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Electrodeposition of Nanoporous Gold Thin Films

Palak Sondhi and Keith J. Stine

Abstract

Nanoporous gold (NPG) films have attracted increasing interest over the last ten years due to their unique properties of high surface area, high selectivity, and electrochemical activity along with enhanced electrical conductivity, and chemical stability. A variety of fabrication techniques to synthesize NPG thin films have been explored so far including dealloying, templating, sputtering, self-assembling, and electrodeposition. In this review, the progress in the synthetic techniques over the last ten years to prepare porous gold films has been discussed with emphasis given on the technique of electrodeposition. Such films have wide-ranging applications in the fields of drug delivery, energy storage, heterogeneous catalysis, and optical sensing.

Keywords: nanoporous gold, electrodeposition, surface area, potential, thin films

1. Introduction

Over the last two decades, nanotechnology and nanoscience have generated great scientific interest focusing mainly on the development of nanomaterials with specific and tunable properties and their applications in various areas [1]. Nanotechnology offers the ability to design, synthesize, and control length scales ranging from <1 to >100 nm. In the literature, reports of discoveries based on novel properties arising from these small size features have been increasing and nano-sized noble metal particles have occupied a central place [2]. Also, nano-technology has grown in significance in the study of fibrous materials, namely nanofibers and silicate nanocomposites wherein the synthesis and characterization along with the unique properties have been studied [3]. An emerging area of great interest is that of nanowire research which will interface with living cells for precise delivery of small molecules, proteins, and deoxyribonucleic acid (DNA) [4]. From the viewpoint of the relationship between nanostructures and proper-ties, remarkable advances have been made in the commercial use of thin films that find wide-ranging applications in almost all the industrial fields such as optics, electronics, mechanics, and even biotechnology [5]. There is a surge of interest seen in the scientific community when it comes to NPG due to its intriguing material properties arising from its high specific surface area, high electrical conductivity, reduced stiffness, and the prospect of easy surface modification. NPG has control-lable pore morphology and ligament size that opens up a wide range of studies of its mechanical and surface properties [6]. Compared to regular gold thin films which are dense inside, NPG films have interconnected ligaments with nanometers-sized

gaps throughout the bulk of the film. The pore size can be modulated depending on the type of synthesis protocol followed ranging from typically 20–50 nm in size but to as small as 5 nm [7]. Additionally, the porous structure of the NPG electrode tremendously increases the number of adsorption sites for various molecules of biological interest making it an attractive candidate in the field of biosensors [8]. Gold electrodes with nanoporous structures possess a higher roughness factor (the ratio between the real surface area and the geometrical area of the electrode) and better electron transport in comparison with their counterparts with smooth surfaces [9]. Metal nanoporous films have been prepared by various methods of high productivity and controllability of which chemical and electrochemical deal-loying laid the foundation for other methods [10]. Moreover, dealloying is a potent approach for the fabrication of both monoporous (i.e., nanoporous or microporous) and hierarchical (i.e., possessing both microporosity and nanoporosity) porous metal structures with novel properties [11]. Multimodal pore size distribution on the nanometer and micrometer scale is highly desirable. The presence of larger size pores enables fast transport of the reactants, while the nanopores are responsible for providing high surface area thereby increasing the rate of electrochemical reactions. High surface area gold could be prepared by the electrodeposition technique, illustrated in **Figure 1**. Porous metals prepared via dealloying often contain some amount of residual less noble metal and therefore other fabrication techniques were explored [12].

The electrochemical deposition of NPG on a solid substrate has been extensively researched in recent years. This facile technique enhances the electrochemical activity of the nanoporous film by offering fine control over the growth and nucleation mechanism which in turn determines the morphology of the deposited film [13]. The three-dimensional (3-D) nanoporous films, membranes or powders of large surface area have received great attention and it has been seen that the templating strategy is the most popular method for their preparation using polycarbonate membranes, colloidal crystals, lyotropic liquid crystalline phases of surfactants, and echinoid skeletal structures as the templates and will be discussed in this chapter [14, 15]. Electroplated gold continues to play an integral role in modern electronics technology, and it is hard to find an equivalent substitute due to the unique combination of properties of the metal. It is speculated that as information technologies continue to expand, the quantity of gold used will continue to
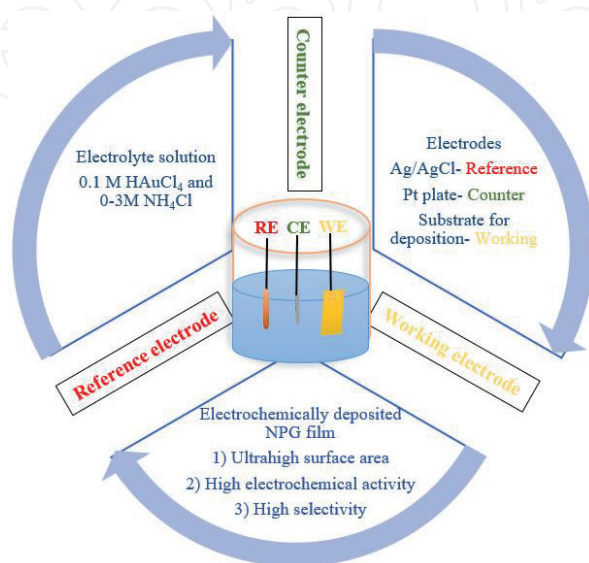

