

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

Gold nanoparticles for cleaning contaminated water

Pollutants in the form of heavy metals, fertilizers, detergents, and pesticides have seriously reduced the supply of pure drinking water and usable water. Gold metal has intriguing potential to deal with the water pollution problem, as recent research on several fronts is advancing the concept of nanoscale gold as the basis for cost-effective nanotechnology-based water treatment. Nanogold has special properties, such as enhanced catalytic activity, visible surface plasmon resonance color changes, and chemical stability that make it more useful than other materials. The article, written by researchers at Rice University in the USA (*J Chem Technol Biotechnol.*, 2013; 88: 735–741) highlights the current use of gold nanoparticles for the efficient removal and the selective and sensitive detection of a variety of pollutants in water. The challenges in further developing nanogold to address water contamination are discussed in this review, which should stimulate future research into improved removal and detection of undesirable chemical compounds.

Nanoparticle-delivered vascular disrupting agents: use of TNF- α conjugated gold nanoparticles for multimodal cancer therapy

Surgery, radiation, and chemotherapy remain the mainstay of current cancer therapy. However, treatment failure persists due to the inability to achieve complete local control of the tumor and curtail metastatic spread. Vascular disrupting agents (VDAs) are a class of promising systemic agents that are known to synergistically enhance radiation, chemotherapy,

or thermal treatments of solid tumors. Unfortunately, there is still an unmet need for VDAs with more favorable safety profiles and fewer side effects. Recent work has demonstrated that conjugating VDAs to other molecules (polyethylene glycol, CNGRCG peptide) or nanoparticles (liposomes, gold) can reduce toxicity of one prominent VDA (tumor necrosis factor α , TNF- α). In this report, the authors from Minnesota and Arkansas (*Mol. Pharmaceutics*, 2013, 10 (5), pp 1683–1694 DOI: [10.1021/mp300505w](https://doi.org/10.1021/mp300505w)) show the potential of a gold-conjugated TNF- α nanoparticle (NP-TNF) to improve multimodal cancer therapies with VDAs. In a dorsal skin fold and hindlimb murine xenograft model of prostate cancer, they reported that NP-TNF disrupts endothelial barrier function and induces a significant increase in vascular permeability within the first 1–2 h followed by a dramatic 80 % drop in perfusion 2–6 h after systemic administration. They also demonstrated that the tumor response to the nanoparticle can be verified using dynamic contrast-enhanced magnetic resonance imaging, a technique in clinical use. Additionally, multimodal treatment with thermal therapies at the perfusion nadir in the sub- and supraphysiological temperature regimes increases tumor volumetric destruction by over 60 % and leads to significant tumor growth delays compared to thermal therapy alone. Lastly, NP-TNF was found to enhance thermal therapy in the absence of neutrophil recruitment, suggesting that immune/inflammatory regulation is not central to its power as part of a multimodal approach. The data demonstrate the potential of nanoparticle-conjugated VDAs to significantly improve cancer therapy by preconditioning tumor vasculature to a secondary insult in a targeted manner. The researchers anticipate their work will help to direct investigations into more potent tumor vasculature specific combinations of VDAs and nanoparticles with the goal of transitioning optimal regimens into clinical trials.

Aptamer-loaded, biocompatible nanoconstructs for nuclear-targeted cancer therapy

Disclosed by US-based researchers (WO2013070763) is a nanoconstruct comprising an aptamer and a gold nanostar.

The nanoconstruct can be used in a method of inducing changes to a nuclear phenotype of a cell comprising transporting the nanoconstruct to a nucleus of a cell, and releasing the aptamer from a surface of the gold nanostar into the nucleus of the cell to afford deformations or invaginations in the nuclear membrane, thereby inducing changes to the nuclear phenotype. The method can be used to treat certain hyperproliferative disorders such as cancer.

Coated article having low-E coating with absorber layer(s)

A coated article is described by Guardian Industries (US2013088773), having a coating supported by a glass substrate where the coating includes at least one color and/or reflectivity-adjusting absorber layer. The absorber layer(s) allows color tuning, and reduces the glass side reflection of the coated article and/or allows sheet resistance of the coating to be reduced without degrading glass side reflection. In certain example embodiments, the absorber layer is provided between first and second dielectric layers which may be of substantially the same material and/or composition. In certain example embodiments, the coated article is capable of achieving desirable transmission, together with desired color, low reflectivity, and low selectivity, when having only one infrared reflecting thin film layer of silver and/or gold. Coated articles according to certain example embodiments of this invention may be used in the context of insulating glass window units, monolithic windows, or the like.

