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Structure and Applications of Gold in Nanoporous Form

Jay K. Bhattarai, Dharmendra Neupane,
Bishal Nepal, Vasilii Mikhaylov,
Alexei V. Demchenko and Keith J. Stine

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Abstract

Nanoporous gold (np-Au) has many interesting and useful properties that make it a material of interest for use in many technological applications. Its biocompatible nature and ability to serve as a support for self-assembled monolayers of alkanethiols and their derivative make it a suitable support for the immobilization of carbohydrates, enzymes, proteins, and DNA. Its chemically inert, physically robust and conductive high-surface area makes it useful for the design of electrochemistry-based chemical/bio-sensors and reactors. Furthermore, it is also used as solid support for organic molecular synthesis and biomolecules separation. Its enhanced optical property has application in design of plasmonics-based sensitive biosensors. In fact, np-Au is one of the few materials that can be used as a transducer for both optical and electrochemical biosensing. Due to the presence of low-coordination surface sites, np-Au shows remarkable catalytic activity for oxidation of molecules like carbon monoxide and methanol. Owing to the importance of np-Au, in this chapter we will highlight different strategies of fabrication of np-Au and its emerging applications based on its unique properties.

Keywords: nanoporous gold (np-Au), dealloying, catalysis, biosensor, actuator, plasmonics

1. Introduction

The importance of the nanoporous materials has been well established historically by the extensive use of zeolite and activated carbon in separation and purification for industrial and clinical applications [1, 2]. Research on nanoporous materials for gas storage, drug delivery, catalysis, sensing, and optoelectronic applications are ongoing with the focus of using the

properties of nanoporous materials to their fullest to improve nanotechnology to the state-of-the-art. In recent years, nanostructures of gold have gained great attention because of their broad range of potential applications in the fields of medicine and energy. Gold nanoparticles (AuNPs) have already been used in a clinical trial for the thermal ablation of solid tumors as a photothermal agent due to its unique optical properties [3]. It has also shown promising results in drug delivery and as a contrast agent for imaging to advance cancer therapy [4]. Gold nanorods (GNs) have also shown promising results in biosensing, drug delivery, photothermal therapy, and imaging.

Gold in the nanoporous form, so-called nanoporous gold (np-Au), has gathered considerable attention recently, as it is a robust 3-dimensional nanostructured form of gold with a very high surface area-to-volume ratio and still maintains the properties of AuNPs and GN [5]. The size of the pores and ligament of np-Au can be easily tuned and are in the range from few nanometers to few hundreds of nanometers [6]. The AuNPs and GNs easily aggregate if suitable conditions were not provided making them less useful for some nanotechnology applications. The np-Au not only circumvents this problem but is simple to prepare and easy to handle for wide varieties of applications.

Through this survey and discussion, we will demonstrate that there is a growing interest in this material, which is justified by its many emerging applications. As a support for enzyme immobilization, the material has accommodated a range of enzymes and is suitable for the development of enzyme reactors. Numerous biosensors for metabolites and for biomarkers have been introduced using np-Au as a support. The applications to catalysis have included many of the oxidation reactions suitable for gold nanoparticles, but with the advantage of possible use in a free-standing intact format. The support of surface plasmons by the material opens up possibilities for use in the development of optical biosensors.

This chapter will cover different synthetic strategies for the preparation of np-Au in different forms. We will also discuss the methods commonly used to characterize np-Au, including scanning electron microscopy, transmission electron microscopy, tomography, and gas adsorption isotherm measurements. Finally, we will focus on the broad range of applications of np-Au, including chemical sensing, electrochemical and optical biosensing, catalysis, and mechanical actuation.

2. Methods of preparation

2.1. Dealloying

The most common method of preparing np-Au is by dealloying [7]. It is a top-down approach where the alloy of gold containing other less noble metals is treated in a corrosive environment with or without applying a potential. The dealloying process selectively removes the less noble metal from Au-M alloy (M=Ag, Cu, Sn, Al, etc.) creating the nanoporous structure having interconnected ligaments [7, 8]. The shape and size of the alloy is important as the np-Au formed after the dealloying process maintains the shape and size of

the alloy. The np-Au can be fabricated as a supported thin film or a free-standing structure. The supported np-Au is physically stable and easy to handle compared to the free-standing np-Au and is most commonly prepared for use as a working electrode in electrochemical experiments. Using supported np-Au, it is convenient to separate the interfacial boundary between np-Au and the clip holding the electrode. **Figure 1A** shows SEM images of the cross-section of np-Au supported on gold wire prepared by first forming the Au-Ag alloy using electrochemical deposition followed by dealloying in HNO_3 for 24 h to selectively remove Ag [9]. **Figure 1A'** is a low magnification SEM image of surface morphology of the as-prepared np-Au and the inset is the high magnification image [9]. Low magnification image shows crack formation throughout the surface due to the volume shrinkage during dealloying whereas high magnification image shows a porous structure having inter-ligament gap (pore size) of 27 ± 7 nm and ligament width of 26 ± 5 nm.

On the other hand, if the electrochemical connection is not desired, the free-standing np-Au is the material of choice for different applications, such as optical biosensing, solid-support organic synthesis, and protein separation. Free-standing np-Au plates, leaves and wires can be easily fabricated by simply dealloying the commercially available 10–12 Karat gold alloys in the desired form. The thicker the alloy, the longer should be the dealloying time for the effective removal of the sacrificial metals. Dealloying time is also important in determining

