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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

Semiconductor-like sensitivity in metallic ultrathin gold nanowire-based sensors

Due to the ease of modification of electronic structure upon analyte adsorption, semiconductors have been preferred materials as chemical sensors. At reduced dimension, however, the sensitivity of semiconductor-based sensors deteriorate significantly due to passivation and often by increased band gap caused by quantum confinement. Using first principles density functional theory combined with Boltzmann transport calculations, scientists from the Indian Institute of Science demonstrate semiconductor-like sensitivity toward chemical species in ultrathin gold nanowires (AuNW) (Roy et al., J. Phys. Chem. C, Just Accepted Manuscript, DOI: 10.1021/jp5042052). The sensing mechanism is governed by the modification of electronic structure of the AuNW as well as scattering of the charge carriers by analyte adsorption. Most importantly, the sensitivity exhibits a linear relationship with the electron affinities of the respective analytes. Based on this relationship, we propose an empirical parameter, which can predict an analyte-specific sensitivity of a AuNW, rendering them as effective sensor for a wide range of chemical analytes.

Gold nanorod enhanced organic photovoltaics: the importance of morphology effects

Organic photovoltaic devices with a 30 % improvement in power conversion efficiency are achieved when gold nanorods (Au NR) are incorporated into the active bulk heterojunction (BHJ) layer, as described by US researchers (Wadams et al., Organic Electronics, Vol. 15, Issue 7, July 2014, pp. 1448–1457. http://dx.doi.org/10.1016/j.orgel.2014.03.039). Detailed analysis of the system is provided through microscopy, device characterization, and spectroscopy, demonstrating that the enhancement effects are predominantly caused by induced morphology changes in the BHJ film rather than plasmonic effects. Wide angle X-ray diffraction provides evidence that the nanorods loaded into the BHJ film have an effect on polymer crystal orientation, leading to a systematic performance increase in the devices as a result of both internal and external efficiency improvements.

Gold nanoparticle dispersion liquid for forming conductive coating film, method for producing the same and conductive coating material composition containing the same

Patent WO2014097639 (A1) describes a gold nanoparticle dispersion liquid for forming a conductive coating film, which is capable of forming a conductive coating film having a low specific resistance by firing at low firing temperatures even in cases where the ratio of gold nanoparticles having a particle diameter of less than 5 nm is suppressed to less than 90 % on a number basis, and a method for producing the gold nanoparticle dispersion liquid for forming a conductive coating film. The present invention provides a gold nanoparticle dispersion liquid for forming a conductive coating film, which contains gold nanoparticles that have a number average particle diameter within the range of 3.98–5.24 nm and a ratio of the number of particles having a particle diameter of less than 5 nm relative to the total number of particles within the range of 64–83 %.

Plasmonic gold nanoparticles modified titania nanotubes for antibacterial application

Close-packed TiO2 nanotube arrays have been prepared on metallic Ti surface by electrochemical anodization by Chinese researchers (Li et al., Appl. Phys. Lett. 104, 261110 (2014); http://dx.doi.org/10.1063/1.4885401). Subsequently, by magnetron sputtering, Au nanoparticles are coated onto the top sidewall and tube inwall. The Au@TiO_2 systems can

effectively kill *Staphylococcus aureus* and *Escherichia coli* in darkness due to the existence of Au nanoparticles. On the basis of classical optical theories, the antibacterial mechanism is proposed from the perspective of localized surface plasmon resonance. Respiratory electrons of bacterial membrane transfer to Au nanoparticles and then to TiO2, which makes bacteria steadily lose electrons until death. This work provides insights for the better understanding and designing of noble metal nanoparticles-based plasmonic heterostructures for antibacterial application.

Nanoparticles heat through light localization

Aqueous solutions containing light-absorbing nanoparticles have recently been shown to produce steam at high efficiencies upon solar illumination, even when the temperature of the bulk fluid volume remains far below its boiling point. Here, Rice University researchers show that this phenomenon is due to a collective effect mediated by multiple light scattering from the dispersed nanoparticles (Hogan et al., Nano Lett., Article ASAP, DOI: 10.1021/nl5016975). Randomly positioned nanoparticles that both scatter and absorb light are able to concentrate light energy into mesoscale volumes near the illuminated surface of the liquid. The resulting light absorption creates intense localized heating and efficient vaporization of the surrounding liquid. Light trapping-induced localized heating provides the mechanism for low-temperature light-induced steam generation and is consistent with classical heat transfer.