Power conversion efficiency enhancement of organic solar cells by addition of gold nanostars, nanorods, and nanospheres

The effects of gold (Au) nanoparticles (NPs) with different morphologies (star, rod, sphere) incorporated into buffer layer, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate), of polymer-based organic solar cells were investigated. Solar cells having gold nanoparticles exhibited significant improvement in device efficiency relative to the reference device. According to the report's authors (*Organic Electronics*, Volume 14, Issue 7, July 2013, Pages 1720–1727), the observed improvement is most likely due to the surface plasmon and enhanced light reflection and scattering properties of the Au NPs. The power conversion efficiency is increased ca. 29 % with Au nanostars, ca. 14 % with Au nanorods, and 11 % with Au nanospheres compared to the device with no Au NP (reference device). Au nanostars provide the strongest contribution to the efficiency among all NP morphologies studied as they have large size, sharp features, and strongest localized surface plasmon resonance effect associate with their morphology.

Bare clusters derived from protein templates: Au_{25}^+ , Au_{38}^+ , and Au_{102}^+

A discrete sequence of bare gold clusters of well-defined nuclearity, namely Au_{25}^+ , Au_{38}^+ , and Au_{102}^+ , formed in a process that starts from gold-bound adducts of the protein lysozyme, were detected in the gas phase by researchers in India (*ChemPhysChem*, Volume 14, Issue 6, pages 1272–1282, April 15, 2013). It is proposed that subsequent to laser desorption ionization, gold clusters form in the gas phase, with the protein serving as a confining growth environment that provides an effective reservoir for dissipation of the cluster aggregation and stabilization energy. First-principle calculations reveal that the growing gold clusters can be electronically stabilized in the protein environment, achieving electronic closed-shell structures as a result of bonding interactions with the protein. Calculations for a cluster with 38 gold atoms reveal that gold interaction with the protein results in breaking of the disulfide bonds of the cystine units, and that the binding of the cysteine residues to the cluster depletes the number of delocalized electrons in the cluster, resulting in opening of a super-atom electronic gap. This shell-closure stabilization mechanism confers enhanced stability to the gold clusters. Once formed as stable magic number aggregates in the protein growth medium, the gold clusters become detached from the protein template and are observed as bare Au_n^+ ($n=25, 38$, and 102) clusters.

Colorimetric detection of mercury ions based on plasmonic nanoparticles

The development of rapid, specific, cost-effective, and robust tools in monitoring Hg^{2+} levels in both environmental and biological samples is of utmost importance due to the severe mercury toxicity to humans. A number of techniques exist, but the colorimetric assay, which is reviewed herein (*Small*, Volume 9, Issue 9–10, pages 1467–1481, May 27, 2013), is shown to be a possible tool in monitoring the level of mercury. These assays allow transforming target sensing events into color changes, which have applicable potential for in-the-field application through naked eye detection. Specifically, plasmonic nanoparticle-based colorimetric assay exhibits a much better propensity for identifying various targets in terms of sensitivity, solubility, and stability compared to commonly used organic chromophores. In this review, 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.

Electronics

Thermal and electrical conduction in 6.4 nm thin gold films

For sub-10 nm thin metallic films, very little knowledge is available so far on how electron scattering at surface and grain boundaries reduces the thermal transport. This report from researchers in the USA and China (*Nanoscale*, 2013, 5, 4652–4656) reveals the first time characterization of the thermal and electrical conductivities of gold films of 6.4 nm average thickness. The electrical (σ) and thermal (k) conductivities of the Au film are found to be reduced dramatically from their bulk counterparts by 93.7 % (σ) and 80.5 % (k). Its Lorenz number is measured as $7.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, almost a twofold increase from the bulk value. The Mayadas–Shatzkes model is used to interpret the experimental results and reveals very strong electron reflection (77 %) at grain boundaries.