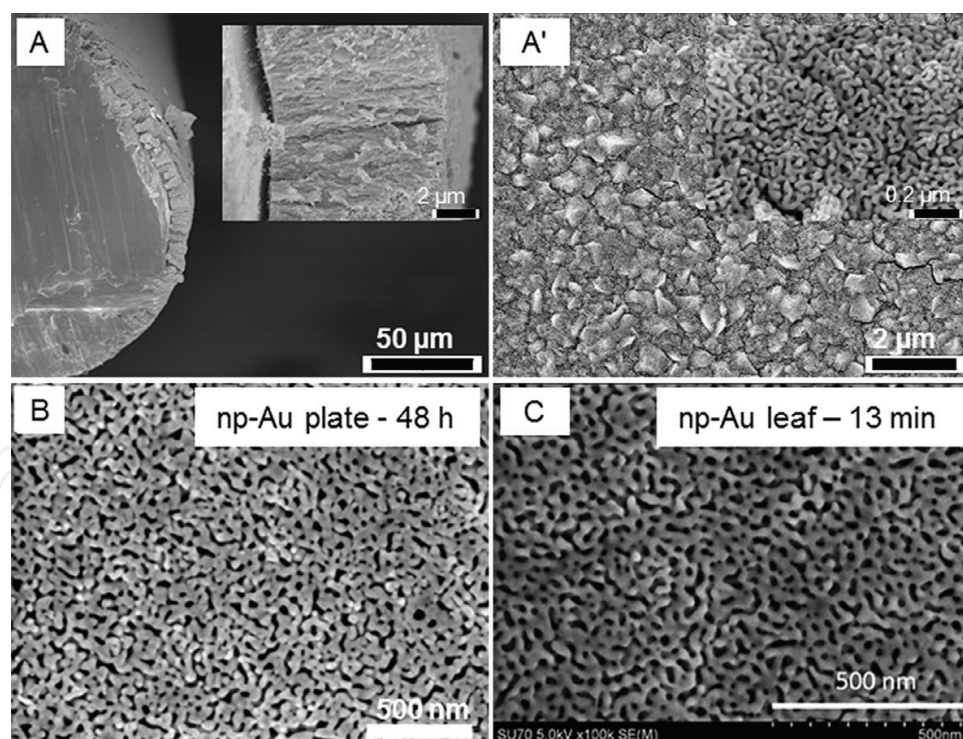


Figure 1. SEM images of np-Au in different form prepared by dealloying in concentrated HNO_3 . (A) Cross-section of Au supported np-Au obtained by 24 h selective dissolution of Ag from Au-Ag alloy, where the alloy was prepared by providing potential of -1.0 V (vs. Ag/AgCl) for 10 min on the gold wire. (A') Top view of the as-prepared np-Au at low magnification. Insets are the corresponding high magnification images. Reproduced and slightly modified with permission from ref. [9], Copyright 2016, Elsevier. (B) np-Au plate dealloyed for 48 h. Reproduced from ref. [10]. (C) np-Au leaf (~ 110 nm) dealloyed for 13 min. Reproduced with permission from ref. [11], Copyright 2011, Elsevier.

the sizes of pores and ligaments. **Figure 1B** and **C** show the np-Au plate ($\sim 250 \mu\text{m}$ thick) dealloyed for 48 h and np-Au leaf ($\sim 110 \text{ nm}$ thick) dealloyed for 13 min in HNO_3 , respectively [10, 12]. It was found that the structure and the composition of np-Au leaf after dealloying for 2 h in nitric acid are comparable to that of np-Au plate dealloyed for 48 h with the pores size nearly 30 nm and nearly 2 atomic percentage of residual silver [11, 13].

When desired, np-Au can also be created in wide varieties of free or surface bound micro and nanostructures. The micro and nanostructures of np-Au can be created using three strategies: (1) template (2) dewetting, and (3) solvent coarsening. The template-based strategy is the most common as wide varieties of desired structures can be created. Silver chloride (AgCl) can be used as a sacrificial template to prepare different types of zero-dimensional np-Au nanostructures, such as nanoframes, bowls and shells [14, 15, 22], **Figure 2A** and **B**. This solution phase synthetic strategy of np-Au can be performed by depositing Au nanoparticles from HAuCl_4 precursor on to AgCl template using hydroquinone as a reducing agent and polyvinyl pyrrolidone (PVP) as a stabilizing agent. The sacrificial AgCl template can then be removed using concentrated NH_4OH , and PVP can be removed by treating the np-Au with piranha solution. The adsorption of PVP on growing Au nanoparticle highly influences the growth of np-Au nanostructure.

Polystyrene (PS) beads are frequently used as a template for np-Au preparation as they are readily available and can be easily removed using heat or chloroform. Nyce and co-workers used PS-bead to synthesize monoliths containing hollow np-Au of nearly $10 \mu\text{m}$ in diameter [17]. First, they created monolithic hollow Au/Ag alloy particle by subsequent electroless deposition of Au and Ag on PS-bead followed by casting and heat removal of the template.

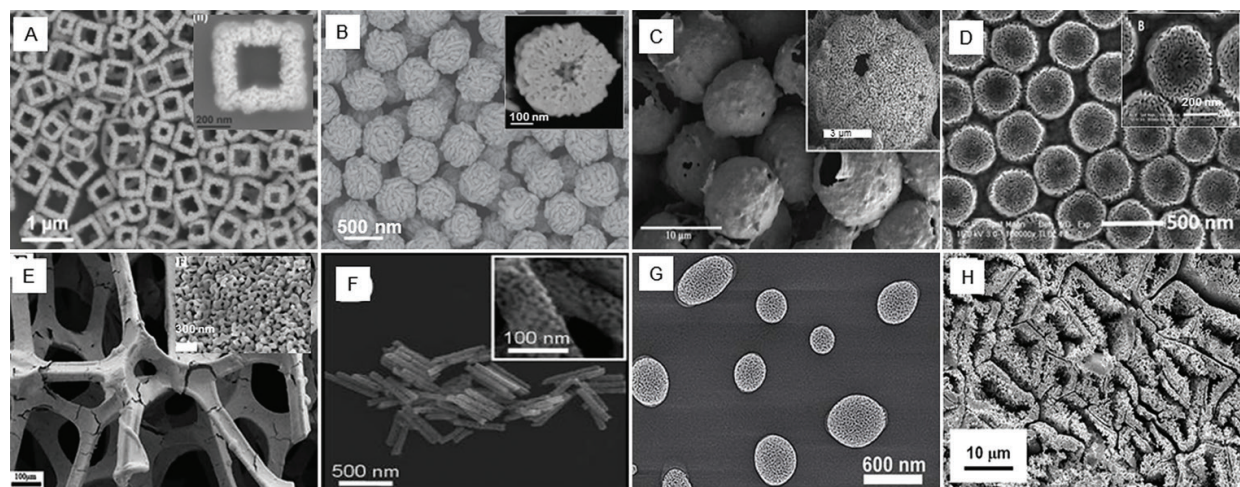


Figure 2. SEM images of np-Au nano- and micro-structures prepared using different methods. (A) and (B) np-Au nanoframes and nanoshells prepared using AgCl as a template. The template used for C, D, E, and F are polystyrene beads, anodized Al_2O_3 films, and Ni macroporous foam, respectively. (G) Nanoparticles formed using dewetting technique on SiO_2/Si surface from 20 nm thick Ag and 10 nm thick Au layer. (H) np-Au coarsened by immersion into concentrated HCl solution for 24 h. Top surface divided into “plots” by coarsened nanoporous walls. The typical side length of the “plots” was approximately from several micrometers to $20 \mu\text{m}$. Reproduced with permission from Refs. [14–21], respectively. (A) Copyright 2015, American Chemical Society, (B) Copyright 2014, Macmillan Publishers Limited, (C) Copyright 2007, American Chemical Society, (D) Copyright 2016, American Chemical Society, (E) Copyright 2014, The Royal Society of Chemistry, (F) Copyright 2008, American Chemical Society, (G) Copyright 2012, The Royal Society of Chemistry, and (H) Copyright 2006, American Chemical Society.