Facile synthesis of pentacle gold–copper alloy nanocrystals and their plasmonic and catalytic properties

The combination of gold and copper is a good way to pull down the cost of gold and ameliorate the instability of copper. Through shape control, the synergy of these two metals can be better exploited. Here, researchers based in China and the USA report an aqueous phase route to the synthesis of pentacle gold–copper alloy nanocrystals with fivefold twinning, the size of which can be tuned in the range from 45 to 200 nm (He et al., Nature Communications, 5, Article number 4327, doi:10.1038/ncomms5327). The growth is found to start from a decahedral core, followed by protrusion of branches along twinning planes. Pentacle products display strong localized surface plasmon resonance peaks in the near-infrared region. Under irradiation by an 808-nm laser, 70-nm pentacle nanocrystals exhibit a notable photothermal effect to kill 4T1 murine breast tumors established on BALB/c mice. In addition, 70-nm pentacle nanocrystals show better catalytic activity than conventional citrate-coated 5-nm Au nanoparticles toward the reduction of *p*-nitrophenol to *p*-aminophenol by sodium borohydride.

Electronics

Room-temperature printing of organic thin-film transistors with π-junction gold nanoparticles

Printing semiconductor devices under ambient atmospheric conditions is a promising method for the large-area, low-cost fabrication of flexible electronic products. However, processes conducted at temperatures greater than 150 °C are typically used for printed electronics, which prevents the use of common flexible substrates because of the distortion caused by heat. Japanese researchers describe a method for the room-temperature printing of electronics, which allows thin-film electronic devices to be printed at room temperature without the application of heat (Minari et al., Advanced Functional Materials, 2014, DOI: 10.1002/adfm.201400169). The development of π-junction gold nanoparticles as the electrode material permits the room-temperature deposition of a conductive metal layer. Room-temperature patterning methods are also developed for the Au ink electrodes and an active organic semiconductor layer, which enables the fabrication of organic thin-film transistors through room-temperature printing. The transistor devices printed at room temperature exhibit average field-effect mobilities of 7.9 and 2.5 $cm^2\ V^{-1}\ s^{-1}$ on plastic and paper substrates, respectively. These results suggest that this fabrication method is very promising as a core technology for low-cost and high-performance printed electronics.

Energy storing electrical cables: integrating energy storage and electrical conduction

A novel device architecture of a coaxial supercapacitor cable that functions both as an electrical cable and an energy-storage device is demonstrated by researchers from the University of Central Florida (Yu and Thomas, Advanced Materials, DOI: 10.1002/adma.201400440). The inner core is used for electrical conduction and the overlying layers are used for energy storage. This unique design provides excellent flexibility, long and stable cycle lifetimes, and high energy and power densities. All these remarkable results demonstrate a clear technological advance achieved by clubbing electrical conduction and energy storage into a single cable.

Gold nanoparticle and gold nanorod embedded PEDOT:PSS thin films as organic thermoelectric materials

Researchers report the thermoelectric properties of organic–inorganic hybrid thin films composed of conductive polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), and inorganic gold nanomaterials (Yoshida and Toshima, Journal of Electronic Materials, Vol. 43, Issue 6, pp. 1492–1497). Two kinds of material with different shapes,

namely rod-shaped gold nanorods (AuNRs) and spherical gold nanoparticles (AuNPs), were used in this study. The PEDOT:PSS/AuNR hybrid films showed an enhancement in electrical conductivity ($\sigma \approx 2{,}000$ S cm^{-1}) and concurrently a decrease in the Seebeck coefficient ($S \approx 12\,\mu$V K^{-1}) with increase in the AuNR concentration. This behavior indicates the presence of the hybrid effect of AuNR on the thermoelectric properties. From scanning electron microscopy (SEM) observation of the highly concentrated PEDOT:PSS/AuNR hybrid films, the formation of a percolated structure of AuNRs was confirmed, which probably contributed to the large enhancement in σ. For the highly concentrated PEDOT:PSS/AuNP films, a dense distribution of AuNPs in the film was also observed, but this did not lead to a major change in the σ value, probably due to the less conductive connections between NPs. This suggests that one-dimensional particles with larger aspect ratio (rods and wires) are favorable nanocomponents for development of highly conductive hybrid materials.

Ambient temperature ball bond

Patent US8767351 (B1) describes systems and methods for attaining a ball bond using less than one thousandth of an inch diameter gold wire using ultrasonic bonding energy and without heating an underlying bonding pad. The ball bond allows the use of particularly small bonding pads that are particularly close to adjacent microelectronic structures that limit the use of other bonding techniques that have shallow takeoff angles.

