Chapter

Nanoporous Metallic Films

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Abstract

Nanoporous metallic films are known to have high surface to volume ratio due to the presence of pores. The presence of pores and ligaments make them suitable for various critical applications like sensing, catalysis, electrodes for energy applications etc. Additionally, they also combine properties of metals like good electrical and thermal conductivity and ductility. They can be fabricated using top-down or bottom-up approaches also known as dealloying and templating which give the fabricator room to tailor properties according to need. In addition, they could find potential applications in many relevant fields in current scenario like drug delivery vehicles. However, there is a long way to go to extract its whole potential.

Keywords: metallic nanostructures, nanoporous metallic films, nano fabrication, optical sensing, catalysis

1. Introduction

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales (1 Bohr radius = 0.5292 Å ≈ 0.05 nm). Due to the influence of the negligible dimensions, materials exhibit remarkable functionality and phenomena. Here properties differ significantly from those at larger scale, because at this level, quantum mechanics and statistical mechanics come into play instead of classical mechanics, and the extremely high surface area to volume ratio of the particles modifies the electrical and chemical activity of the substance, thus the effective concentration of reactants confined in nanostructures may be very high. Typical nano-systems may contain from hundreds to tens of thousands of atoms.

Presently scientists and engineers are finding a wide variety of ways to deliberately make materials at the nano-scale to take advantage of their enhanced properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale counterparts [1], and these products have various applications and a niche market in the fields of electronics, chemistry and biomedicine; semiconductor technology being of the most significance. Needless to say, this branch of science has a great of scope for research and innovation for years to come, on its way to increasing process efficiency, cost effectiveness, and broadening the range and accuracy of human perception.

Out of all the nanostructures, nanoporous film has attracted many research groups in the past decade due to the presence of nano holes in it which acts as a nanoparticle and increases the specific surface area. Also, the increase in chemical stability plays a role in the attraction of several research groups. In order to investigate it further various metals have been used to fabricate nanoporous metallic films. Nanoporous Ag cathode has been used photoelectrochemical carbon dioxide

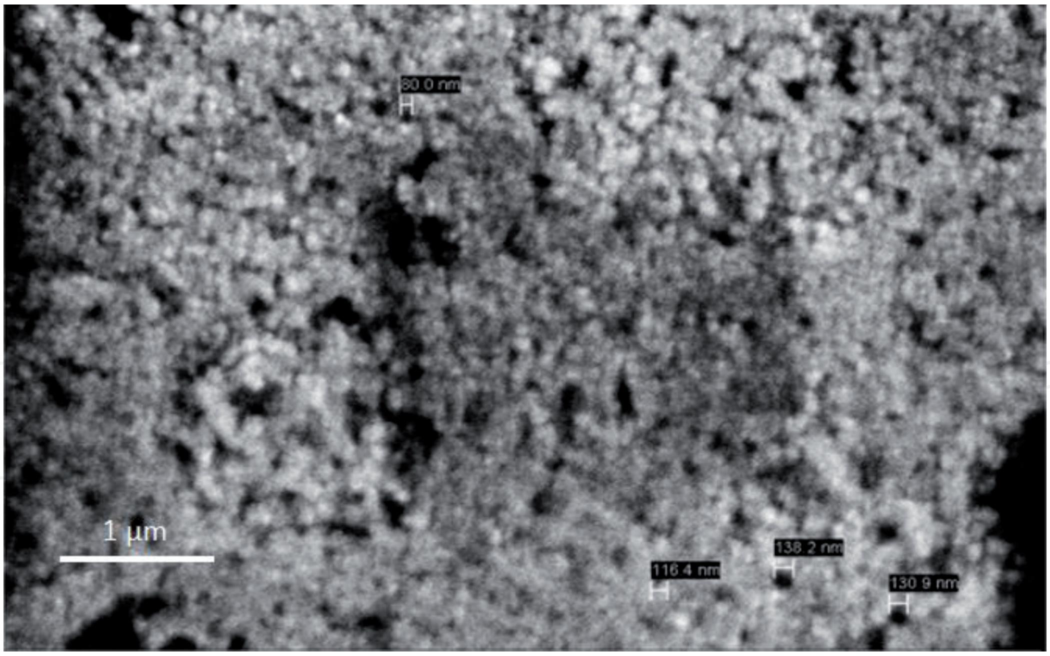

Figure 1.
SEM image: Electroless plated Au on e-beam evaporated Cu on silicon substrate [5].

reduction [2] and nanoporous palladium have been used for reductive dichlorination [3]. But among all the metallic porous films, the nanoporous gold (NPG) film is used mostly due to its chemical stability and unique surface chemistry.