Finally, the hollow Au/Ag alloy was dealloyed in HNO_3 to create monolithic hierarchical np-Au, **Figure 2C**. PS-bead can also be used as a mask to generate a semi-random array of np-Au disk on silicon or glass surface [16, 19]. For this, silicon or glass support is sputter deposited with gold and silver alloy on top of which the monolayer of PS-beads is prepared. Oxygen plasma treatment is then employed to shrink the immobilized PS-bead and separate it from the neighboring beads followed by sputter-etching in argon plasma to transfer the pattern of the bead to the alloy film. Finally, PS-beads were dissolved in chloroform to obtain the alloy disk and dealloyed in concentrated nitric acid to obtain the np-Au disk, **Figure 2D**.

Three-dimensional (3D) structures of metals and metal oxides can be used as a template for preparation of np-Au of different shapes and sizes. 3D-macroporous Ni foam was used as a template to prepare the three-dimensional np-Au film supported on Ni surface [19, 23]. In this method, Au-Sn alloy film was first electrodeposited onto the surface of Ni foam followed by removal of Sn in NaOH and H_2O_2 solution by treating for 3 days at room temperature, resulting in three-dimensional np-Au, **Figure 2E**. Significant advances in preparing monodisperse np-Au nanorods and nanowires of desired size have been made by using porous anodic aluminum oxide (AAO) as a template. The AAO having pore sizes of around 100–200 nm and wide varieties of thickness can be used as a template for preparing np-Au nanorods [18], nanowires [24], and nanotubes [25], **Figure 2F**. In this method, one side of the alumina template is closed by sputtering or evaporating a conducting copper film, followed by electrochemical cathodic deposition of gold and silver alloy through the template. The alloy nanostructures can be stripped as a free structure when Al_2O_3 and deposited Cu film is dissolved in suitable solutions. KOH can be used to dissolve Al_2O_3 , and a mixture of CuCl_2 and HCl can be used to dissolve the Cu film. Finally, removing Ag from Au-Ag alloy gives the nanoporous nanostructures. By decreasing or alternating gold/silver composition ratios to prepare the alloy on Al_2O_3 template followed by dealloying, step-like np-Au nanowires such as nano-cones and nano-barbells can be prepared [26].

Dewetting bilayers of gold and sacrificial less noble metal on SiO_2 or TiO_2 surface at elevated temperature leads to the inter-diffusion between bilayered metals to form an alloy while shrinking the volume to generate the isolated particles or droplets [20, 27, 28], **Figure 2G**. Removal of the sacrificial less noble metal using dealloying or etching creates the np-Au nanoparticle similar in shape and size to the alloy particle [29, 30]. Using this technique, ordered array of np-Au nanoparticles can be created on nanoimprint lithography prepatterned SiO_2/Si substrates, where the size of the np-Au particles can be easily controlled by varying the metal layer thickness [31].

The np-Au ligaments and pores can be easily modified by keeping it in corrosive solvent for different period of time. It has been found that keeping np-Au in HNO_3 for longer time creates the stress to the ligaments, which start merging at some locations decreasing the size of pores or completely closing the pore while at the other locations ligaments keeps separating further generating large pores. This process results into larger but fewer numbers of pores and ligaments [10]. We have found that after 42 days of dealloying in nitric acid, the average inter-ligament gaps and ligaments width increases to 115 ± 32 and 160 ± 47 nm, respectively from 27 ± 7 and 38 ± 8 nm obtained after 24 h dealloying. Interestingly, when np-Au is immersed

in concentrated hydrochloric acid for 24 h, the ligaments of np-Au gets coarsened by several hundred nanometers and divides into regions of few micrometers to 20 μm in size, generating np-Au prism [21], **Figure 2H**.

2.2. Electrochemical etching of gold electrode

Thin layer np-Au films can be created on the surface of gold electrodes by applying a potential with or without the use of sacrificial metals from electrolyte solution. Different strategies have been utilized to prepare np-Au using this method, including holding a high anodic potential for different times [32], ramping up the potential from 0 V to very high potential (>20 V) in few seconds [33, 34], cycling the potential between two points at a specific rate in suitable electrolyte [35], and using the combination of these methods. Chloride-containing electrolytes are commonly used for this technique, which create np-Au through electro-dissolution of Au into AuCl_2^- and AuCl_4^- , disproportionation of AuCl_2^- to Au atom and AuCl_4^- , and deposition of Au atom back on gold electrode to form np-Au [32]. Deng and co-workers demonstrated that by simply holding the potential at 0.9 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$, sat.) in 2 M HCl, np-Au film can be created on the gold surface within a minute [32]. Later, the same group proved the effectiveness of the chloride ions for np-Au formation by taking 1 M KCl as an electrolyte. By providing 1.29 V versus saturated calomel electrode for 300 s the authors were able to create np-Au in neutral KCl solution [36]. The work has been further elaborated using 0.5 M NH_4Cl as an electrolyte to prepare np-Au structure by providing the anodic potential of 1.32 V (vs. SCE) [37]. It has been found that the roughness factor, the ratio of the electrochemical active surface area to the geometric area, of np-Au depends on potential step time, which can be enhanced when hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) solution is mixed with NH_4Cl to prevent bubble formation during the np-Au formation step. Non-chloride-containing electrolytes like citric acid have also been used to prepare np-Au on gold rod by providing the anodic potential of 4.0 V for 3 h to create the ultra-high surface area with the roughness factor higher than 1000 [38].

Instead of simply sweeping the anodic potential linearly, multi-cycle potential scans can be used to prepare np-Au on the polished gold electrode using suitable electrolytes. In the cathodic potential scan, the sacrificial metal ions from the solution can be electrodeposited to create gold alloy in situ which on the subsequent anodic potential scan is removed from the surface of the gold electrode [39]. After the multiple cathodic/anodic cycles, np-Au with a high surface area can be generated, **Figure 3**. Hu and co-workers prepared a thin layer of np-Au on the gold electrode surface by etching the electrode by providing multiple electrochemical cycles in the potential range -0.72 to 1.88 V at 10 mV s^{-1} in benzyl alcohol electrolyte containing 1.5 M ZnCl_2 at 120°C [35]. In this study, Zn plate and a Zn wire were used as the counter and reference electrodes, respectively.