Fuel cell technologies

Patent WO2014087878 (A1) describes a fuel cell separator comprising a substrate, a first plating layer formed on the substrate, and a gold plating layer formed on the first plating layer by electroless plating, said fuel cell separator being characterized in that an arithmetic average roughness (Ra) of the surface of the first plating layer facing the gold plating layer is 80 nm or less. According to the present invention, the gold plating layer can be uniformly formed on an uneven portion constituting a gas flow path, and a non-forming portion and pin holes are prevented from occurring in the gold plating layer without increasing the film thickness of the gold plating layer, thereby enabling a fuel cell separator excellent in corrosion resistance and conductivity to be provided.

Catalysis

NO_X purification catalyst

The invention described in patent US2014194281 (A1) relates to a catalyst able to exhibit an NO_X purification performance at a low temperature and/or in an oxidizing atmosphere, that is, a nitrogen oxide purification catalyst including gold atoms and nickel atoms in a solid and a state of close proximity.

Alkoxyboration: ring-closing addition of B–O σ bonds across alkynes

For nearly 70 years, the addition of boron–X σ bonds to carbon–carbon multiple bonds has been employed in the preparation of organoboron reagents. However, the significantly higher strength of boron–oxygen bonds has thus far precluded their activation for addition, preventing a direct route to access a potentially valuable class of oxygen-containing organoboron reagents for divergent synthesis. We herein report the realization of an alkoxyboration reaction, the addition of boron–oxygen σ bonds to alkynes. Functionalized O-heterocyclic boronic acid derivatives are produced using this transformation, which is mild and exhibits broad functional group compatibility. Our results demonstrate activation of this boron–O σ bond using a gold catalysis strategy that is fundamentally different from that used previously for other boron addition reactions. (Hirner et al., J. Am. Chem. Soc., 2014, 136 (12), pp 4740–4745, DOI: 10.1021/ja500463p).

Green synthesis of core–shell gold–palladium@palladium nanocrystals dispersed on graphene with enhanced catalytic activity toward oxygen reduction and methanol oxidation in alkaline media

Well-defined core–shell gold–palladium@palladium nanocrystals (AuPd@Pd) are facilely prepared by a simple and green wet-chemical method at 25 °C described by Chinese researchers (Zheng et al., Journal of Power Sources, Vol. 262, pp. 270–278. http://dx.doi.org/10.1016/j.jpowsour.2014.03.131). A Good's buffer, 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES), is used as a reducing agent and a shape-directing agent, while there is no template, seed, organic solvent, or surfactant involved. The AuPd@Pd nanocrystals are uniformly dispersed on graphene nanosheets by ultrasonication, resulting in the formation of graphene supported AuPd@Pd (G-AuPd@Pd). The as-prepared nanocomposites exhibit the improved catalytic activity, good tolerance, and better stability for oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) in alkaline media, compared with the G-Pd and commercial Pd black catalysts. The as-developed method may provide a promising pathway for large-scale fabrication of AuPd-based catalysts.

Volcano-shape glycerol oxidation activity of palladium-decorated gold nanoparticles

Bimetallic PdAu catalysts are more active than monometallic ones for the selective oxidation of alcohols, but the reasons for

improvement remain insufficiently detailed. A metal-on-metal material can probe the structure–catalysis relationship more clearly than conventionally prepared bimetallics. In this study from the Wong group at Rice University (Zhao et al., Chemical Sciences, 2014 DOI: 10.1039/c4sc01001a), Pd-on-Au nanoparticles with variable Pd surface coverages (sc%) ranging from 10 to 300 sc% were synthesized and immobilized onto carbon (Pd-on-Au/C). Tested for glycerol oxidation at 60 °C, pH 13.5, and 1 atm under flowing oxygen, the series of Pd-on-Au/C materials showed volcano-shape catalytic activity dependence on Pd surface coverage. Increasing surface coverage led to higher catalytic activity, such that initial turnover frequency (TOF) reached a maximum of ~6,000 h^{-1} at 80 sc%. Activity decreased above 80 sc% mostly due to catalyst deactivation. Pd-on-Au/C at 80 sc% was >ten times more active than monometallic Au/C and Pd/C, with both exhibiting TOF values less than ~500 h^{-1}. Glyceric acid was the dominant primary reaction product for all compositions, with its zero-conversion selectivity varying monotonically as a function of Pd surface coverage. Glyceric acid yield from Pd-on-Au/C (80 sc%) was 42 %, almost doubles the yields from Au/C and Pd/C (16 and 22 %, respectively). Ex situ X-ray absorption near edge structure analysis of two Pd-on-Au/C materials with comparable activities (60 and 150 sc%) showed that the former had less oxidized Pd ensembles than the latter and that both catalysts were less oxidized compared to Pd/C. That Au stabilizes the metallic state of surface Pd atoms may be responsible for activity enhancement observed in other PdAu-catalyzed oxidation reactions. Decorating a Au surface with Pd generates a catalyst that has the deactivation resistance of Au, the higher glyceric acid selectivity of Pd, and the synergistically higher activities that neither metal has.