Effect of applied load in the nanoindentation of gold ball bonds

Researchers have analyzed the effects of nanoindentation at applied loads of 10 and 20 mN on the micromechanical properties of gold (Au) ball bonds with and without cracks (*Journal of Electronic Materials*, June 2013, Volume 42, Issue 6, pp 1063–1072). The depth profile and the plastic zone size for each indentation were determined to identify the substrate effect and its relationship with the observed micromechanical properties. The substrate effect occurred for indentations at 20 mN applied load, but did not occur near cracks for either 10 or 20 mN loads. Because of the substrate effect and the presence of cracks, the average hardness or yield strength decreased for indentations on Au ball bonds. Therefore, to minimize the substrate effect, an applied load of 10 mN is best for characterizing Au ball bonds.

Layer-by-layer-assembled reduced graphene oxide/gold nanoparticle hybrid double-floating-gate structure for low-voltage flexible flash memory

A hybrid double-floating-gate flexible memory device by utilizing an rGO sheet monolayer and a Au NP array as upper and lower floating gates has been reported by researchers in Hong Kong (*Advanced Materials*, Volume 25, Issue 6, pages 872–877, February 13, 2013). The rGO buffer layer acts as a charge-trapping layer and introduces an energy barrier between the Au NP lower floating gate and the channel. The

proposed memory device demonstrates a strong improvement in both field-effect-transistor and memory characteristics.

Metallurgy

Gold alloy with improved hardness

Swatch Group R&D describe a gold-based alloy (I) comprising gold (at least 75 wt.%), a second metal (0.1–2.1 wt.%) selected for its ability to form precipitates with gold, and at least one filler metal (balance) selected for its ability to sustain a stable face-centered cubic structure and for its ability to increase the solubility of the second metal in gold, where the mixture further comprises at least one precipitate of the second metal with gold selected to obtain a hardness of greater than 250 HV. An independent claim is included for preparing (I) comprising: selecting the second metal; selecting the filler metal; creating the insertion condition in a face-centered cubic structure resulting of the dissolution of a mixture of gold, the second metal, and the filler metal and precipitates of the second metal with gold; preparing the mixture; placing the mixture at 400–700 °C, rapid cooling, after rapid cooling, treating obtained material at 200–400 °C for producing the selected precipitate of the second metal with gold; increasing the selected precipitate to obtained material for a sufficient time to obtain the required hardness; and cooling the material in room temperature. See patent EP2588635 (A2).

Fuel cells

Highly stable platinum alloy catalyst for methanol electrooxidation

A catalyst for use in at the anode of direct methanol fuel cells is made from nanoparticles having a core-shell structure has been described by researchers at Northeastern University (see patent US2013089812). The core is an alloy of platinum and gold. The core is surrounded by a first shell of ruthenium and a second shell containing a ternary alloy of platinum, gold, and ruthenium. The catalyst can be made by a reverse-micelle method or by a single-phase scalable method. The catalyst is highly stable under conditions of use and resists dissolution of ruthenium or platinum.

Direct $\text{NaBH}_4\text{--H}_2\text{O}_2$ fuel cell based on nanoporous gold leaves

Direct borohydride-hydrogen peroxide fuel cell (DBHFC) has proved a promising power source and made plenty of progress during last decade. In this work (*International*

Journal of Hydrogen Energy, In press, <http://dx.doi.org/10.1016/j.ijhydene.2013.01.016>), nanoporous gold (NPG) leaves, derived from dealloying 12 carat Au/Ag alloy, are applied as catalyst to promote the performance of DBHFCs, at an ultralow loading of 0.12 mg cm^{-2} . The effects of etching time, operation temperature, solution concentration, and membrane thickness on cell performance are studied. At 80°C , the cell with Nafion 212 can generate a power density of nearly 400 mW cm^{-2} at 0.66 V , under the supplying of 10 wt\% NaBH_4 and $20 \text{ wt\% H}_2\text{O}_2$. Moreover, commercial 40 wt\% Pt/C catalyst and self-made Pt/NPG catalyst are also investigated. All the results indicate that the NPG catalyst is a promising and cost-efficient electrocatalyst of DBHFC for both the anode and the cathode.

Fuel cell flow field plate including nonstoichiometric metal oxide layer

General Motors researchers disclose a flow field plate or bipolar plate for a fuel cell that includes a combination of nonstoichiometric and a conductive material that makes the bipolar plate conductive, hydrophilic, and stable in the fuel cell environment (see patent US2013095251). The nonstoichiometric and the conductive material can be deposited on the plate as separate layers or can be combined as a single layer. Either the nonstoichiometric layer or the conductive layer can be deposited first. In one embodiment, the conductive material is gold.