Nanoporous gold can also be formed by first polarizing the pure gold electrode, holding it at a certain potential for specific time, and finally reversing the potential to clean the gold surface. By polarizing the gold electrode from 0.0 to 2.0 V at the scan rate of 0.02 V s^{-1} in 0.5 M H_2SO_4 , holding the potential at 2.0 V for 60 min to form a gold oxide (orange-yellowish surface) followed by reverse potential scan to reduce the oxide layer on the gold surface (black surface), Sukeri et al. succeeded in preparing np-Au film on pure gold surface [40]. Similarly, Nishio

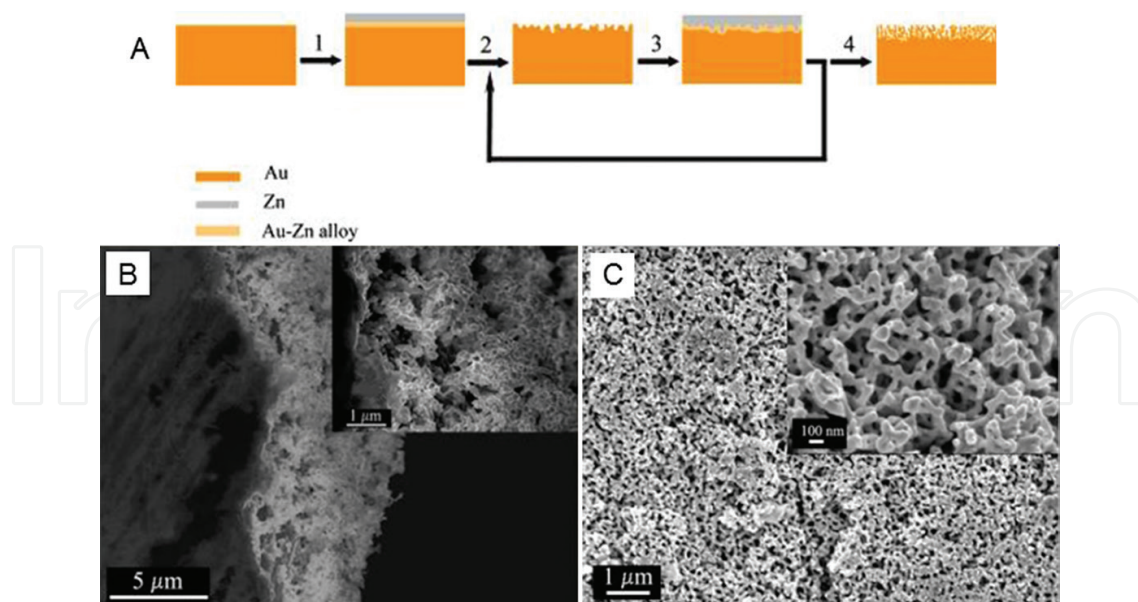


Figure 3. (A) Schematic illustration of the formation of np-Au film electrode by a multicyclic electrochemical alloying/dealloying method. Step 1, electrodeposition of Zn and formation of Au-Zn alloy; step 2, electrochemical dealloying; step 3, electrodeposition of Zn and formation of Au-Zn alloy again; step 4, formation of np-Au film after multicyclic alloying/dealloying. (B) and (C) SEM images of np-Au electrodes after 30 cycles of alloying/dealloying in ZnCl₂/BA electrolyte at 120°C, where (B) is cross-sectional view and (C) is planar view. The inset in (B) and (C) are the corresponding images with higher magnification. Reproduced with permission from Ref. [39], Copyright 2007, American Chemical Society.

and Masuda used oxalic acid to create the carbonaceous passivation film on gold surface by holding the potential at 1.8 V versus Hg/Hg₂SO₄ reference electrode, which on the reverse scan breaks down to form np-Au film with a uniform hole size of 20 nm [41]. The study has also shown that acidity is not the key factor for the np-Au formation by anodizing the sample in neutral sodium oxalate solution. Fang et al. used 1:1 (v/v) mixture of hydrofluoric acid and dimethylformamide as an etching electrolyte while suddenly ramping up the potential from 0 V to 40 V over 12 s or from 0 to 20 V over 24 s [33]. The latter slower voltage ramp was found to create the larger pores. On the other hand, the pore size created by directly holding the potential for 20 V or 40 V in the same electrolyte solution for similar time was found to create the smaller pore sizes. Xu and co-workers anodized the cleaned gold wire using potential of 5 V for 180 s in 0.15 M phosphate buffer to form oxides on electrode surface (evident by salmon pink color of the electrode surface) followed by reduction of gold oxide by 1 M ascorbic acid solution at room temperature to prepare np-Au (evident by change in color of the electrode surface to black) [42].

3. Characterization

The shape and size of nano- and micro-structured np-Au along with their pores and ligaments size is characterized by scanning electron microscopy (SEM). SEM images are also important to determine the cracks on the surface of np-Au. For the very thin np-Au samples and for distinguishing the foreign elements incorporated within np-Au at high resolution, transmission

electron microscopy (TEM) images are useful [43]. Filled nanoporous spaces by foreign elements appear dark on TEM images, which can be distinguished from the control np-Au appearing light. High-resolution transmission electron microscope (HRTEM) can further reveal the lattice spacing of the foreign element which may either vary significantly from that of the np-Au or show the epitaxial relationship with the continuous lattice fringes [44]. It can also reveal different kinds of lattice defects present within np-Au [7]. Transmission electron tomography can be used to generate bicontinuous 3D-structure of np-Au showing the internal structure of the np-Au [45].

Energy dispersive X-ray spectroscopy (EDS) can be used to confirm the removal of less noble metal from np-Au through which the time needed for the complete removal of sacrificial metals can be estimated. Change in grain size and crystal structures of alloy or np-Au are studied using X-ray/electron diffraction. Based on the appearance of the characteristic X-ray diffraction peaks, the np-Au hybrid electrode with wide varieties of metals can be prepared [23].

When sufficient mass of np-Au is available, the surface area and pore size of np-Au can be determined using nitrogen adsorption/desorption isotherms. BET surface area analysis and BJH pore size distribution analysis provide the information about surface area and pores, respectively [46]. These methods are mainly useful for characterizing unsupported np-Au monoliths. For the supported np-Au electrode, a simpler and easier method to determine the surface area is through the cyclic voltammetry (CV) using oxide stripping method. In this method, charge under the cathodic peak generated due to the stripping of oxide from the gold surface is used to calculate the actual surface area of np-Au. However, electrochemically active or accessible surface area of np-Au can be determined using CV of redox probes or mediators.

