the use of any expensive equipment or clean room processing. The demonstrated approach paves the way to significantly low-cost and high-throughput production of sensor chips or 3D-configured surfaces for remote sensing applications (ACS Nano, 2012, 6 (3), pp 2056–2070, DOI: 10.1021/nn203661n).

MEDICINE

### Negatively charged gold nanoparticles inhibit Alzheimer's amyloid-β fibrillization, induce fibril dissociation, and mitigate neurotoxicity

Amyloids are pathogenic hallmarks in many neurodegenerative diseases such as amyloid-β (Aβ) fibrils in Alzheimer's disease (AD). In this research, the effect of gold nanoparticles (AuNPs) on amyloids is examined using Aβ as a model system. It is found that bare AuNPs inhibited Aβ fibrillization to form fragmented fibrils and spherical oligomers. Adding bare AuNPs to preformed Aβ fibrils results in ragged species where AuNPs bind preferentially to fibrils. Similar results are demonstrated with carboxyl- but not amine-conjugated AuNPs. Co-incubation of negatively charged AuNPs with Aβ relieved Aβ toxicity to neuroblastoma. Overall, it is demonstrated that AuNPs possessing negative surface potential serve as nanochaperones to inhibit and redirect Aβ fibrillization, which could contribute to applications for AD (Small. doi:10.1002/smll.201201068).

FUEL CELLS

### Fuel cell metal separator and noble metal coating method therefor

Separator plates are key components of PEM fuel cells. This invention by Honda Motor Company relates to the use of gold coatings on separator plates. The gold coating layer includes a main gold coating portion and a reticulate gold coating portion that extends around the main gold coating portion. US2012258383 (A1)

### Highly stable Pt monolayer on PdAu nanoparticle electrocatalysts for the oxygen reduction reaction

Stability is one of the main requirements for commercializing fuel cell electrocatalysts for automotive applications. Platinum is the dominant catalyst for oxygen reduction in cathodes, but it undergoes dissolution during potential changes while driving electric vehicles. The authors report a new class of highly stable, active electrocatalysts comprising platinum monolayers on palladium–gold alloy nanoparticles. In fuel cell tests, this electrocatalyst with its ultra-low platinum content showed minimal degradation in activity over 100,000 cycles between potentials 0.6 and 1.0 V. Under more severe conditions with a potential range of 0.6–1.4 V, the authors registered no marked losses in platinum and gold despite the dissolution of palladium. These data coupled with theoretical analyses demonstrated that adding a small amount of gold to palladium and forming highly uniform nanoparticle cores make the platinum monolayer electrocatalyst significantly tolerant and very promising for the automotive application of fuel cells (Nature Communications 3, Article number:1115 doi:10.1038/ncomms2124)