Study of the synergistic interaction between nickel, gold, and molybdenum in novel modified NiO/GDC cermets, possible anode materials for CH_4 fueled SOFCs

Greek and French researchers describe the structural and physicochemical characterization of novel Au–Mo–NiO/GDC cermets, alongside with measurements of their carbon tolerance (*Applied Catalysis A: General*, Volume 456, 10 April 2013, Pages 223–232). This is an investigation on whether commercially available NiO/GDC powder that is modified with Au and/or Mo can yield possible electrocatalysts as anodes for CH_4 fueled SOFCs. Specifically, the performed preparation methods of deposition–precipitation and deposition–coprecipitation permitted the modification of a commercial electrocatalyst and lead to cermets that exhibit different reaction kinetics for the catalytic dissociation of CH_4 and different performance for CH_4 steam reforming. The most interesting structural findings were observed in the reduced form of the prepared powders, where a bimetallic Ni–Au solid solution is formed in the Au-modified sample. In the ternary composite material, a trimetallic Ni–Au–Mo solid solution is formed, which induces a controversial synergistic

effect on the sample's catalytic performance. On the other hand, the presence of Au compared to Mo shows the best combination of results in terms of structural properties, carbon tolerance, and selectivity to the desirable products of H_2 and CO, for the reaction of CH_4 steam reforming.

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](https://doi.org/10.1126/science.1227813)), very small gold clusters (3 to 10 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.

Nonmercury catalytic acetylene hydrochlorination over bimetallic Au–Co(III)/SAC catalysts for vinyl chloride monomer production

Several gold-based catalysts including Au, Au–La(III), Au–Co(II), and Au–Co(III) were prepared by Chinese researchers (*Green Chem.*, 2013, 15, 829–836, DOI: [10.1039/C3GC36840H](https://doi.org/10.1039/C3GC36840H)) and assessed for acetylene hydrochlorination, combining with characterizations of low-temperature N_2 adsorption/desorption, thermogravimetric analysis, X-ray diffraction, temperature-programmed reduction, inductively coupled plasma-atomic emission spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. The best catalytic performance was obtained over Au1Co(III)3/SAC catalysts with an acetylene conversion of 92 % and a selectivity to VCM of 99.9 %. It is indicated that the additives of Co(III), Co(II) and La(III) are preferential to stabilize the catalytic active Au^+ species and inhibit the reduction of Au^{3+} to Au^0 in the preparation process of Au-based/SAC catalysts. The addition of these additives can greatly inhibit the occurrence of coke deposition on the catalyst surface, and also inhibit the catalyst sintering, thereby improving the activity and long-term stability of the Au-based catalysts

Method for preparing a palladium–gold alloy gas separation membrane system

Researchers at Shell Oil have developed a method for preparing a palladium–gold alloy gas separation membrane system comprising a gold–palladium alloy membrane on a porous substrate coated with an intermetallic diffusion barrier, as described in patent US2013104740 (A1). The method includes an abrading step to increase surface roughness of the palladium to a desired range, a gold plating step with a solution of chloroauric acid (AuCl_4H) and hydrogen peroxide, followed by annealing to produce a palladium–gold alloy membrane.

Combining gold and photoredox catalysis: visible light-mediated oxy- and aminoarylation of alkenes

A room temperature intramolecular oxy- and aminoarylation of alkenes with aryldiazonium salts has been developed by researchers in Germany (*J. Am. Chem. Soc.*, 2013, 135 (15), pp 5505–5508, DOI: [10.1021/ja400311h](https://doi.org/10.1021/ja400311h)) using a novel gold and photoredox dual-catalytic system. The compatibility of these two catalytic modes has been established for the first time and demonstrates the potential of this system as a method to expand the scope of nucleophilic addition reactions to carbon–carbon multiple bonds.

