

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.

1. Catalysis and chemistry

Spectroscopic observation of dual catalytic sites during oxidation of CO on a Au/TiO₂ catalyst

The prevailing view of CO oxidation on gold–titanium oxide (Au/TiO₂) catalysts is that the reaction occurs on metal sites at the Au/TiO₂ interface. Here, researchers from the University of Virginia (Green et al., *Science*, 5 August 2011: vol. 333 no. 6043 pp. 736–739) observed dual catalytic sites at the perimeter of 3-nm Au particles supported on TiO₂ during CO oxidation. Infrared-kinetic measurements indicate that O–O bond scission is activated by the formation of a CO–O₂ complex at dual Ti–Au sites at the Au/TiO₂ interface. The team employed density functional theory calculations, which provided the activation barriers for the formation and bond scission of the CO–O₂ complex, confirming this model as well as the measured apparent activation energy of 0.16 eV. The observation of sequential delivery and reaction of CO first from TiO₂ sites and then from Au sites indicates that catalytic activity occurs at the perimeter of Au nanoparticles.

Selective oxidation of D-galactose over gold catalysts

The selective oxidation of D-galactose to galactonic acid over Au/Al₂O₃ was studied isothermally in a semi-batch shaker reactor under pH-controlled conditions at atmospheric pressure by Finnish researchers. The team prepared and calcined a series of Au/Al₂O₃ catalysts at different

temperatures to achieve different gold particle sizes, as reported by Kusema et al. (*ChemCatChem.*, doi: [10.1002/cctc.201100183](https://doi.org/10.1002/cctc.201100183)). The catalytic properties of the gold nanoparticles were affected by the cluster size. A detailed comparison of activity and selectivity of these catalysts was made, which demonstrated that Au/Al₂O₃ with a mean particle size of 2.6 nm exhibited the highest activity. The influence of the pH value of the reaction medium on the selective oxidation of D-galactose was elucidated. Alkaline conditions were characterized by high catalyst activity and selectivity to aldonic acid whilst inhibition of the catalytic activity was observed in the acidic medium. The intermediate species was present at low pH values, and this resulted in low conversion and selectivity to the main product, galactonic acid. The electrochemical potential of the catalyst was correlated to the catalytic activity.

Gold polymer nanostructure-supported scandium catalyst and use of the same

WO 2011111482 (A1)

Japanese scientists disclose a scandium catalyst that can be used with water and a water-soluble organic solvent, and does not leak scandium. In a liquid phase, this is a gold polymer nanostructure-supported scandium catalyst formed by mixing Lewis acid metallic compounds represented by gold clusters with particle diameters on the order of 1–50 nm, disulfide monomer, disulfide sulfonate, and ScY₃ (in the formula, Y represents OSO₂CF₃) and polymerizing in the presence of an initiator of radical polymerization, the disulfide monomer represented by the following formula CH₂=CH–R₁–S–S–R₁–CH=CH₂ (in the formula, R₁ represents a bivalent hydrocarbon radical that can include an ether bond), and the disulfide sulfonate represented by the following formula MO₃S–R₂–S–S–R₂–SO₃M (in the formula, R₂ represents a bivalent hydrocarbon radical that

can include an ether bond; M represents alkali metal). The catalyst is used for an aldol reaction in water or a water-soluble organic solvent, a cyano reaction, an allyl reaction, a Michael reaction, a Mannich reaction, a Diels–Alder reaction or a Friedel–Crafts reaction.

Gold complexes

WO 2011107736 (A1)

Gold (I) hydroxide complexes of the form Z–Au–OH and digold complexes of the form Z–Au–([mu]OH)–Au–Z, where groups Z are two electron donors, are provided in this disclosure from the University of St Andrews in Scotland. The groups Z may be carbenes, for example, nitrogen containing heterocyclic carbenes (NHCs), phosphines, or phosphites. The complexes can be used as catalysts, for example, in reactions such as hydration of nitriles, skeletal arrangement of enynes, alkoxycyclisation 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.