Figure 1.
A representation of the electrochemical deposition set up.

increase [16]. Experimental parameters have been seen to influence the morphology of gold and therefore, this chapter will give insights into the various methods used for fabricating NPG thin films with special emphasis on electrodeposition strategies. Along with the synthetic approaches, applications and the characterization of the NPG film will be discussed.

2. Fabrication techniques

There are various methods for fabricating porous gold films, and these are categorically described below.

2.1 Dealloying methods

De-alloying is an effective corrosion method for the fabrication of NPG films wherein the presence of less noble metals in the gold alloy has been exploited in a way that they are chemically or electrochemically dissolved to produce monolithic metal bodies with nanoscale pore structure. Au-Ag alloys are considered ideal due to their similar atomic volumes and continuous solid solubility allowing for coherent transformation from the master alloy to the nanoporous structure, see **Table 1** [17, 18]. Chemical dealloying has been studied employing Metropolis Monte Carlo simulations wherein the simulation of the dealloying process in the first stage describes the equilibrated systems followed by the second stage of dealloying with the exclusion of interaction parameters [19]. A simple method to dealloy the precursor alloy is to immerse it in nitric acid leading to selective etching of silver forming a 3-D pattern resulting in the formation of an open, bicontinuous highly porous network of gold with tunable ligament and channel width by varying the alloy composition, electrochemical potential, or by thermal annealing after dealloying [20]. **Figure 2** depicts the outcome of NPG structures upon a change in the experimental parameters.

Fabrication techniques	Advantages	Application
Dealloying	This approach enables the fabrication of NPG thin films, either free-standing or supported on a conductive substrate	Enhanced electrocatalytic activity towards methanol oxidation, potential in the field of catalysis, optics, and sensor technology
Self-assembly	Thin films formed exhibit enhanced thermal stability and capability of electron transfer. This method can be applied to various conductive surfaces without harmful pretreatment	Energy storage, photovoltaics, sensing, and electrochemical usage
Sputter deposition	Simple green method, reproducible and generates low-price final product	Electrochemical biosensing, used as supercapacitors, in microelectronics and photovoltaics
Electrodeposition	One-step fabrication of thin films directly on a substrate, control of particle morphology, size, and density is relatively easy. Uniform deposition is seen along with good stability	Electroanalytical and catalytic field

Table 1.
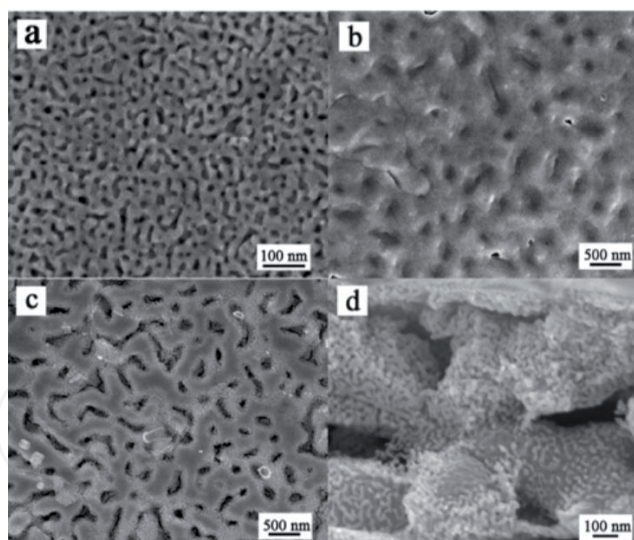*Summary of the fabrication techniques used to synthesize NPG thin films.*

Figure 2.
SEM images of NPG structures. (a) NPG membrane made by dealloying 1 μm thick gold leaf in nitric acid for 1 h. (b) Coarsened NPG structure generated via annealing of (a) at 400°C for 8 h. (c) Hierarchical porous membrane structure produced by performing second dealloying (of sample b) in nitric acid for 5 min and annealing at 400°C for 4 h. (d) Cross-section micrograph of sample (c). Reproduced with permission from reference [20], Copyright 2003, American Chemical Society.