Diesel oxidation catalyst comprising palladium, gold and ceria

The invention described in patent US2014161695 (A1) relates to a diesel oxidation catalyst comprising a carrier substrate and a first washcoat layer disposed on the substrate, the first washcoat layer comprising palladium supported on a support material comprising a metal oxide, gold supported on a support material comprising a metal oxide, and a ceria comprising compound, as well as a process for the preparation of such catalyst.

Synergistic gold-bismuth catalysis for non-mercury hydrochlorination of acetylene to vinyl-chloride monomer

Gold has been proposed as an environmentally friendly catalyst for acetylene hydrochlorination for vinyl-chloride monomer synthesis by replacing the commercially used mercury catalyst. However, long life with excellent activity is difficult to achieve since gold is readily reduced to metallic nanoparticles. The stability of gold limits its industrial application. In this paper, US researchers promoted gold with bismuth for the hydrochlorination of acetylene (Zhou et al., ACS Catal., Just Accepted Manuscript, DOI: 10.1021/cs500530f). It was found that the Bi promotion leads to partial reduction to AuCl, rather than the complete reduction of Au to metallic nanoparticles in the absence of Bi. The optimized catalyst with a molar ratio of Bi:Au=3:1 (0.3 wt% Au) showed comparable reactivity to 1.0 wt% Au catalyst and significantly improved stability. Furthermore, the gold-bismuth catalyst had higher activity and stability than the commercial mercury catalyst and is less toxic and more environmental-friendly, making it a potentially green mercury-free industrial catalyst for acetylene hydrochlorination.

Chemistry

Chemistry and biology of two novel gold(I) carbene complexes as prospective anticancer agents

Two novel gold carbene compounds manifested similarly potent cytotoxic actions in vitro against A2780 human ovarian carcinoma cells, and both were able to completely overcome resistance to cisplatin in the A2780R line according to Italian researchers (Messori et al., Inorg. Chem., 2014, 53 (5), pp 2396–2403 DOI: 10.1021/ic401731a). Relevant metalation effects were highlighted with the Atox-1 protein, suggesting that the investigated gold carbene complexes most probably act through selective metalation of a few proteins bearing specific gold binding motifs.

A golden future in medicinal inorganic chemistry: the promise of anticancer gold organometallic compounds

From wedding rings on fingers to stained glass windows, by way of Olympic medals, gold has been highly prized for millennia. Nowadays, organometallic gold compounds occupy an important place in the field of medicinal inorganic chemistry due to their unique chemical properties with respect to gold coordination compounds. In fact, several studies have proved that they can be used to develop highly efficient metal-based drugs with possible applications in the treatment of cancer. This perspective penned by researchers from France and Germany summarizes the results obtained for different families of bioactive organometallic gold compounds including cyclometallated gold(III) complexes with C,N-donor ligands, gold(I), and gold(I/III) N-heterocyclic (NHC) carbene complexes, as well as gold(I) alkynyl complexes, with promising anticancer effects (Bertrand and Cassini, Dalton Trans., 2014, 43, 4209–4219. DOI: 10.1039/C3DT52524D). They focus on recent

developments in the field and discuss the potential of this class of organometallic compounds in relation to their versatile chemistry and innovative mechanisms of action.

Medicine

Photothermal killing of cancer cells by the controlled plasmonic coupling of silica-coated Au/Fe_2O_3 nanoaggregates

Tumor ablation by thermal energy via the irradiation of plasmonic nanoparticles is a relatively new oncology treatment. Hybrid plasmonic-superparamagnetic nanoaggregates (50–100 nm in diameter) consisting of SiO_2-coated Fe_2O_3 and Au (≈30 nm) nanoparticles were fabricated by researchers in Switzerland using scalable flame aerosol technology (Sotiriou et al., Advanced Functional Materials, 2014, DOI: 10.1002/adfm.201303416). By finely tuning the Au interparticle distance using the SiO_2 film thickness (or content), the plasmonic coupling of Au nanoparticles can be finely controlled bringing their optical absorption to the near-IR that is most important for human tissue transmittance. The SiO_2 shell facilitates also dispersion and prevents the reshaping or coalescence of Au particles during laser irradiation, thereby allowing their use in multiple treatments. These nanoaggregates have magnetic resonance imaging (MRI) capability as shown by measuring their r2 relaxivity while their effectiveness as photothermal agents is demonstrated by killing human breast cancer cells with a short, 4-min near-IR laser irradiation (785 nm) at low flux (4.9 W cm^{-2}).