Making the golden connection: reversible mechanochemical and vapochemical switching of luminescence from bimetallic gold–silver clusters associated through aurophilic interactions

Aiming at the development of new architectures within the context of the quest for strongly luminescent materials with tunable emission, Lasanta et al. (J. Am. Chem. Soc., doi: [10.1021/ja206845s](https://doi.org/10.1021/ja206845s)) utilized the propensity of the robust bimetallic clusters $[Au_2Ag_2(RI/RII)_4]$ ($RI=4\text{-C}_6F_4I$, $RII=2\text{-C}_6F_4I$) for self-assembly through aurophilic interactions. With a de novo approach that combines the coordination and halogen-bonding potential of aromatic heteroperhalogenated ligands, they generated a family of remarkably luminescent bimetallic materials that provide grounds to address the relevance, relative effects, and synergistic action of the two interactions in the underlying photophysics. By polymerizing the green-emitting ($\lambda_{\text{maxem}}=540$ nm) monomer $[Au_2Ag_2RII4(\text{tfa})_2]_2$ —(tfa=trifluoroacetate) to a red-emitting ($\lambda_{\text{maxem}}=660$ nm) polymer $[Au_2Ag_2RII4(\text{MeCN})_2]_n$, they have demonstrated that the degree of cluster association in these materials can be effectively and reversibly switched simply by applying mechanochemical and/or vapochemical stimuli in the solid state as well as by solvatochemistry in solution, the reactions being coincident with a dramatic switching of the intense, readily perceptible photoluminescence. The key event in the related equilibrium is the evolution of a metastable yellow emitter ($\lambda_{\text{maxem}}=580$ nm) for which the structure determination in the case of

the ligand RII revealed a dimeric nonsolvated topology $[Au_2Ag_2RII4]_2$. Taken together, these results reveal a two-stage scenario for the aurophilic-driven self-assembly of the bimetallic clusters $[Au_2Ag_2(RI/RII)_4]$: (1) initial association of the green-emitting monomers to form metastable yellow-emitting dimers and desolvation followed by (2) resolution of the dimers and their self-assembly to form a red-emitting linear architecture with delocalized frontier orbitals and a reduced energy gap. The green emission from $[Au_2Ag_2RII4(\text{tfa})_2]_2$ —($\lambda_{\text{maxem}}=540$ nm) exceeds the highest energy observed for $[Au_2Ag_2]$ -based structures to date, thereby expanding the spectral slice for emission from related structures beyond 140 nm, from the green region to the deep-red region.

Oxidative esterification of 1,2-propanediol using gold and gold–palladium supported nanoparticles

The oxidative esterification of 1,2-propanediol to methyl lactate and methyl pyruvate has been investigated using gold and gold–palladium nanoparticles supported on a variety of supports by a team of researchers on either side of the Atlantic (Brett et al., Catal. Sci. Technol., 2011, doi: [10.1039/C1CY00254F](https://doi.org/10.1039/C1CY00254F)). Methyl lactate can be used in cosmetics and personal care products, whereas methyl pyruvate is useful in the treatment of diseases of the nervous system. They have shown that gold–palladium alloy catalysts can be very effective for the oxidative esterification of 1,2-propanediol to methyl lactate and methyl pyruvate. Five supports, titania, carbon, silica, iron oxide, and ceria are contrasted. The addition of palladium to gold significantly enhances the activity and retains the high selectivity to methyl lactate using O_2 as oxidant. Using ceria as support, a significant improvement in the selectivity to methyl lactate was observed, whereas using silica as support, high selectivity to methyl pyruvate was achieved. The use of colloidal methods and the effect of support and Au/Pd molar ratio are also discussed.

Linear alkane polymerization on a gold surface

In contrast to the many methods of selectively coupling olefins, few protocols catenate saturated hydrocarbons in a predictable manner. Here, Zhong et al. (Science, 14 October 2011: vol. 334 no. 6053 pp. 213–216) report the highly selective carbon–hydrogen (C–H) activation and subsequent dehydrogenative C–C coupling reaction of long-chain ($>\text{C}_{20}$) linear alkanes on an anisotropic gold(110) surface, which undergoes an appropriate reconstruction by adsorption of the molecules and subsequent mild annealing, resulting in nanometer-sized channels (1.22 nm in width). Owing to the orientational constraint of the reactant molecules in these one-dimensional channels, the reaction

takes place exclusively at specific sites (terminal CH₃ or penultimate CH₂ groups) in the chains at intermediate temperatures (420 to 470 K) and selects for aliphatic over aromatic C–H activation.