NPG film provides a suitable microenvironment for immobilization of biomolecules (like enzymes) by maintaining their biological activity and facilitates electron transfer between the immobilized proteins and electrode surfaces, leading to its intensive usage in electrochemical biosensors with enhanced analytical performance compared to other biosensor designs [4].

Figure 1 shows surface morphology of NPG film which was manufactured by e-beam deposition of Cu on silicon substrate and then electroless plated with Au. The characteristics of Au nanoporous film such as high surface-to-volume ratio, high surface energy, ability to decrease proteins metal inter-particulate distance, and the functioning as electron conducting pathway between prosthetic groups and the electrode surface have been claimed as the reasons to facilitate electron transfer between redox proteins and electrode surfaces. And these are the properties that make the NPG film so coveted for the fabrication of electrochemical sensors and biosensors.

In this chapter, the processes to make nanoporous metallic films followed by effect on properties of the film are discussed. The applications of nanoporous metallic films and finally, the future scope are also elucidated.

2. Fabrication methods

The fabrication techniques for the preparation of nanoporous structures vary with the requirement of the application. The nanoporous films can be either etched out from an alloy (top-down approach), known as dealloying process or can be fabricated using a template and removing it after deposition of required metal on it (bottom-up approach), known as a templating process [6]. The stability of a nanoporous film is dictated by their pore and ligament sizes.

In dealloying, the undesirable material of the alloy is dissolved under appropriate corrosive condition leaving a stable porous desirable metal [7]. Dealloying can also be further divided into free corrosion dealloying and dealloying by using electrochemical methods. The key factor for choosing an alloy for dealloying by free corrosion is the parting limit which suggests that the composition of undesirable material should be higher than a threshold value. The parting limit for $Au_x Ag_{x-1}$ found by experiments done by Newman [8] is 0.4 for x. Selective dealloying has been used by various research groups to fabricate porous structures below 100 nm. The formation of pores during the dealloying process can be divided into three stages according to SAXS (small-angle X-ray scattering) analysis [9]. The time of each stage is inversely proportional to the dealloying temperature. In the first stage, there are some changes in the SAXS data but physically the commencement of pore formation cannot be detected. The second stage shows some physical changes with the increase in visibility of pits on the surface, subsequently, there is a drastic change in the intensity of the SAXS curve. The third stage corresponds to the growth of pores and a visible increase of ligaments in the structure until a stable structure is achieved. When strictly focusing on NPG films of some suitable alloys like AuAg [10], AuCu [11] and AuNi [12], the most commonly used is AuAg alloy.

Introduction of electric potential to facilitate the dealloying process have also been attempted and is known as dealloying by using an electrochemical method. The major component of this process is an anode (the alloy), cathode, reference electrode and electrolyte. Two common electrolytes for AuAg alloy are aqueous perchloric acid ($HClO_4$) for relatively big pore size and neutral silver nitrate solution (AgNO3) for small pore size [13]. This method requires a more sophisticated set-up than free dealloying process but in return, more uniform nanoporous film and a higher degree of process control are achieved. Similar to parting limit, this method also requires a positive potential value known as critical potential (E_c). The selective dissolution takes place by the rapid increase of Ag dissolution rate. As would be explained later in this chapter, any factor which enhances the surface diffusivity would have an impact on pore as well as ligament size.

Dealloying by the electrochemical process has also been divided into two types, potentiostatic dealloying and galvanostatic dealloying. The experimental set-up for both potentiostatic and galvanostatic methods is the same. In potentiostatic dealloying, the potential value is kept just above the critical potential (E_c) value, which facilitates the gradual dissolution of Ag giving a robust and uniform structure at the end. Whereas in galvanostatic dealloying, the potential value starts above E_c and gradually increased till a maximum limit which is also known as cut-off potential. The two competing factors of Ag dissolution which increases the stress and Au diffusion which decreases the stress in NPG film contribute to the quality of pores in a NPG film [13]. Galvanostatic dealloying by controlling Ag dissolution rate and Au diffusion rate through a periodic increase in potential provides a more robust and crack-free NPG film when compared to that of potentiostatic dealloying.