4. Modification of np-Au surface

4.1. Self-assembled monolayers

Self-assembled monolayers (SAMs) of thioalkyl derivatives on the planar gold surface are a well-studied field [47]. Different types of biomolecules, such as protein, DNA and carbohydrates can be strongly bound and presented on the surface of gold as a SAM mimicking the cell surface or their natural form [48]. Biomolecules can be either modified with the thiolated linker first and allowed to form a SAM or immobilized on the previously formed SAM by reacting with the terminal functional group. Np-Au surface can be modified with different types of SAM in the same way as done in a planar gold surface by immersing the np-Au in the ethanolic solution of desired SAM-forming molecules for few hours to overnight [9]. SAM formation on np-Au surface is of higher interest because high surface area of np-Au allows large number of desired molecules on the surface. However, SAM on np-Au is not as well organized as that on planar gold surface and chances of intermolecular interactions between the terminal functional group are higher [49]. The nature and size of the terminal group and length of the linker determine how deep the monolayers are formed and are functionally active in the interior of np-Au. When np-Au-based glucose sensor was constructed by immobilizing glucose oxidase (GOD) onto the SAMs of carboxylic acid terminated alkanethiol having different

chain lengths, it was found that the sensitivity of the biosensor decreases with the increase in chain length [50]. This phenomenon has been explained by the better SAM formation of the longer chain length molecules on the np-Au surface, helping to immobilize higher number of enzymes and hence creating more difficulty for the electron transfer to occur. However, increase in thickness due to the longer chain length may also be the reason behind the difficulty for electron transfer to occur. The type of terminal functional group and chain length of SAM play vital roles in loading and releasing of drugs in np-Au. A negatively charged fluorescein (a small-molecule drug surrogate) shows lower loaded inside np-Au when np-Au surface was functionalized with carboxy-terminated SAM compared to when modified with amine-terminated SAM [51]. This is due to the repulsive interaction of negatively charged fluorescein with the carboxylic group and attractive interaction with the amine group. It was also found that increasing the chain length (11 carbons) of SAMs changed the pore area decreasing the access of fluorescein to the interior of np-Au and hence reducing loading capacity [51].

4.2. Metal and metal oxides

Modification or decoration of the np-Au surface with other metal or metal oxide can build up functionalities to the already versatile np-Au structures. Modifying the np-Au with a tiny amount of platinum, palladium and TiO_2 nanoparticles not only greatly increase the effective surface area but also enhance the electrocatalytic performance toward methanol oxidation [52–54]. Modifying the np-Au with platinum and palladium also significantly improves the structural stability of np-Au whereas TiO_2 suppresses the coarsening of the nanoporous structure after multiple uses. Modifying np-Au surface with metals and metal oxides, such as Pt, Pd, Cu, Ni, Ru, CuO, TiO_2 , and CoO have shown significantly enhanced sensitivity toward the nonenzymatic detection of glucose with very good selectivity in the biological matrix [55–62]. When np-Au is modified with Ru to form np-Au/Ru nanocomposite and immobilized further into GCE with chitosan as a capping agent to create an electrode, it can act as a better non-enzymatic glucose sensor with good sensitivity and selectivity compared to bare np-Au [58]. The modified GC/np-Au-Ru/CHIT electrode shows six-fold higher amperometric sensitivity of $240 \mu\text{A mM}^{-1} \text{cm}^{-2}$. Modifying the np-Au with ultrathin nickel (Ni) film enables detection of glucose with the sensitivity as high as $5070.9 \text{ mA mM}^{-1} \text{cm}^{-2}$, which is nearly 340 times higher compared to that on the polished gold electrode [63].

The immersion-electrodeposition method is one of the simplest methods to modify the np-Au surface with metals and metal oxides [52]. In this method, np-Au is immersed in a suitable salt solution, allowed to soak for certain time and electrodeposited by applying a suitable potential. Platinum was decorated on np-Au by first immersing np-Au in H_2PtCl_6 solution for 10 min followed by electrodeposition by sweeping the potential at 50 mV s^{-1} between 0 and 1.1 V (vs. RHE) for 3 cycles in 0.1 M HClO_4 solution [52]. Similarly, iridium oxide was electrodeposited on np-Au using multiple cyclic voltammetry scans [64]. This method is suitable for modifying the external surface or thin films of np-Au with metal and metal oxides, but modifying the interior part of the thicker np-Au structure is challenging mainly because of the mass transport limitation leading to the closing of external pores before completely modifying the interior surface. There are different alternatives to overcome this situation. Underpotential deposition of the reactive metal to form a monolayer followed by galvanic displacement of the reactive metal by the atoms of

desired metal can modify the np-Au surface while conserving the original structure of np-Au. Np-Au surface can be modified with Ni using galvanic displacement reaction of underpotential deposited zinc [63]. Similarly, Cu can be underpotential deposited on the np-Au surface to decorate it with Pt using a galvanic displacement reaction [43]. However, the residual metal such as silver, which is left while dealloying np-Au, can also be used in galvanic replacement reaction to decorate Pt using H_2PtCl_6 solution [65]. Water dispersed TiO_2 nanoparticles were loaded inside np-Au followed by annealing to embed the TiO_2 particles on the np-Au surface [53]. The desired noble metal can also be included as one of the constituents of the alloy, which remains on the np-Au surface after the dealloying process removing less noble metal/s [54].

5. Applications

5.1. Chemical sensor

Nanoporous gold without any further modification with other metals or biological molecules can act as a chemical sensor owing to its high surface area, ability to catalyze certain analytes at low potentials, resistance against surface fouling and pH, and fast mass transportation [66]. It has been successfully used to detect arsenic [As(III)], a toxic metal ion whose exposure can lead to many health issues including cancer, using square wave anodic stripping voltammetric technique to the concentration as low as 0.0315 ppb with the sensitivity of $44.64 \mu\text{A cm}^{-2} \text{mM}^{-1}$ [67]. World Health Organization's recommended limit of arsenic in the drinking water is 10 ppb. Phenolic compounds, such as phenol and catechol have been considered as priority toxic pollutants by US-EPA but still extensively used by many chemical companies for various applications. A suitable detection method for these compounds is a need for monitoring its concentration in environment and food products. By applying a suitable detection potential, np-Au electrode can not only detect the phenolic compounds down to few micromolar range [68] but also selectively distinguish one from another [69]. However, np-Au can also be easily modified with biomolecules and different types of other metals for its use in bio/chemical sensing.

5.2. Enzyme immobilization

Nanoporous gold is a suitable solid support for the immobilization of enzymes because of its biocompatible nature, ability to form self-assembled monolayers on the surface, and high surface area-to-volume ratio [5]. Once the enzyme is immobilized on the electrode surface, it is very important that it maintains its enzymatic activity for further usage. Np-Au increases the stability and functionality of the immobilized or entrapped enzymes by decreasing their tendency to unfold due to its constrained environment [70, 71]. Lignin peroxidase (LiP) immobilized on np-Au was found to retain 55% of its initial activity after 2 h at 45°C whereas free LiP was completely deactivated under similar conditions [71]. Another study reported that alcohol dehydrogenase (ADH) or glucose oxidase (GOD) immobilized on np-Au lost only 5.0 and 4.2% of the original current response, respectively, after storage for 1 month at 4°C [70]. By creating the appropriate pore size of the np-Au, the leaching can also be drastically reduced from the electrode [70]. The larger the pore size of np-Au, the higher will be the leaching. On the other hand,

smaller pores may block the enzymes from entering the np-Au interior portion. Fortunately, due to the ability of np-Au to form SAMs, enzymes can be strongly and covalently bound on np-Au surface increasing the loading and activity of the enzyme while decreasing the leaching [72, 73]. Nevertheless, physical adsorption of enzyme on np-Au is widely used to prepare the enzyme-based biosensor, because of comparative stability, the ease of preparation and few steps required [74]. The leakage of the physically immobilized enzymes can be reduced by using polymers like chitosan [75] and Nafion [70]. The high surface area of np-Au helps to amplify the response signal of the analyte during biosensing due to the large numbers of immobilized enzymes.