Variables such as acid concentration, etching time, and solution temperature are known to influence the size of pores and ligaments. NPG films with ultrafine pores have been produced by a pulse electrochemical dealloying carried out at a potential of 0.6 V with 50 ms on-time and 10 ms off-time in 8 M HNO_3 at 23°C [21]. It has been seen that with the use of strong acid or alkali corrosion, the rearrangement is very rapid leaving little scope for porosity adjustment in such nanoporous products. Therefore, instead of the traditional corrosive acid etching, a two-step dealloying method has been reported which utilized $FeCl_3$ to synthesize NPG wherein the pore size was easily tunable by using a surfactant like polyvinyl pyrrolidone (PVP) or replacing corrosion reaction solvent with ethylene glycol (EG) [22]. Dealloying can be further classified into three categories namely, (i) chemical dealloying, (ii) electro-chemical or potentiostatic dealloying, and (iii) liquid metal dealloying. The driving force towards the selective dissolution of the active component is varied in the above-mentioned categories. It is a corrosive solution such as an acid in the case of chemical dealloying, the constant potential for electrochemical dealloying and the nature of liquid metal medium and temperature are the crucial deciding factors in the emerging field of liquid metal dealloying [11]. Extensive investigations have demonstrated that nanoporous metals with 3-D bicontinuous structures fabricated by the dealloying method, has many active sites for the excitation of localized surface plasmons and can, therefore, serve as a potential substrate for practical surface-enhanced Raman scattering (SERS) application [23]. Unlike single-sized porous materials, a hierarchi-cal (bimodal) porous structure can impart novel properties to the material wherein large pores can favor increased mass transport and small pores can impart high specific surface area [24].

2.2 Self-assembly

Self-assembly is one of the most versatile, simple, and inexpensive methods aiding the formation of porous polymer films with finely controlled topography [25]. The self-assembly strategy is a powerful approach to create functional nano-materials due to the high selection capability of the precursor materials and inclu-sion of functional groups, and nanoarchitectonics. The process is usually carried

out under ambient and mild conditions, making the process suitable for biological materials, see **Table 1** [26]. The self-assembled nanostructured film is a rapidly emerging field of great fundamental and practical interest due to the prospective applications in the field of microelectronics, non-linear optics, catalysis, and sensor science. Controlled covalent attachment of nanoparticles to functionalized surfaces is a versatile approach for producing thin-film structures. It has been seen that self-assembly of gold nanoparticles (AuNPs) on thiol modified surfaces exhibited non-metallic optical and electronic properties [27]. The self-assembly process of the AuNPs via aggregation and coalescence leads to the porous structure directly without relying on external assistance. Zhang and coworkers successfully fabricated porous gold films from a colloidal gold solution by evaporation induced self-assembly method (EISA) [28]. A facile synthetic approach for the self-assembly of AuNPs on sulfide functionalized polydopamine surface in high-density has been reported. AuNPs were seen to self-assemble strongly on the modified surface due to the strong interaction between gold and sulfur atoms [29]. Nanostructural control is very critical in material chemistry to bring out unique physical and chemical properties. So far, many mesoporous materials with varying compositions have been reported via self-assembly of amphiphilic organic molecules and have attracted keen interest due to their wide range of potential applications in energy storage, separation, catalysis, ion exchange, sensing, and drug delivery [30]. Another useful technique to immobilize gold thin films on micro- and nanopatterns is via the use of directed self-assembly on templates that are prepared by phase- separated mixed Langmuir Blodgett (LB) films. Atomic force microscopy (AFM), Auger electron spectroscopy, and scanning Auger electron mapping of the gold thin films revealed that the immobilized layer was following the patterns of the original mixed LB films [31]. Systematic analysis of the thermodynamics and kinetics of self-assembly in thin films of supramolecular nanocomposite has been studied in detail to extract information about the interfacial area defects, chain mobility, and activation energy needed for the diffusion of materials. Co-assemblies of nanoparticles and organic moieties are promising, and the resultant material will combine the properties of both the families of building blocks. Hierarchically structured nanocomposite thin films over macroscopic distances have been created by a fast ordering process with minimal usage of solvent via a deep understanding of the kinetic pathways [32].