Low pore size and high ligament size related to the high thermal and electrical conductivities is reported by various research groups [14, 15]. For a 1.3 μm thick NPG film, the ligament size can range from 22 to 155 nm [16]. Hakamada [17] while fabricating nanoporous Ni, Ni-Cu and Cu found an inverse correlation between the atomic ratio of Ni in alloy and ligament size. Another important factor that determines the ligament size is surface diffusion at the metal/electrolyte interface. Correlation between surface diffusion coefficient (D_s) and ligament size (d) is given by Equation [18];

$$D_s = \frac{d^4 kT}{32\,\gamma t a^4} \tag{1}$$

where k is Boltzmann constant, T is the absolute temperature, γ is the surface energy, t is the dealloying time and a is lattice parameter. According to the above relationship, surface diffusion also depends on dealloying temperature and time. Qian and Chen [18] quantified the temperature dependence of NPG films by increasing temperature from −20 ◦C to 25 ◦C leading to an increase in diffusivity by two orders of magnitude. Apart from the above-mentioned factors, the dealloying process gets affected by properties of precursor alloy and dealloying solution [19, 20].

The disadvantages of dealloying is the effect of acids and bases used as a solution on the workforce as well as wastage of the dissolved metal. To cope with this problem, Zhang [21] have used ultrasonic irradiation (UI) to assist the dealloying process. This additional method uses lower acid concentration and simultaneously reduce environmental pollution. The UI reduces the surface energy which further enhances the diffusion leading to more coarsening of the ligaments [22]. This experiment proved that the coarsening rate of the ligament increases by introducing UI in dealloying process.

Similar to the use of ultrasonic irradiation, ultrasonic agitation has been used to achieve finer ligaments and pores of palladium-nickel nanoporous thin films [23]. The ultrasonic agitation reduced the time by a factor of 5 without disturbing the desired structure. There has been a similar effect of the magnetic field highlighted on the nanopores of Ag [24].

Another method for the fabrication of NPG films is the templating process. The templating process can be explained in two steps, the preparation of Au or Ag-Au coated core/shell particles followed by the removal of core material to get pure metal foam [25]. The preferred material for template assisted fabrication of NPG film is silica or polystyrene beads. This method gives a higher level of control over pore and ligament size as these would be dependent on the size of beads that can be readily controlled during template fabrication.

3. Properties of nanoporous gold films

3.1 Mechanical properties

Using the analogy of foam to describe nanoporous materials, mechanical properties of foam depends on the cell size similarly pore size dictates the mechanical behaviour of nanoporous materials. Though there is a resemblance between both structures, the effect of scale cannot be neglected and the equation of foams for mechanical behaviour cannot be applied. Also, the introduction of capillary actions and the plastic behaviour of ligaments cannot be unforeseen at lower dimensions. Hodge et al. [26] attempted to present an equation from experimental data for yield strength and it should be emphasized that as the ligament size approaches 1.0 μm the data begin to approach the Gibson and Ashby scaling prediction.

$$\sigma^{*} = C_s\left[\sigma_o + kL^{-\frac{1}{2}}\right]\left(\frac{\rho^{*}}{\rho_s}\right)^{3/2} \quad (2)$$

Where * denotes foam properties and s denotes solid properties, C_s is a fitting coefficient, σ_o is the bulk material yield strength (σ_s), k is the Hall–Petch-type coefficient for the theoretical yield strength of Au in the regime, $\rho*/\rho_s$ is the ratio between densities of the porous structure and corresponding dense material and L is the ligament size. The real picture of what is happening at the nanoscale can only be found by experimenting, so experimental results of yield strength and tensile strength. On the experiment front, the results from pillar compression tests revealed that the yield strength comes closer to theoretical yield strength of Au when the size of pillars decreases. The tensile test on NPG revealed some macroscale brittleness in it which is opposite to the inherent ductile behaviour of Au [13]. This contradiction in behaviour has been checked through another test known as fracture toughness.