Truncated ditetragonal gold prisms as nanofacet activators of catalytic platinum

Lu et al. (J. Am. Chem. Soc., doi: [10.1021/ja207848e](https://doi.org/10.1021/ja207848e)) report a facile, seed-mediated method to synthesize nanoscale gold-truncated ditetragonal nanoprisms (TDPs) enclosed by 12 high-index {310} facets. The method leads to the formation of nanoparticles with high size and shape monodispersity and allows for easy surfactant removal. The dependence of particle shape on the synergistic contribution of metallic ions, halide ions, and surfactant adsorbates during synthesis is described. The resulting high-index nanoparticle facets were demonstrated as efficient activators of a supported catalytic material (platinum). A Pt monolayer deposited onto the Au TDP nanofacets with sharp electrochemical signatures exhibits an enhanced catalytic activity.

A novel carbonylation reaction: activated metallic gold as an agent for direct methoxycarbonylation

Xu et al. (J. Am. Chem. Soc., doi: [10.1021/ja207389z](https://doi.org/10.1021/ja207389z)) have discovered that metallic gold is a highly effective vehicle for the low-temperature vapor-phase carbonylation of methanol by insertion of CO into the O–H bond to form methoxycarbonyl. This reaction contrasts sharply to the carbonylation pathway well known for homogeneously catalyzed carbonylation reactions, such as the synthesis of acetic acid. The methoxycarbonyl intermediate can be further employed in a variety of methoxycarbonylation reactions, without the use or production of toxic chemicals. More generally, they observed facile, selective methoxycarbonylation of alkyl and aryl alcohols and secondary amines on metallic gold well below room temperature. A specific example is the synthesis of dimethyl carbonate, which has extensive use in organic synthesis. This work establishes a unique framework for using oxygen-activated metallic gold as a catalyst for energy-efficient, environmentally benign production of key synthetic chemical agents.

Selective oxidation of glycerol by highly active bimetallic catalysts at ambient temperature under base-free conditions

Au–Pt alloy nanoparticles deposited on Mg(OH)₂ show high activity in the selective oxidation of polyols using molecular oxygen as oxidant at mild and base-free conditions as described by Brett et al. (Angew. Chem. Int. Ed., 2011, 50, 43, 10136 doi: [10.1002/anie.201101772](https://doi.org/10.1002/anie.201101772)).

2. Novel materials

Organic electronics on natural cotton fibers

In this work published in *Organic Electronics* (volume 12, issue 12, December 2011, 2033–2039 pp.) the authors report on nanoscale modification of natural cotton fibers with conformal coatings of gold nanoparticles. Deposition of thin layers of the conductive polymer poly(3,4-ethylenedioxithiophene) and a combination of these two processes were employed to increase conductivity of plain cotton yarns. This innovative approach was especially designed to fabricate two classes of devices: passive devices such as resistors obtained from electrically conductive cotton yarns, and two types of active devices, namely organic electrochemical transistors and organic field effect transistors. The detailed electrical and mechanical analysis performed on treated cotton yarns revealed that they can be used as conductors, whilst still maintaining good flexibility. This study opens opportunities for integration between organic electronics and traditional textile technology and materials.

Cyanide-based electrolytic gold plating solution and plating method using the same

Disclosed in this recent patent WO 2011118537 (A1) from Metalor Technologies in Japan is a composition of matter claim for a new cyanide-based electrolytic gold plating solution containing a dicyanoaurate (I) alkali salt or dicyanoaurate (I) ammonium salt.