2.3 Sputter deposition

Sputter deposition is an industry-relevant, high-rate, large-scale, and well-controllable deposition technique used to prepare gold films and other device fabrication processes. It is a large-scale deposition method, allowing high-rate vacuum coating with nanoscale precision, see **Figure 3**. Sputter deposition is an ideal method for preparing nanometer-thick films along with precise control over the deposition rate, highly adhesive films, large area uniformity, uniform temperature, and the ability to coat a variety of substrates including the non-heat resistant [33].

Sputtering is a pollution-free ("green") technique that offers the advantage of reproducibility and low price of the final product. Nanostructured gold film adhesion and electrical contact properties are strongly influenced by interface structure, see **Table 1** [34]. Thin gold films prepared by this strategy are found to be continuous and relatively homogeneous, with distinct grain surfaces without showing the formation of islands. Films of thickness ranging between 5 and 52 nm have been prepared for the study of third-order non-linear properties where the third-order susceptibility was found to be of the order of 10^{-9} esu. This non-linear optical interaction enhancement has helped to construct nanodevices to be used in metrology, sensing, imaging, and telecommunications [35]. It has been shown that pure
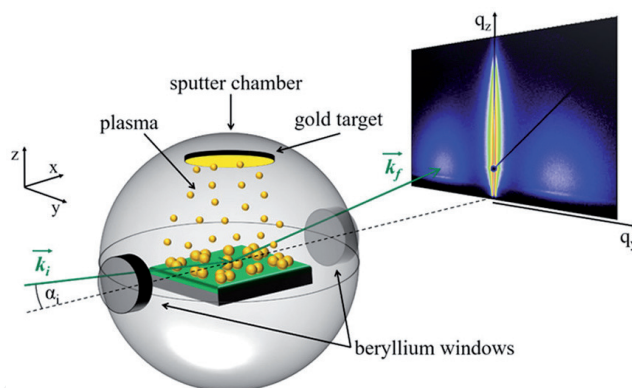
Figure 3.
Schematic illustration of the in situ grazing-incidence small-angle X-ray scattering (GISAXS) set up showing sputtering of gold atoms on spiro-OMeTAD film. A two-dimensional detector is detecting the signal produced by scattered X-rays. Reproduced with permission from reference [33], Copyright 2020, American Chemical Society.

sputtered gold films can match the hardness of gold electrodeposits. The hardness of sputtered films and the grain size of the deposit is controlled by maintaining the temperature of the substrate during deposition [36]. It has been reported that ultrathin semi-transparent gold films have been deposited using radio frequency (RF) magnetron sputtering at room temperature over a small area (23 mm^2) of the porous silicon layer. Various film thicknesses were obtained by changing the sputtering time from 5 to 20 s at constant chamber pressure and argon gas flow rate [37]. Thin films have been deposited by varying the experimental conditions concerning the substrate tilt angle and background pressure. Growth regimes of thin gold films deposited via magnetron sputtering at oblique angles and low temperatures have been studied from both theoretical and experimental points of view [38]. The growth and morphology of a room temperature sputter-coated thin gold film on a soft polymeric substrate from nucleation to thin film formation has been investigated using AFM. It was observed that an initial 3-D island-type growth starts with the deposition and with increasing time the morphology evolved from hemispherical islands to partially coalesced worm-like island structures, to percolation, and finally to a rough and continuous film [39]. In a study, it was seen that after the stage of nucleation, the growth of gold clusters proceeds mainly in the lateral direction. As the discontinuous islands change into a continuous thin film, a rapid decline in the resistance of the gold layer has been observed [40]. A unique method for synthesizing porous gold films by co-deposition of Au-Cu alloy has been done via co-sputtering Au and Cu using a multi-target sputtering system at room temperature. Selective removal of Cu was done via corrosive dealloying leading to the formation of the porous gold film via the physical–chemical combination method [41]. Sputter deposited thin porous gold films find applications in the field of electrochemical biosensing for enhancing redox signals by modulating the nanopore size and film thickness. Higher detection resolution is exhibited to that obtained by conventional bulk gold electrodes [42]. The atom sputtering deposition technique has allowed scientists to study the optical and electrical properties, density, and crystalline structure of gold nanostructures sputtered on glass [40].