Another mechanical property which is of importance is fracture toughness. It was found that fracture toughness of NPG is low even though gold is inherently ductile [27]. But when the previous phenomena of a tensile test revealing the macroscale brittleness are combined with the above results, the contradictory behaviour becomes clear. In nanoporous films, the ligament acts as a pillar to support the structure. So, the combined behaviour of the structure is coming from the intrinsic behaviour of ligaments. Li and Sieradzki [28], also correlated the ligament size and fracture behaviour. Research groups also concluded the rupturing of ligaments below 100 nm in size [29, 30]. The change in facture behaviour has been observed when the amount of Ag was varied in the final product. For less than 1% of Ag in final nanoporous structure, the rupture is smoother than the other increased value of Ag suggesting the rupturing is intragranular for lesser Ag content [13]. This observation means for less than 1% Ag, the grain boundary strength is higher or the whole system is more brittle as it broke without showing a significant change in appearance. But when the amount of Ag is increased the crack propagates through grain boundaries. Though there is significant data for these behaviours, intensive research is required to fully understand the phenomena.

3.2 Optical properties

The optical properties of metals are dictated by the to and fro motion of the electrons in the outer shell of metal that are triggered by any electromagnetic radiation. The motion can simply be understood by imagining photoelectric effect. The surface electrons are known as surface plasmons (SPs). The variables in this phenomenon are metal since each metal releases a unique amount of energy which acts as the fingerprint of that metal and frequency of electromagnetic radiations. Therefore, by changing these variables a nanoporous structure can be used for a huge number of applications like sensors [31], medical imaging, diagnostics [32] etc. Based on the movement of surface plasmons (SPs), the optical characterization techniques have been classified into surface plasmon polaritons (SPPs) and localized SPRs (LSPRs). With the help of excitation from grating or prism couplers, SPPs are known to propagate for tens or hundreds of micrometers [33]. As the name suggests the second one, localized SPRs (LSPRs) are non-propagating type and since the resonance in a confined space has been associated with a strong electromagnetic field, LSPRs contribute to several significant phenomena like surface-enhanced Raman spectroscopy [34], phononic effects [31]. This strong electromagnetic field becomes more prominent when the nanostructures have sharp features.

So, an ideal nanostructure would be the one which supports both localized as well as propagating systems. The simultaneous presence of a planar structure and nanostructure makes nanoporous materials an ideal candidate with good optical properties. This bicontinuous structure facilitates high field enhancements and good directional control [13]. The relation between irradiation wavelength and propagation of NPR has also been established. The longer the laser wavelength, the farther the propagating SPRs [35].

4. Applications of nanoporous gold films

The nanoporous materials field has gained much attention from the industry due to its enormous specific surface area, well-defined pore sizes and functional sites [36]. Surely, these properties can be achieved for other nanostructures too, but the low capital, high throughput and ease of control of morphology involved in the manufacturing make nanoporous materials more attractive. Among all the metals used for nanoporous structures, Au stands as an outstanding material due to its high surface area (~10 m^2/g), electrochemical activity, biocompatibility and ease of preparation [37, 38]. Due to the enormous surface to volume ratio of NPG, they have shown exceptional sensitivity and selectivity [39]. Particularly sensitivity becomes very crucial in medical or manufacturing safety field, concerning the placement of sensors on which sometimes many lives depend. This is the reason; NPG is finding its way into medical and manufacturing safety field more rapidly.

4.1 Optical sensing

As described in the previous section, the generation of surface plasmon resonance is due to the reduction of the dimension of metals to the scale of the mean free path of electrons [40]. When the electromagnetic radiations of the surroundings interact with electrons, there is inelastic scattering which depends on the pore size. In general, the smaller the pore size the higher the sensitivity [39].

Lang [41] studied the effect of varying nanoporosity on the enhancement of fluorescence. A new method of fabrication was introduced using a combination of dealloying and electroless plating to fabricate NPG structure with high ligament size. This enlarged ligament size facilitated the weakening of plasmon dampening leading to the enhancement in surface-enhanced fluorescence. It was further reported by Lang et al. [42] that fluorescent intensity of molecules absorbed on human-serum-albumin (HSA)-coated NPG films is inversely proportional to the nanopore size. The 45 times increase of fluorescence intensity was reported for a pore size of ~10 nm using this method. Whereas Zhang [43] fabricated a NPG film based optical sensor for sub-ppt detection of mercury ions. A Cy5-labelled aptamer NPG sensor was used with resonant excitation laser, to achieve 0.2 ppt Hg^{2+} sensitivity. This sensor could be extended further for detection of other heavy metal ions.