Gold and iron oxide hybrid nanocomposite materials

This critical review, penned by Leung et al. (Chem. Soc. Rev., 2012, doi: [10.1039/C1CS15213K](https://doi.org/10.1039/C1CS15213K)) provides an overview of current research activities that focused on the synthesis and application of multi-functional gold and iron oxide (Au–Fe_xO_y) hybrid nanoparticles and nanocomposites. An introduction of synthetic strategies that have been developed for generating Au–Fe_xO_y nanocomposites with different nanostructures is presented. Surface functionalisation and bioconjugation of these hybrid nanoparticles and nanocomposites are also reviewed. A variety of applications such as theranostics, gene delivery, biosensing, cell sorting, bio-separation, and catalysis is discussed and highlighted. Finally, future trends and perspectives of these sophisticated nanocomposites are outlined. Underpinning the fundamental requirements for effectively forming Au–Fe_xO_y hybrid nanocomposite materials would shed light on future development of nanotheranostics, nanomedicines, and chemical technologies. The authors propose that it would be interesting to

investigate such multi-component composite nanomaterials with different novel morphologies in the near future to advance chemistry, biology, medicine, and engineering multi-disciplinary research.

Development of biofuel cells based on gold nanoparticle-decorated multi-walled carbon nanotubes

This study, authored by Naruse et al. (Biosens. Bioelectron., volume 30, issue 1, 2011, 204–210) focused on developing the synthesis of Au nanoparticle-decorated functionalized multi-walled carbon nanotubes (Au NPs/f-MWCNTs) for monosaccharide (biofuel) oxidation reactions and practical application in air-biofuel cells. They describe the development of a scalable and straightforward method to synthesize Au NPs/f-MWCNTs which allowed control of the loading and size of the Au NPs. The Au NPs/f-MWCNTs exhibited better catalytic activities and stability than the Au sheet and subsequently resulted in a threefold increase in the power density of the air-glucose fuel cell with an exceptionally high open-circuit voltage (~1.3 V). The catalytic efficiency was confirmed by high-performance liquid chromatography with the superior of the Au NPs/f-MWCNTs over a bare gold electrode. In addition, the application of this advanced catalyst to other monosaccharide oxidation reactions showed that the configuration of –OH groups at C₂ and C₃ of the reactants plays an important role in the initial adsorption process, and thus, affects the required activation energy for further oxidation. The different monosaccharides lead to significantly different fuel cell performances in terms of power density, which coherently corresponds to the difference in the configuration of C₂ and C₃. Because two small air-glucose fuel cells using Au NPs/f-MWCNTs can run a LED lamp, the authors propose that further applications of other monosaccharides as fuel in biofuel cells for equivalent required power devices may be feasible.

3. Nanotechnology

Gold nanoparticles for high-throughput genotyping of long-range haplotypes

Completion of the Human Genome Project and the HapMap Project has led to increasing demands for mapping complex traits in humans to understand the etiology of diseases. Identifying variations in the DNA sequence, which affect how diseases develop and respond to pathogens and drugs, is important for this purpose, but it is difficult to identify these variations in large sample sets. In this *Nature Nanotechnology* article (Chen et al., Nat. Nanotechnol., volume: 6, 639–644 pp. (2011)), the authors show that through a combination of

capillary sequencing and polymerase chain reaction assisted by gold nanoparticles, it is possible to identify several DNA variations that are associated with age-related macular degeneration and psoriasis on significant regions of human genomic DNA. This method is accurate and promising for large-scale and high-throughput genetic analysis of susceptibility towards disease and drug resistance.

Nanoparticle superlattice engineering with DNA

A current limitation in nanoparticle superlattice engineering is that the identities of the particles being assembled often determine the structures that can be synthesized. Therefore, specific crystallographic symmetries or lattice parameters can only be achieved using specific nanoparticles as building blocks (and vice versa). Now, MacFarlane et al. (Science, 14 October 2011: vol. 334 no. 6053 pp. 204–208) present six design rules that can be used to deliberately prepare nine distinct colloidal crystal structures, with control over lattice parameters on the 25- to 150-nm length scale. These design rules outline a strategy to independently adjust each of the relevant crystallographic parameters, including particle size (5 to 60 nm), periodicity, and interparticle distance. As such, this work represents an advance in synthesizing tailorabile macroscale architectures comprising nanoscale materials in a predictable fashion.