2.4 Electrodeposition

Electrodeposition is a simple, controllable, and cost-effective method that can control the growth process by varying deposition current density. Kinetic control over the growth process can give insights into the mechanisms in the synthesis of deposits with various sizes and shapes. The mass of gold on the electrode is controlled by the electric charge passed during the electrodeposition process, based

on Faraday's laws of electrolysis [43]. Deng and co-workers gave a mechanistic viewpoint to the facile method of electrodeposition in the electrochemical cell, where a process of electrodissolution-disproportion-deposition is involved. Upon the potential step, the gold substrate undergoes active electrodissolution in HCl providing the diffusion control, forming $AuCl_2^-$ and $AuCl_4^-$. With the progress of the reaction, HCl depletes and $AuCl_2^-$ starts accumulating near the gold surface immediately giving off Au atoms and $AuCl_4^-$ wherein the newly formed Au atoms aggregate and deposit on the substrate to form NPG film [44, 45]. NPG morphology evolution has a direct relationship with the topography of the underlying substrate. A study has very well demonstrated that micropattern widths that are within the magnitude of film thickness produce tunable pores with less cracking [46]. Porous nanomaterials particularly NPG has drawn tremendous research interests mainly in the development of electrochemical sensors due to the high surface area and the trait of being electrocatalytically active. Electrosynthesis can impart precise control over the bicontinuous network of interconnected nanometric gold grains and multiple sized pores [47].

Conductive substrates coated with AuNPs can be exploited as biochemical sensors and electrodes owing to their excellent electrocatalytic activity. A simple, powerful, and cost-effective way for attachment of AuNPs onto a substrate has been electrodeposition with pulsating current resulting in smoother, brighter, finer, and less porous Au grains concerning the direct current [48]. A simple template-less, surfactant-less and effective electrochemical method for the preparation of AuNP arrays with an average diameter of ~14 nm onto indium tin oxide (ITO) glass has been reported. The system exhibits excellent catalytic properties due to the presence of large active sites on the surface [49]. The deposition of thin metallic films onto non-conductive surfaces by the wet processing technique of electrodeposition is another route for fabricating various unique electronic devices and systems. Amine terminated self-assembled monolayer (SAM) modified insulator surface has been employed for the lateral growth of electrodeposited gold. Controlled morphology and thickness of laterally grown metal films has paved a way to create nanogap electrodes [50].

Electrochemical deposition methods have been classified into two groups namely, templated electrodeposition and self-templated electrodeposition. Template technology offers advantages for designing new types of electrode materials aided by "hard" or "soft" templates that give rise to functional materials with diverse structures and morphologies, such as, one-dimensional nanostructures, two-dimensional films, and 3-D porous frameworks. In templated electrodeposition, porous gold is deposited on a template by reducing gold near the electrode surface via fixed potential application followed by the removal of the template. The self-templated approach initializes with the generation of H_2 bubbles in the solution containing a supporting electrolyte by applying a potential of at least −2 V vs. saturated calomel electrode (SCE), allowing a gold reduction in the interstitial space [51, 52]. The monolithic NPG film has been synthesized using a bottom-up synthesis from a bicontinuous microemulsion (BME) acting as a dynamic soft template, depicted in **Figure 4**. The aqueous phase of BME acted as a medium for gold electrodeposition and the intertwined structure came from the aqueous and oil phases of BME compartmentalized by surfactant and cosurfactant. The resultant film nanostructure has been controlled by adjusting the initial BME composition and by varying kinetic parameters such as deposition potential and time [53].

The role of electrodeposition potential on the growth morphologies has been seen in a study where gold deposition from sulfite electrolyte exhibits a range of geometries from vertically oriented nanowires to lenticular grains and dendrites at more negative potentials [54].
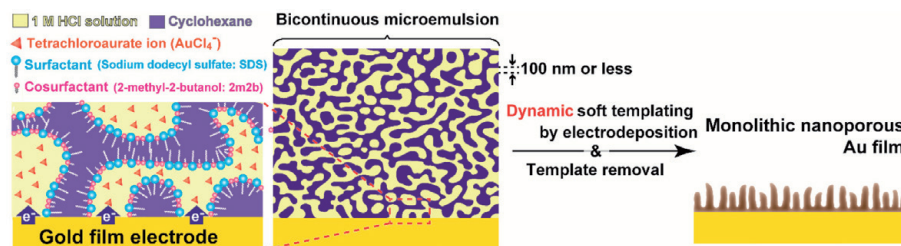
Figure 4.
Schematic representation of the dynamic soft templating of a nanoporous thin gold film from BME by electrodeposition. Reproduced with permission from reference [69], Copyright 2013, American Chemical Society.