Similarly, there have been many studies on the surface-enhanced Raman spectroscopy. Zhang [44] have modified the nanoporous structures with wrinkles to include more "hot spots" for ultrahigh SERS enhancements. This was achieved with the help of thermal contractions of prestrained polystyrene microparticles (PS). The wrinkled NPG was found to have 100 times higher signal than the normal NPG films. Another interesting optical application was reported by Shih [5] where they have used NPG gold disks to sense chemical and find refractive index simultaneously. The NPG disks modified with octadecanethiol (ODT) and the surface-enhanced near-infrared absorption (SENIRA) spectroscopy was used to detect hydrocarbon compounds from crude oil samples.

Figure 2 shows the enhancement in SERS spectra when Au nanostructures are formed Pt substrates rather than on Cu substrate [45]. This research work also proves the importance of selection of substrate for use in optical sensing phenomena.

4.2 Electrochemical sensing

Electrochemical sensors are an electrode which goes through a redox reaction to detect the substance attached to the sensors. Now, the sensitivity and selectivity of the sensor become the prominent property to tune for respective applications. A schematic diagram of the sensor has been shown in **Figure 3**.

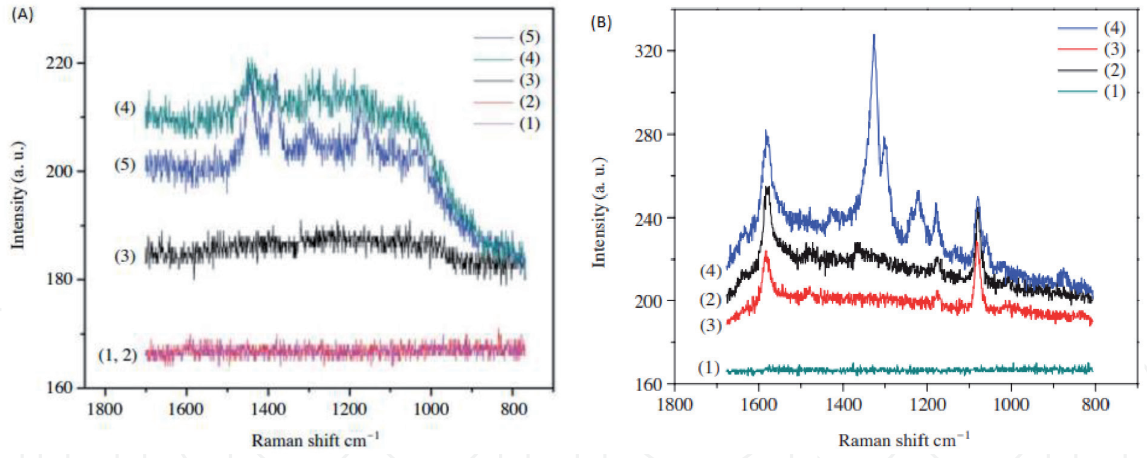

Figure 2.
(A) SERS spectra constituting SERS signal from (1) bare e-beam Au sample and Cu substrate whose reaction times are (2) 0 min, (3) 2 min, (4) 18 h and (5) 24 h respectively. (B) SERS spectra obtained from Pt substrate whose reaction times are (1) 0 min, (2) 2 min, (3) 19 h and (4) 24 h respectively [45].

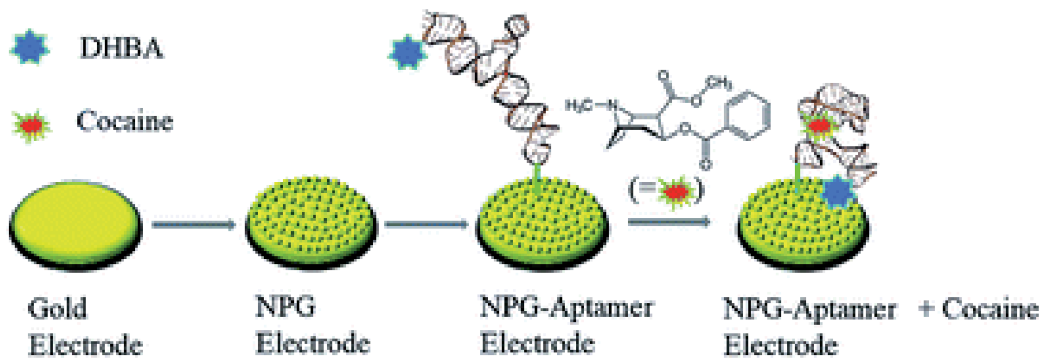

Figure 3.
Working of a NPG electrochemical sensor [46].