5.3. Electrochemical biosensor

Supported np-Au is a suitable solid support for immobilization of different types of protein (e.g., antibodies, enzymes, and lectins), carbohydrates, and RNA/DNA molecules because of its clean surface, robust structure, high surface area and biocompatible nature [76]. These immobilized biomolecules on np-Au, called receptors, can be used as biosensors for the detection of various analytes, such as poisonous metal ions, small organic molecules, and other biomolecules. Because of the highly conductive nature of np-Au electrode, it can be used as a transducer for the detection of analytes using different electrochemical techniques. The commonly used electrochemical techniques for np-Au-based biosensing are cyclic voltammetry (CV), chronoamperometry (CA), chronocoulometry (CC), electrochemical impedance spectroscopy (EIS), differential pulse voltammetry (DPV) and square wave voltammetry (SWV). Except EIS which is based on the resistance of the electrode, all the other techniques are based on the measurement of current or charge whose signal is directly proportional to the concentration of the analyte. DPV and SWV are pulse-based techniques, which have the ability to discriminate against the charging current by only sampling the Faradaic current at the end of the pulse. As a result, a very small concentration of a sample can be detected precisely. Electrochemical biosensors can be classified as DNA aptasensor, enzymatic biosensor, and immunosensor based on the type of receptor molecule used. Recently, Zeng et al. prepared regenerable DPV-based aptasensor on the np-Au surface for the detection of Hg^{2+} with the limit of detection as low as 0.0036 nM [77]. The non-enzymatic amperometric glucose sensor is possible using np-Au electrode [11] or by modifying the np-Au surface with other metals or metal oxides [78]. However, np-Au surface can be modified with glucose oxidase to use the synergistic catalytic properties of both np-Au and glucose oxidase for the detection of glucose. In one such study, high sensitivity of $12.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with the linear responses ranging from 50 μM to 10 mM was obtained with a low detection limit of 1.02 μM [79]. The prepared structure possesses strong anti-interference capability against many molecules present in human serum. Np-Au surface was used for detecting various cancer biomarkers based on sandwich-type immunosensing. Np-Au electrode immobilized on graphene surface was combined with horseradish peroxidase-encapsulated liposomes as labels and thionine as electron mediator for the detection of cancer antigen 15-3 using DPV [80]. The linear range of the immunoassay was found to be 2×10^{-5} –40 U mL^{-1} with a limit of detection of 5×10^{-6} U mL^{-1} . Similarly, DPV was used to detect carcinoembryonic antigen (CEA) by immobilizing anti-CEA on np-Au [81] and CV was used to detect prostate specific antigen (PSA) by immobilizing anti-PSA [82].

5.4. Actuator

The phenomenon of change in surface stress and strain of np-Au due to the adsorption or desorption of gas or water can be used to convert chemical energy into a mechanical response [83, 84]. One way to prepare such surface driven actuator is by alternate exposure to ozone and carbon monoxide on np-Au surface [85]. Exposure of ozone on np-Au surface leads to adsorption of oxygen on clean Au, whereas CO exposure cleans the Au surface by reacting with adsorbed oxygen to release carbon dioxide, **Figure 4A** and **B**. Another way to generate such stress on np-Au surface is by volumetric changes of np-Au by physical adsorption and desorption of polar water molecules [84]. This method can create reversible strain amplitudes up to 0.02% in response to a 15% change in relative humidity. The ligaments of np-Au actuator coarsen with time leading to a substantial loss in performance. In such case, np-Au can be modified with platinum or polyaniline to prepare a composite porous structure [83, 86]. Np-Au/Pt alloys prepared by dealloying ternary alloy of Ag-Au-Pt to create very small structure size and large specific surface area can significantly enhance the stress and strain in the bulk of the material reaching linear strain $\sim 1.3\%$ [83].

5.5. Plasmonic response

Propagating surface plasmon resonance (SPR) is the evanescent electromagnetic waves found in the interface of thin metal (e.g., Au and Ag)-dielectric interface, which propagates at the distance on the order of tens to hundreds of microns along x - and y -axis, but decays on the order of 200 nm along the z -axis [87]. However, if the oscillation of surface plasmons is confined within the surface of the nanostructures of the metal (e.g., Au and Ag), it is called LSPR [88].

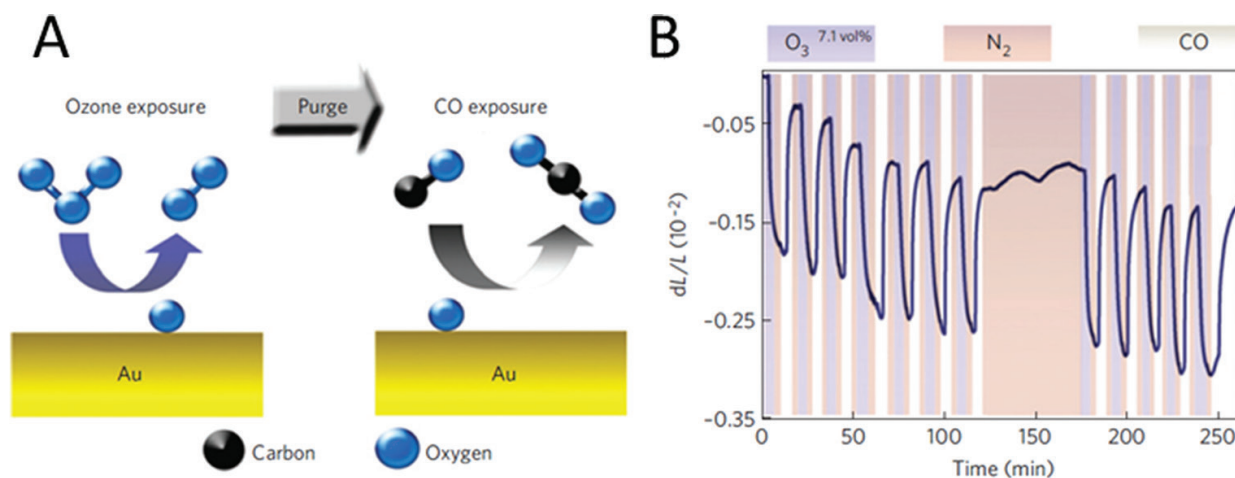


Figure 4. (A) Illustration of surface-chemistry-driven actuation in np-Au. Au surfaces can be switched back and forth between an oxygen-covered and clean state by alternating exposure to ozone (O_3) and carbon monoxide (CO). (B) Performance of a surface-chemistry-driven np-Au actuator. Strain versus time as the np-Au actuator is alternately exposed to a mixture of $\sim 7\%$ O_3 in O_2 and pure CO. Between exposures, the sample compartment was purged for 3 min with ultrahigh-purity N_2 . Ozone exposure causes contraction, whereas CO exposure restores the original sample dimension. The response is mostly elastic, with only a small irreversible component. The system is very stable, and interrupting the exposure sequence for 1 h causes only a small drift of the signal. Reproduced with permission from Ref. [85], Copyright 2009, Macmillan Publishers Limited.