In recent years, studies have been performed to produce 3D porous materials that have the advantage of increasing the mass transport for electrolytes but also allow rapid electrochemical reactions due to considerable active surface area. A new way of producing such materials is via concurrent generation of hydrogen bubbles with simultaneous metal deposition at high cathodic current densities. The reduction of H+ giving rise to hydrogen bubbles acts as a dynamic template for metal electrodeposition [15]. The electrodeposition parameters such as time and potential are the deciding factors for the pore size and film density. The dynamic hydrogen bubble template (DHBT) method results in a gold nanoporous structure with outstanding properties, like high specific surface area, large pore volume, uniform nanostructure, good conductivity, and enhanced electrochemical activity [55]. A simple method has been proposed for the one-step electrodeposition of NPG-islands films on the surface of the glassy carbon (GC) electrode via the hydrogen bubble template approach. The 3-D structure generated via the DHBT method is more attractive as it is clean and porous in an efficient way in the absence of inorganic and organic templates and exhibited improved electrocatalytic activity for oxygen reduction and hydrogen evolution reactions (HER) [56]. Recently, self-supported 3D metal foams of copper, tin, and silver have been reported. 3D porous noble metals such as gold have higher equilibrium potential and lower overpotential for HER and therefore, a two-step rout was taken involving the deposition of the less noble element followed by its galvanic displacement. Chung and coworkers have therefore shown a fast one-step preparation of high surface area NPG with a multimodal pore-size distribution utilizing a DHBT [12].

Another study produced porous gold incorporating nanocorrals on gold screen-printed electrodes (SPEs) utilizing hydrogen bubbles as a dynamic template. The structure produced using this one-step electrodeposition using high overpotential had a high roughness factor [57]. Moreover, distinct pore morphology can be obtained by taking advantage of electrical conductivity and morphological plasticity of NPG. Pore morphology can be tuned using the novel and versatile technique of electro-annealing on NPG thin films at low temperatures [58]. The microstructure of electrodeposited gold films and their deposition characteristics are affected by base metal ions. It has been seen that gold deposits obtained from Co and Ni-containing electrolytes are generally hard, while Pb and Tl-containing electrolytes tend to give soft gold deposits [59]. The crystallographic structure of gold films is also dependent on the current density at which electrodeposition has been carried out. It has been seen that Au electrodeposited at a current density less than $0.25 \ mA \ cm^{-2}$ from dicyanoaurate baths with or without Cu^{2+} or Tl^+, gave rise to the formation of hexagonal structure [60].

The electrochemical potential and the concentration of $HAuCl_4$ have been modified to create a variety of morphologies in the final structure. Nanopyramidal, nano rod-like, and spherical gold nanostructures were fabricated on polycrystalline gold substrates via one-step, non-templated electrochemical overpotential

deposition (OPD) [61]. Moreover, the chemical nature of the organic ions present in the organic electrolytes has a huge role to play on the morphology of the deposits produced. The organic species adsorb onto the electrodeposits due to high surface energy and finally influence the shape of the growing grains and the roughness of gold electrodeposits [62]. Recently, a study described the electrodeposition of gold nanostructures at the interface of a Pickering emulsion. The controlled electrodeposition of AuNPs on the surface of an emulsion droplet gave rise to intricate structures with fine control over the locus or duration of nanoparticle growth. Decamethylferrocene present in the emulsion droplet acted as a heterogeneous electron transfer agent for the reduction of aqueous phase Au (III) resulting in its deposition as nanoparticles [63]. In one of the studies, it was found that SERS of the electrodeposited gold was correlated to the roughness and the size of surface nanostructures where these two parameters were largely controlled by the applied potential during deposition [64]. Over the last decade, researchers have focused on improving methods for fabricating reproducible substrates for surface-enhanced resonance Raman scattering (SERRS). Amongst these, deposited gold films have been the most heavily researched, and therefore, Bartlett and his group fabricated ordered-spherical-cavity gold films using colloidal templated electrodeposition method for the first time. The net enhancements are found to be ~10^9 for SERRS over normal Raman [65]. Nanostructured gold films for use in localized surface plasmon resonance (LSPR) spectroscopy have been prepared from flat gold film substrate made by stripping off epoxy coated glass slides off the gold-sputtered silicon wafers and then subsequent two-step chronoamperometry to electrodeposit gold from potassium dicyanoaurate solution [66].

Solid thin film deposition on the soft ionic liquid (IL) substrate was used for L-arginine detection. A gold monolayer was deposited on the surface of the IL substrate using the conventional electro-co-deposition (CECD) technique using an electrochemical workstation with three electrodes system in 0.5 M NaCl and 3 mM $KAuCl_4$ electrolyte solutions [67]. A new study described the bottom-up approach of lithographically patterned nanowire electrodeposition (LPNE) for synthesizing noble metal nanowires on glass or oxidized silicon surfaces. The process of LPNE starts with the preparation of a nickel nanoband electrode which acts as the surface for electrodeposition [68].