Hydrogen production by dehydrogenation of formic acid on atomically dispersed gold on ceria

Atomically dispersed gold species catalyze the decomposition of formic acid through the dehydrogenation pathway at near-ambient temperatures. US-based researchers have demonstrated that gold on ceria is an effective and stable catalyst (*ChemSusChem*, Volume 6, Issue 5, pages 816–819, May 2013). By using this catalyst, mechanistic insights are obtained that can lead to the use of trace amounts of gold to achieve robust and cost-effective catalysts

Epoxidation of styrene by t-butyl hydroperoxide over gold nanoparticles supported on Yb_2O_3 : effect of gold deposition method, gold loading, and calcination temperature of the catalyst on its surface properties and catalytic performance

Surface properties and epoxidation performance of $\text{Au}/\text{Yb}_2\text{O}_3$ catalyst are influenced by the method of gold deposition [viz. deposition–precipitation (DP), homogeneous deposition–precipitation (HDP) or impregnation], gold loading (0.9–6.6 wt%), and the catalyst calcination temperature (400–900 °C). According to researchers in India and Australia (*Journal of Catalysis*, Volume 300, April 2013, Pages 217–224) the catalyst showed the best epoxidation performance when it

was prepared by the HDP method and calcined at 500 °C. The $\text{Au}/\text{Yb}_2\text{O}_3$ catalyst even after calcination at 900 °C showed good activity and epoxide selectivity. Both Au^0 and Au^{3+} surface species were found in the catalyst calcined at 800 °C, but only Au^0 species were observed at the lower calcination temperatures (<600 °C). The selectivity for styrene oxide increased continuously with the reaction temperature (from 75 to 97 °C) and time (1–5 h), indicating that styrene oxide did not undergo secondary reactions under these conditions

Photocatalytic water gas shift using visible or simulated solar light for the efficient, room temperature hydrogen generation

Gold nanoparticles supported on P25 TiO_2 is a highly efficient photocatalyst to promote the simultaneous H_2O reduction to H_2 and CO oxidation to CO_2 , according to recently published research from a Spanish university (*Energy Environ. Sci.*, 2013, Accepted Manuscript, DOI: [10.1039/C3EE40656C](https://doi.org/10.1039/C3EE40656C)). This photocatalytic process can be performed using simulated solar light as well as light from a LED quasi monochromatic centered at 450 nm, indicating that not only UV but also visible light promotes the reaction. This novel photocatalytic reaction corresponds to the water gas shift which is an endothermic process that is currently carried out at large industrial scale at temperatures about 350 °C. In contrast, the photocatalytic process is performed at ambient temperature with no other energy requirement than sun light. Other related TiO_2 and CeO_2 photocatalyst containing noble metals (Pt or Pd) behave similarly, but with lower efficiency both in the UV and in the visible region than Au/TiO_2

Au – Pd nanoparticles supported on carbon fiber cloth as the electrocatalyst for H_2O_2 electroreduction in acid medium

A novel synthesis of Au – Pd alloy nanoparticles supported on carbon fiber cloth (Au – Pd NPs/CFC) via a potential pulse technique is described by Chinese researchers (*Journal of Power Sources*, Volume 233, 1 July 2013, Pages 252–258). Different composition stoichiometry of Au – Pd nanoparticles are deposited from the aqueous solutions of $\text{HAuCl}_4/\text{PdCl}_2$ mixtures in molar ratios of 5:1, 2:1, 1:1, 1:2 and 1:5. The electrode is characterized by scanning electron microscopy coupled to energy dispersive X-ray analysis, transmission electron microscopy, and X-ray diffractometer. H_2O_2 electroreduction in H_2SO_4 solution on Au – Pd nanoparticles is studied by linear sweep voltammetry and chronoamperometry. The catalytic performance on different composition stoichiometry of Au – Pd nanoparticles increases with the increase of Pd content. Additionally, the flower-like Au – Pd NPs/CFC electrode exhibits the excellent catalytic properties and good stability to H_2O_2 electroreduction in acid solution and it outperforms pure Au or Pd catalyst supported on carbon fiber cloth.

Gold catalysis: highly functionalized cyclopentadienes prepared by intermolecular cyclization of ynamides and propargylic carboxylates

Highly electrophilic gold carbenoids available from propargylic esters by means of 1,2-acyloxy migration open up new reaction pathways for ynamide gold chemistry. In this way, highly functionalized cyclopentadiene derivatives

become accessible, as described by German researchers (Angewandte Chemie International Edition, Volume 52, Issue 22, pages 5880–5884, May 27, 2013).

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