On-demand intracellular amplification of chemoradiation with cancer-specific plasmonic nanobubbles

Chemoradiation-resistant cancers limit treatment efficacy and safety. Researchers from Rice University, Northeastern and MD Anderson show here the cancer cell-specific, on-demand intracellular amplification of chemotherapy and chemoradiation therapy via gold nanoparticle- and laser pulse-induced mechanical intracellular impact (Lukianova-Hleb et al., *Nature Medicine* (2014) doi:10.1038/nm.3484). Cancer aggressiveness promotes the clustering of drug nanocarriers and gold nanoparticles in cancer cells. This cluster, upon exposure to a laser pulse, generates a plasmonic nanobubble, the mechanical explosion that destroys the host cancer cell or ejects the drug into its cytoplasm by disrupting the liposome and endosome. The same cluster locally amplifies external X-rays. Intracellular synergy of the mechanical impact of plasmonic nanobubble, ejected drug, and amplified X-rays improves the efficacy of standard chemoradiation in resistant and aggressive head and neck cancer by 100-fold in vitro and 17-fold in vivo, reduces the effective entry doses of drugs and X-rays to 2–6 % of their clinical doses, and efficiently spares normal cells. The developed quadrapeutic technology combines four clinically validated components and transforms a standard macrotherapy into an intracellular on-demand theranostic microtreatment with radically amplified therapeutic efficacy and specificity.

Drug repositioning: auranofin as a prospective antimicrobial agent for the treatment of severe staphylococcal infections

Auranofin (AF), a gold(I) complex in clinical use for the therapy of rheumatoid arthritis, is reported here to produce remarkable bactericidal effects in vitro against *Staphylococcus* sp. (Cassetta et al., BioMetals, August 2014, Vol. 27, Issue 4, pp. 787–791). Noticeably, a similar antimicrobial action and potency are also noticed toward a few methicillin-resistant *S. aureus* strains but not toward *E. coli*. The time and concentration dependencies of the antimicrobial actions of AF have been characterized through recording time kill curves and a concentration-dependent profile highlighted. Overall, the present results point out that auranofin might be quickly and successfully repurposed for the treatment of severe bacterial infections due to resistant *Staphylococci*.

Auranofin and related heterometallic gold(I)–thiolates as potent inhibitors of methicillin-resistant *Staphylococcus aureus* bacterial strains

A series of new heterometallic gold(I)–thiolates containing ferrocenyl phosphines were synthesized by researchers in Spain and the USA (Hokai et al., Journal of Inorganic Biochemistry, Vol. 138, September 2014, pp. 81–88). Their antimicrobial properties were studied and compared to that of FDA-approved drug, auranofin (Ridaura), prescribed for the treatment of rheumatoid arthritis. MIC in the order of one digit micromolar were found for most of the compounds against Gram-positive bacteria *S. aureus* and CA **methicillin-resistant *S. aureus*** (MRSA) strains US300 and US400. Remarkably, auranofin inhibited S. aureus, US300 and US400 in the order of 150–300 nM. This is the first time that the potent inhibitory effect of auranofin on MRSA strains has been described. The effects of a selected heterometallic compound and auranofin were also studied in a non-tumorigenic human embryonic kidney cell line (HEK-293).

Cisplatin-tethered gold nanospheres for multimodal chemo-radiotherapy of glioblastoma

Glioblastoma multiforme (GBM) remains the most aggressive and challenging brain tumor to treat. We report first successful chemo-radiotherapy on patient-derived treatment resistant GBM cells using a cisplatin-tethered gold nanoconjugate.

After preferential uptake by the GBM cells, the nanoconjugate effects DNA damage which initiates caspase-mediated apoptosis in those cells. In the presence of radiation, both gold and platinum of cisplatin, serve as high atomic number radiosensitizers leading to the emission of ionizing photoelectrons and Auger electrons. This resulted in enhanced synergy between cisplatin- and radiotherapy-mediated cytotoxicities and photo/Auger electron-mediated radiosensitization leading to complete ablation of the tumor cells in an in vitro model system. This study demonstrates the potential of designed nanoparticles to target aggressive cancers in patient-derived cell lines providing a platform to move toward treatment strategies (Setua et al., Nanoscale, 2014, Accepted Manuscript, DOI: 10.1039/C4NR03693J).