Electrochemical sensors are being used in biomedical applications on a large scale due to its sensitivity and selectivity. Chen [47] fabricated an electrochemical NPG film sensor to detect glucose based on the current response. As it was observed in optical sensors, lower pore size gave better sensitivity for glucose in this electrochemical sensor. The sensor was fabricated with the help of dealloying method and then cyclic voltammogram (CV) curves for NPG was used to detect OH^- adsorptions as it has direct correlations with electro-oxidation of glucose. In order to check the selectivity and sensitivity towards glucose of the sensor, glucose concentration was varied by keeping the pore size (18 nm) and current potential constant (0.1 and 0.3 V). On comparison, the current density at 0.1 V decreased while it increased linearly for 0.3 V proving the sensitivity of electrochemical sensor towards oxidation and subsequently towards the concentration of glucose. Additionally, the sensor was evident of excellent selectivity by avoiding interference caused by other substance present in the solution.

Electrochemical NPG sensor was used by a research group for the detection of DNA [48]. The biosensor showed an excellent sensitivity with a limit of detection up to 28 aM. The fact that the nanopores capture DNA and immobilizes it makes it more selective. Likewise, simple fabrication technique of dealloying makes it more feasible. Qui [49] went one step further to enzyme-modify NPG electrochemical biosensors to detect glucose and ethanol. The NPG was modified with the help of alcohol dehydrogenase (ADH) or glucose oxidase (GOD) that enhanced its sensitivity towards glucose and ethanol. The promising fact about these sensors is even after leaving them for 1-month storage at 4 ◦ C, the ADH- and GOD- based biosensor lost only 5% and 4% efficiencies, respectively. In this connected world, where some product is manufactured at one place and then transported to another sustained efficiency is of prime importance.

4.3 Catalysis

Catalysis is another activity which is highly dependent on the surface area for its efficiency. The first catalytic activity of gold nanoparticles was reported to be back in 1987 when CO was oxidized far below room temperature [50]. Due to inherent inert behaviour of gold, this experimental result came as a surprise. Moreover, a nanostructure is constructed on a substrate. So, when a reaction was taking place of these nanostructures used to come off from the substrate as a result of poor adhesion. This is where NPG gained its importance in this field for its bicontinuous structure [51]. In case of oxidation, the high surface area acts as an important site for adsorption giving exposure to a higher number of reactant molecules to interact with the surface. Another reason for high oxidation behaviour is the presence of some amount of Ag in NPG films. It is known that Ag bind oxygen and activate them [52].

Shi et al. [53] used NPG functionalized with praseodymium-titania mixed oxide to catalyze water-gas shift reaction. Both electron energy loss spectroscopy (EELS) and flow reactor tests revealed that Pr-TiO_x functionalized NPG is highly active as well as very stable to high temperature such as 180–400°C. This study exhibited the interaction between Au substrate and the oxide deposit which plays a vital role in the dissociation of water. The problem with the use of any nanostructure was decay in catalytic activity with time due to coarsening of the nanostructure. Use of Pr-TiO_x formed a mixed Pr-TiO_x solid solutions which prevented further coarsening of NPG making the catalyst stable to use for a long period. The catalytic activity of Au is also vital in recent reports of hydrogen fuel. Albeit the produced hydrogen contains a small amount of CO that can further deactivate the electrodes [54], a highly sensitive and selective catalyst is required for this purpose. NPG films form potential candidate for such catalytic applications.

Similar to CO oxidation, research has also been started in H_2 oxidation. Qadir et al. reported very low H_2 oxidation activity by bare np-Au [55]. The activity was manipulated by deposition of titania on the catalyst. This exercise also proves that tuning the amount of titania deposit can increase the oxidation activity of the structure.