Both the SPR and LSPR are sensitive to change in refractive index around the metal-dielectric interface. This property can be used to design a label-free, sensitive and high-throughput biosensor to study the interaction of biomolecules.

Thin films (~100 nm) of np-Au can generate both the SPR and LSPR simultaneously [89]. Kim et al. studied biotin-streptavidin interaction on the surface of np-Au film fabricated by oblique angle deposition using SPR [90]. They found that there is an enhancement in SPR response due to np-Au compared to when studied on conventional bare gold film. The reason for enhancement in SPR response is attributed to excitation of local plasmon field and an increased surface area for the reaction. In the absorption spectra, two characteristic LSPR peaks can be observed for np-Au, one near 490 nm and other around 550–650 nm [91, 92]. The LSPR peak of np-Au at 490 nm is nearly independent of change in refractive index [92] and the peak at 550–650 nm is relatively wider compared to that obtained from Au nanoparticles and nanorods. The wide peak decreases the sensitivity of the biosensor limiting the use of np-Au in biosensing experiments. However, preparing np-Au nanostructures, such as np-Au disks can greatly enhance the plasmonic response due to high-density internal plasmonic “hot-spots” [19, 93]. By using these structures, the plasmonic bands can be tuned from 900 to 1850 nm by changing the diameter of the disk from 300 to 700 nm. The disk with a diameter of 300 nm shows the LSPR peak in relatively lower wavelength region and is sharper compared to the disk with higher diameter.

5.6. Heterogeneous catalysis

With the discovery of nanoparticles and nanoporous structures of gold, studies and understanding of the gold as a heterogeneous catalyst have been emerging. Heterogeneous catalysis is vital for (1) environmental waste management, as green chemistry reactions are possible and (2) synthesizing desired products, which is either not possible with homogeneous catalysis or requires poisonous chemicals if done without a catalyst. Gold nanoparticles, because of their high surface area and other unique properties, have shown promising results in heterogeneous catalysis. However, for the nanoparticles to be used in liquid phase catalysis, they should be functionalized with a suitable stabilizing agent or else they may undergo undesired aggregation decreasing the surface area and hence the catalytic activity. The functionalized stabilizing agent can also decrease the effective surface area and may passivate the surface faster. Unsupported np-Au, a bulk 3D-structure of gold having nanometer-sized pores and ligaments, can overcome these shortcomings. Besides having high surface area, it is easy to prepare, stable at harsh reaction conditions, and has less possibility of contamination. Furthermore, the structure can be easily reused and recycled, making it an ideal green catalyst for many reactions. Np-Au has already shown significant catalytic activity in many important gas-phase and liquid-phase reactions, such as oxidation of CO, alcohols, and carbohydrates. We will briefly discuss some of the reactions below.

5.6.1. CO-oxidation

CO-oxidation is one of the important reactions necessary in controlling air pollution, such as through automotive or industrial emission and in hydrogen purification in fuel cells [94]. One of the early experiments to show the use of unsupported np-Au in CO-oxidation was conducted

independently by Xu et al. [95] and Zielasek et al. [96]. Their experiment not only presented some of the important information on CO-oxidation but also became a crucial step toward the use of unsupported np-Au for gas-phase heterogeneous catalysis. Unlike palladium and platinum-based catalysts, np-Au shows important catalytic activity for CO-oxidation even at very low temperature down to -30°C and are tolerant to CO poisoning [97], **Figure 5**. It was found that unlike in supported gold catalysts, preactivation steps by passing O_2 at high temperature is not the necessary step for unsupported np-Au [95]. CO conversion rate of 99.5% and $>85\%$ could be achieved for nearly 20 h when reaction performed at room temperature and -30°C , respectively. However, catalytic efficiency was found to decrease faster at room temperature due to coarsening of the porous structure [95]. Residual silver [96] or Cu [98] in the np-Au have been linked to strongly influence the catalysis of CO, however, there is no evidence to support the ability of residual silver or copper alone on catalysis below 100°C . There is no consensus among the scientists over the exact mechanism of CO-oxidation over np-Au catalyst. Some suggest that

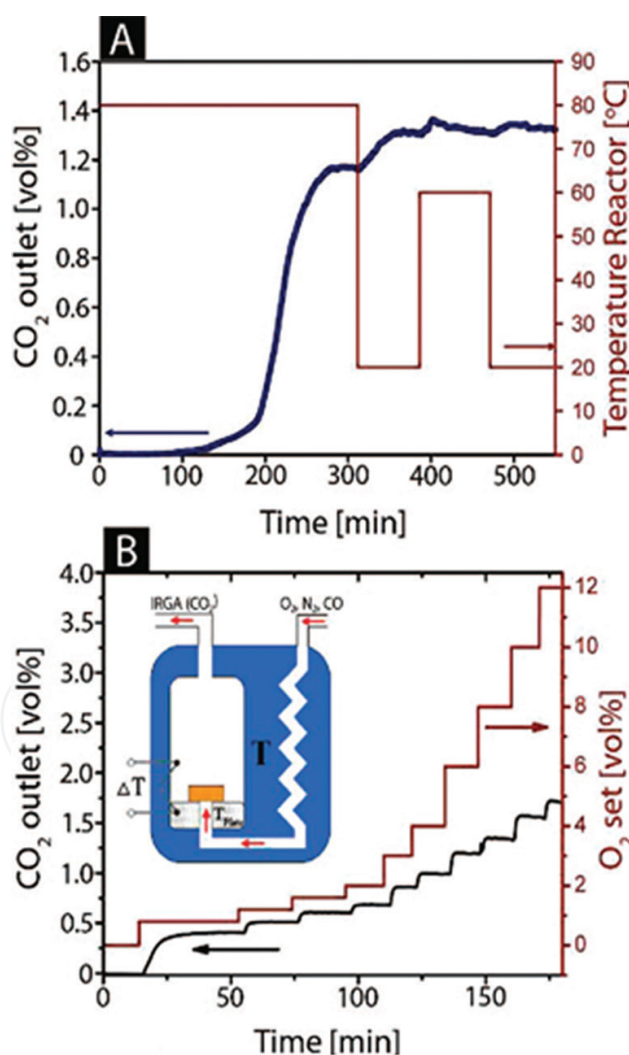


Figure 5. Catalysis: (A) CO₂ signal typically detected at the reactor out during activation of a np-Au disk; (B) CO₂ signal (outlet) for increasing O₂ concentration at the reactor inlet (CO as carrier gas, reactor temperature 20°C). Reproduced with permission from Ref. [97], copyright 2009, American Chemical Society.

the residual metal helps to activate the molecular oxygen and hence np-Au should be considered a bimetallic catalyst [97] while others think low coordinated gold atoms present on the ligaments surface due to various steps and kinks are responsible for activating molecular oxygen [6]. Long-term stability of the np-Au catalysts for CO-oxidation at room temperature is still a challenge.