LPNE has been combined with colloidal lithography to create a novel low-cost method for the lithographically patterned electrodeposition of metallic nanoring close-packed arrays over large areas. By altering the width and radius of the nanoring during the fabrication, near-infrared (NIR) plasmonic resonances could be tuned from 3500 to 8000 cm^{-1} with potential applications in the fabrication of plasmonic antennae, plasmonic semiconductors, and negative-index metamaterials [69]. Direct electrodeposition of porous gold nanowire arrays has been developed utilizing a one-step electrodeposition methodology utilizing nanochannel alumina templates. Current density during deposition is the deciding factor for the microstructure of gold nanowires and the resulting structure has shown excellent electrochemical biosensing ability towards the detection of glucose [70].

It has been known that the surface roughness and the structure of gold deposits can be influenced by periodically reversed or pulsed current and in some electronic applications pulse plated gold deposits are considered superior to DC plated deposits. Electrodeposition of gold using pulse plating produces a dense fine-grained structure with half the resistivity of normal DC plated films [71]. The pulse potentiostatic method (PPSM) offers numerous advantages in terms of controllability, particle size, stronger adhesion, and uniform film morphology. PPSM has been used to deposit gold nanoflowers (AuNFs) onto a polymer film. Through this simple and rapid method, a new organic–inorganic hybrid film has been fabricated with

superior electroactivity, electrochemical, and interfacial characteristics suggesting the suitability of such electrodes for sensors, electrocatalysis, and diode applications [72]. Epitaxial, ultrathin, semitransparent, and catalytic gold films were electrodeposited on n-type silicon (n-Si) to protect the substrate from photo-passivation, see **Figure 5**. In addition to being a good redox catalyst, the ultrathin gold layers serve to induce band bending in n-Si thereby making it a diode of an ideal quality factor due to minimal electron–hole recombination [73].

Fabrication methods have been used in combination in the past to generate a promising eco-friendly biosensor platform with advantages coming from both the techniques. One such study has been done to fabricate a glucose biosensor wherein AuNPs and glucose oxidase multilayer films were generated via electrodeposition and self-assembly respectively [74]. As an eco-friendly alternative, deep eutectic solvents (DESs) are a new class of green and sustainable solvents extensively used for electrodepositions due to their intrinsic properties of good solubility, non-flammability, low toxicities, and suitable electrochemical windows. Recently, an electrochemical method has been developed to fabricate NPG electrodes by alloying and dealloying the precursor alloy in $ZnCl_2$-urea deep eutectic solvent [75]. The wide acceptance of DES in metal/alloy electrodeposition processes has been seen in recent times due to their ability to act as stabilizers and reducing agents in metal nanoparticle synthesis. Moreover, the nucleation rates are enhanced leading to a
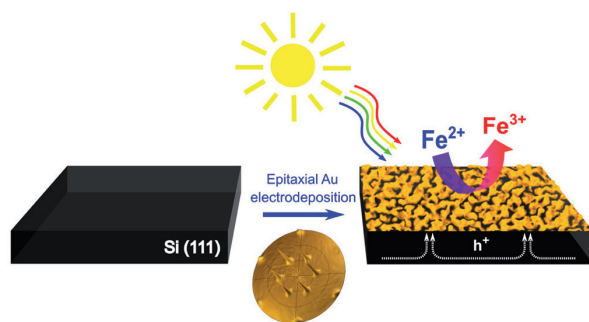

Figure 5.
Illustration showing the formation of an ultrathin epitaxial gold layer electrodeposited on n-Si (111) to form a Schottky junction in a regenerative photoelectrochemical cell. Reproduced with permission from reference [73], Copyright 2018, American Chemical Society.
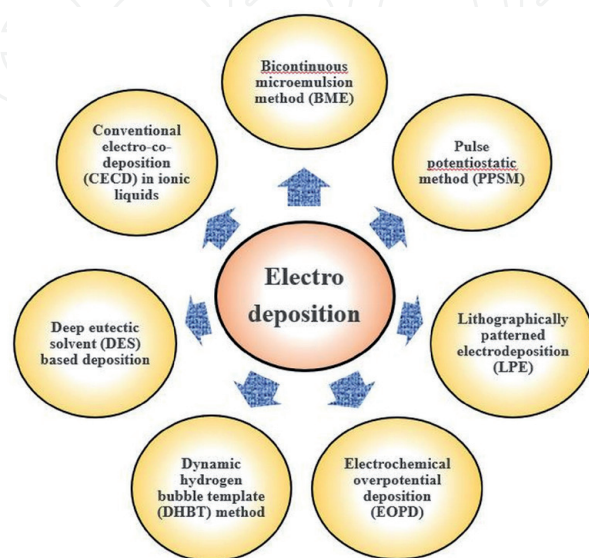