4.4 Biomolecular sensing

Modified electrodes are being widely employed in modern electrochemistry for electrocatalytic reactions and as electrochemical sensors. Gold electrodes are useful to construct electrochemical sensors because of their chemical inertness. The well-established strategy of a self-assembled monolayer formation for immobilization of compounds onto gold surfaces are based on the attachment of thiol (-SH) or disulfide (-S-S-) functional groups to Au (111) [56].

In order to develop new reliable, efficient and functional micro/nanoscale devices, control over the surface properties is essential. The surface properties of microscale and nanoscale devices can easily be controlled and manipulated in a versatile manner through surface modification technology. The properties such as wetting, biocompatible, bioselective, optical and electronic characteristics of various inorganic and polymeric surfaces can be adjusted and controlled by modifying the surface.

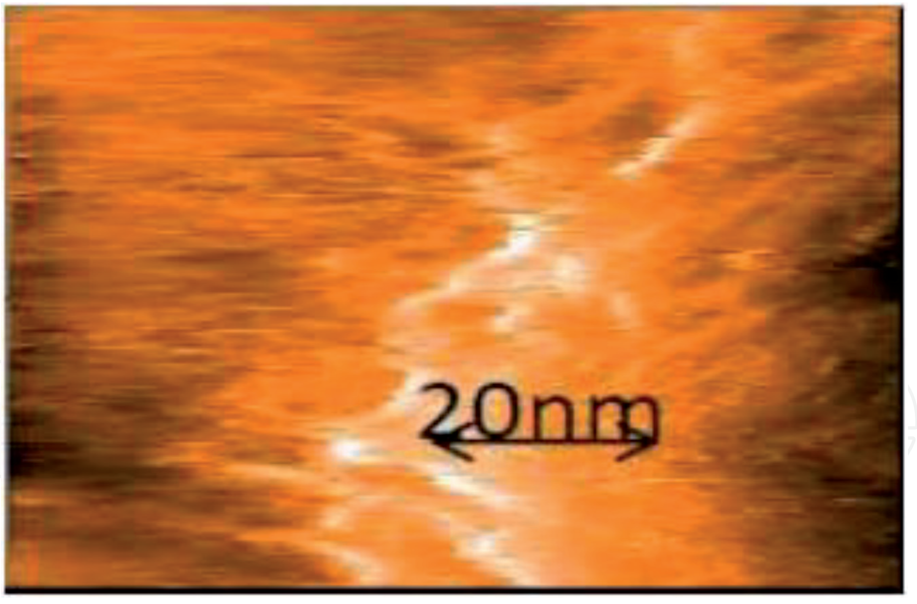

Figure 4.
STM image of gold on mica with surface modification by L-cysteine molecules [57].

Furthermore, a wide variety of terminal functional groups such as amino group, carboxylic acid group can be implemented to detect the trace heavy metal ions, DNA, RNA or antibodies.

Surface modifications can be grouped into two broad categories: (a) Chemically or physically altering the atoms or molecules in the existing surface (treatment, etching, chemical modification) (b) Coating over the existing surface with a material having a new composition (solvent coating or thin film deposition by chemical vapour deposition, radiation grafting, chemical grafting or RF-plasmas).

The Self Assembled Monolayers (SAMs) are nanostructures that are formed by organic assemblies owing to the adsorption of molecular constituents from solution or gas phase onto the surface of solids or arrays on liquid phase. The molecules or ligands that form SAMs have a chemical functionality called "headgroup" which has a special affinity towards a substrate. Typically, the thickness of a SAM is typically 1–3 nm.

SAMs are well-suited for studies in nanoscience and nanotechnology because: They are easy to prepare. They do not require ultrahigh vacuum (UHV) or other specialized equipment. SAMs can be easily prepared by immersing the substrates into the known solution. They form on objects of all sizes and are critical components for stabilizing and adding function to preformed, nanometer-scale objects for example, thin films, nanowires, colloids, and other nanostructures. They can couple the external environment to the molecular, electronic and optical properties of metallic structures. The most extensively studied class of SAMs is derived from the adsorption of alkanethiols (-SH) on gold, silver, copper, palladium, and mercury. SAMs also provide a convenient approach for ultra-low-level analyte recognition and have been important in the development of electroanalytical devices and electrochemical sensors [56].