Nanowired three-dimensional cardiac patches

Engineered cardiac patches for treating damaged heart tissues after a heart attack are normally produced by seeding heart cells within three-dimensional porous biomaterial scaffolds. These biomaterials, which are usually made of either biological polymers such as alginate or synthetic polymers such as poly(lactic acid), help cells organize into functioning tissues, but poor conductivity of these materials limits the ability of the patch to contract strongly as a unit. Here, Dvir et al. (Nat. Nanotechnol., 6, 720–725 (2011)) show that incorporating gold nanowires within alginate scaffolds can bridge the electrically resistant pore walls of alginate and improve electrical communication between adjacent cardiac cells. Tissues grown on these composite matrices were thicker and better aligned than those grown on pristine alginate, and when electrically stimulated, the cells in these tissues contracted synchronously. Furthermore, higher levels of the proteins involved in muscle contraction and electrical coupling are detected in the composite matrices. It is expected that the integration of conducting nanowires within three-dimensional scaffolds may improve the therapeutic value of current cardiac patches.

4. Medical and dental

Polyrotaxane/gold nanoparticle hybrid nanomaterials as anticancer drug delivery systems

Gold nanoparticles (Au NPs) have been widely used in various biomedical applications, including photothermal therapy, imaging, and drug delivery. This study (Adeli et al., *J. Mater. Chem.*, 2011, doi: [10.1039/C1JM12412A](https://doi.org/10.1039/C1JM12412A)) deals with the synthesis of new hybrid nanostructure-based drug delivery systems (DDSs), consisting of Au NP cores and polyrotaxane shells (Au NPs@PR). In order to prepare the polyrotaxanes (PRs), cyclodextrin rings were threaded onto poly(ethyleneglycol) axes, and then, the pseudopolypyrotaxanes were capped by Au NPs. The electrostatic interactions between the Au NPs and the polyrotaxane backbone led to the Au NPs@PR hybrid nanomaterials. Anticancer drugs, such as cisplatin (diamminedichloroplatinum) and doxorubicin were conjugated to Au NPs@PRs, and their controlled release, through the photothermal properties of the Au NP cores, was investigated. To prove the efficacy of the DDSs, they were endocytosed by cancer cells (mouse tissue connective fibroblast adhesive cell line, L929) and the anticancer drugs were released by a photothermal explosion of the Au NPs@PR hybrid nanomaterials. It was found that these systems are able to release drugs and kill cancer cells controllably.

Gold nanoparticles: promising nanomaterials for the diagnosis of cancer and HIV/AIDS

Gold nanoparticles (Au NPs) are currently playing a significant role for human welfare in the field of clinical diagnosis as well as several biomedical applications.

More and more research shows that Au NPs-based technologies are becoming promising approaches in cancer research and AIDS treatment. In this paper, Kumar et al. (*J. Nanomater.* (2011), Article ID 202187, doi:[10.1155/2011/202187](https://doi.org/10.1155/2011/202187)) have focused mainly on the exploitation of unique and characteristic properties of Au NPs such as surface plasmon resonance, surface enhanced Raman scattering, magnetic properties (MRI), and fluorescence behavior shown upon conjugation with biological and biocompatible ligands. These properties find wide prevalence in biodiagnostics like plasmon-based labeling and imaging, enzyme-linked immunosorbent assay, and electrochemical-based methods that can pave the way for developing novel techniques towards diagnosis and therapy of cancer and HIV/AIDS.

Oligonucleotide delivery by cell-penetrating “striped” nanoparticles

Gold nanoparticles coated with homogeneous (MUS) or “striped” (MUS-OT) ligand shells can be conjugated with double- or single-stranded DNA, and particles with either ligand configuration effectively carry DNA into melanoma tumor cells. When endocytosis is inhibited, however, MUS-OT particles continue to mediate DNA delivery, while the delivery ability of MUS particles is abolished as described by Jewell et al. (*Angew. Chem. Int. Ed.*, 2011, doi: [10.1002/anie.201104514](https://doi.org/10.1002/anie.201104514)).

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