5.6.2. Methanol oxidation

Methyl formate is an important precursor for the manufacture of formic acid, formamide, and dimethyl formamide, which is prepared in the industry at thousands of tons each year by combining poisonous carbon monoxide gas with methanol for the better selectivity [99]. However, it is possible to synthesize methyl formate from partial oxidation of methanol using suitable catalyst without using CO [100]. Monolithic unsupported np-Au has shown promising potential to be used in a gas-phase catalysis for selective conversion of methanol to methyl formate [101]. This is due to its high surface area, presence of considerable number of low-coordinated surface Au atoms, and availability of small percentage of Ag as a residual atom [101, 102]. Unlike nanoparticles, nanoporous structures are highly resistance to sintering and are successful in circumventing the limitation of bulk structure for dissociating the bound oxygen on its surface [103]. Strongly bound oxygen on the surface decreases the catalytic efficiency of the gold. Wittstock et al. used unsupported monolithic np-Au disc for the selective gas-phase oxidative coupling of methanol to methyl formate at low temperature with selectivity above 97% and high turnover frequencies [103]. Thin film of supported np-Au prepared on aluminum microfiber to form a composite structure was found to be cost effective, highly active, selective, and stable for oxidative coupling of methanol to methyl formate [104]. The composite structure is capable of achieving ~100% methyl formate selectivity with ~25% methanol conversion at 100°C and stable for more than 300 h without any sign of sintering.

On the other hand, the electrocatalytic oxidation of methanol using precious metal catalysts is of great interest for its use in direct methanol fuel cells. Pt-based catalyst strongly chemisorbs the intermediate species generated during electrooxidation of methanol poisoning the catalyst. However, these intermediate species have weak interactions with gold surface. Np-Au has high surface area and can transfer electrons better than the bulk and Au nanoparticle-supported electrode, making it a suitable catalyst for electrochemical oxidation of methanol [105]. Unfortunately, it was observed that the np-Au structures are coarsened quickly with the multi-cycling of the potential [52]. However, decorating the surface of np-Au by small amount of Pt to form nanoporous bimetallic Au-Pt alloy nanocomposites can greatly enhance the structural stability and the electrocatalytic activity toward methanol oxidation [106]. The nanoporous bimetallic Au-Pt alloy nanocomposites can also be prepared by dealloying the ternary alloy of gold, platinum, and other less noble metal [107]. This type of modified np-Au can work as a suitable catalyst for electrooxidation of other small organic molecules, such as formic acid, formaldehyde, and ethanol [108].

5.6.3. Liquid-phase catalysis

Recent works have proved that np-Au has remarkable catalytic activity in liquid-phase catalytic reactions. This type of reactions are not only selective but also work without any

additives or stabilizing agents while avoiding cumbersome work-up procedures like filtration or centrifugation. Yin et al. used unsupported np-Au for the aerobic oxidation of D-glucose to D-gluconic acid with the high selectivity of 99% under the mild reaction conditions [109]. At pH = 7.0 the conversion to gluconic acid was ~33% which reached 78% at pH = 9.0. Interestingly, the catalytic activity was found to link with the size of the ligaments with that of 6 nm showing highest catalytic activity and resistant to deactivation. It was also observed that low-coordinated Au surfaces are the active reaction site whereas the presence of residual Ag does not favor the glucose oxidation. However, the np-Au-catalyzed reaction for the direct preparation of formamide from the reaction of alcohols and amines under aerobic conditions shows that the presence of small percentages of Ag in np-Au enhances the oxidation process [110]. Yamamoto group have extensively studied the use of unsupported np-Au in liquid-phase catalysis for wide varieties of organic reactions [111]. They catalyze aerobic oxidation reaction of alcohols in batch and flow systems while monitoring the adsorptions of O₂ and alcohol onto np-Au surface using thermal desorption spectroscopy analysis [112]. The aerobic oxidation of 1-phenylbutanol with flow system using np-Au as the catalyst and methanol as solvent at 60°C for 20 min yields 99% of the corresponding ketone with the 100% conversion. Similarly, np-Au catalyst is used for the activation of bis(pinacolato)diboron that allows the direct diboration of alkynes [113]. It was observed that np-Au can cleave the B-B bond of bis(pinacolato)diboron without the use of any additives. Np-Au catalyst is also used to reduce aldimines (R¹HC=NR²) in the presence of aldehydes (R¹CHO) giving corresponding amines (R¹H₂C-NHR²) with high yields and 100% selectivity [111]. Unsupported np-Au also helps to obtain excellent chemical yields with remarkable chemo-selectivity in the hydrogenation of aldehydes and semi-hydrogenation of alkynes [114, 115].

6. Summary

A substantial progress has been made during the last two decades in the synthesis, modification and functionalization of np-Au due to their many important and unique properties. Chemical dealloying is a quick and easy means of creating np-Au whether it is a self-supported bulk or solid-supported thin film; however, electrochemical dealloying is useful for control tuning of pores and ligament size of the thin films and might not be as useful for dealloying bulk structures. Recent knowledge on techniques to control the shape and size of np-Au and size of its pores and ligament has increased its importance in wide range of disciplines, including catalysis, optical and electrochemical chemical and biomolecules sensing, actuator, bioreactors, biomedicine, and energy.

In summary, np-Au is a versatile nanostructured framework that has diverse application not only as a pure material but also by functionalizing it with diverse types of organic molecules and metal or metal oxide nanostructures to convert it into multifunctional composite material. Converting np-Au into the multifunctional nanostructures can greatly increase its potential applications in different other fields of nanotechnology that were not previously envisioned.

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Author details

Jay K. Bhattarai, Dharmendra Neupane, Bishal Nepal, Vasili Mikhaylov, Alexei V. Demchenko and Keith J. Stine*

*Address all correspondence to: kstine@umsl.edu

Department of Chemistry and Biochemistry, University of Missouri – St. Louis, Saint Louis, MO, USA

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