Above **Figure 4** shows the surface coverage of L-Cysteine molecules on NPGF and with the increased surface coverage L-Cysteine molecules would be able to trap more heavy metal ions leading to lesser limit of detection (LOD) [57].

5. Future of NPG

The future for NPG films is promising though there are many unanswered questions. Like the understanding of relationship between constituent of an alloy and its morphology after dealloying and pressure flow relationship NPG sieves as well as

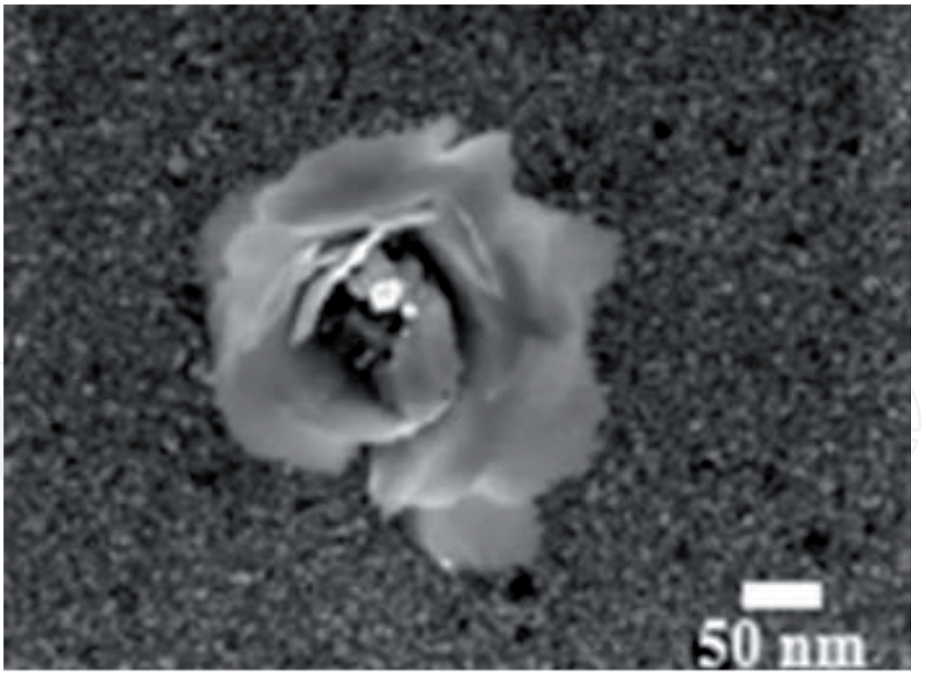

Figure 5.
SEM image of nanoflower [45].

its membrane architecture [58]. Also, the degree of sensitivity is going to play a vital role in coming days which will strengthen its foothold in the sophisticated sensing applications. The research work is already underway for different structures such as NPG leaves, nanowires, nanoflowers (**Figure 5**), etc. Looking at the promising optical and mechanical properties there is a long way to go before the full potential of NPG is reached. Additionally, with the onset of the decade where data is going to be of so much importance, correct data and large amount of data would be of high importance for precise decision-making purposes.

With the passage of time, the resources are becoming scarce triggering the requirement of tools which utilizes fewer materials to give more information. Also, selectivity would be of prime importance. For increased selectivity the sensors or catalysts should be manipulated from the bottom and this can be possible through NPG film like structures only. The use of minimal material would ensure less environmental impact. Hereby, the research should be more focused in areas like hydrogen fuel which is environmentally friendly and can pave way for potential applications in transportation industry.

6. Conclusion

Nanoporous metals is known to exhibit strong electrochemical, optical and mechanical properties due to their unique three-dimensional and quasi-periodic nanoporosity. Nevertheless, there are many challenges that remain. Performance of electrochemical sensors in energy applications depends strongly on their structure and composition [59]. So, new electrochemical fabrication method with the ability of tailoring of the size and shape of nanomaterials is required. Similarly, understanding of nanoporous metals with improved optical performances is necessary as it needs superior reproducibility, facile synthesis and excellent stability [13]. Additionally, in the field of medical research nanoporous metals are can be used for controlled drug-delivery [60]. Nanoporous metallic films would be attractive materials for future applications research that would result in huge advancement of the field of technology with strong conviction.

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