Figure 6.
A general overview of the techniques used for electrodeposition to form thin nanoporous films.

decrease in the particle size in the presence of DES as it has relatively low surface tension [76]. Remarkable optical behavior has been observed when the bulk material is transformed into nanostructured surfaces. A simple two-step electrochemical process has been developed wherein electrodeposition and anodization is used in conjunction to generate black gold surfaces that can absorb more than 93% of the incident light over the entire visible spectrum due to the canopy of dendritic nanostructures within a nanoscale roughness with potential applications in photovoltaic solar cells [77]. **Figure 6** summarizes the general methods used for electrodeposition to form thin nanoporous films.

3. Characterization techniques for NPG thin films

The physical and morphological properties of nanoporous thin films are strongly linked with material's porosity (defined as the ratio of void volume to the total volume of the film). Hence, many efforts have been devoted to developing a reliable self-consistent quantitative characterization of their porosity [78]. The physical characteristics of thin films have been characterized by a combination of X-ray photoelectron spectroscopy (XPS), grazing-incidence small-angle X-ray scattering (GISAXS) along with adsorption isotherm surface area measurements. Porosity and internal feature sizes range from a few to tens of nanometers [79]. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments have the potential to find the electrochemically active surface area of the NPG film. Studies have shown that using CV and EIS it was shown that NPG films have 4–8.5 times more accessible surface area than thermally evaporated gold (EG) films [80]. Potential step (PS) chronoamperometry has also been combined with surface plasmon resonance (SPR) for probing electrochemical deposition, conformational changes linked with redox-initiated film reorganization, and the quantification of electrodeposited thin film thickness [81]. A well-recognized approach to determine the specific surface area of nanoporous materials is the Brunauer, Emmett, and Teller (BET) method which is based on physical adsorption of gas molecules to determine the specific surface area [82]. Many groups have extensively used scanning electron microscopy (SEM) for rapidly exploring pore size and ligament size due to their ease of use and applicability to varying types of samples. Elastic modulus is an important mechanical property to calculate residual stress in free-standing beams. This in turn determines film stiffness and therefore, sensor performance [83]. SEM and AFM techniques have been used by many researchers to characterize the surface morphology, size, and shape of the pores as well as the surface roughness of the porous gold films [84]. Maaroof and coworkers have measured the optical properties of porous gold film using the techniques of spectrophotometry and ellipsometry. The spectral response was delivered using a homogeneous Lorentz-Drude (L-D) model and showed that the optical properties of NPG films are dependent on void occupancies [44]. Nanoporous metals have significant geometric complexity in the form of random bicontinuous structures possessing bubbles within ligaments, regions of very high negative, positive, and saddlepoint curvature, and multiple facets. Erlebacher introduced methods to geometrically quantify the structure of nanoporous metals using large-scale kinetic Monte Carlo simulations using mesh-smoothing algorithms [85]. Atom probe tomography (APT) analysis of NPG material, produced by dealloying can give huge information regarding the compositional variation within the structure of nanoscale ligaments. 3-D analysis of materials at the sub-nanometer scale is possible by careful preparation of samples through a reproducible process for complete pore filling through electrodeposition of copper into finely sized pores. Compositional profiling and

mapping of ligaments are now possible by APT analysis [86]. Electrodeposition of gold nanostructures having sharper features yield higher refractive index sensitivity and therefore, can be used as transducers in LSPR spectroscopy for probing many types of biomolecular interactions [66].

4. Applications

Nanoporous materials such as carbon nanotubes, nanoporous anodic alumina, nanotubular titania, porous silicon, and NPG have significant potential in the field of biomedicine involving high drug loading capacity and its controlled release. It was seen that a sub-micron-thick sputter-coated NPG thin films have a loading capacity of 1.12 $\mu g/cm^2$ and molecular release half-lives between 3.6 hours to 12.8 hours [87]. NPG is a promising material for drug delivery applications and for studying the influence of surface modification on the drug release kinetics due to its high effective surface area, well-known surface gold-thiol chemistry, and tunable pore morphology and is depicted in **Figure** 7 [88].

Rough and activated noble metals exhibit some unexpected properties in comparison with their smooth counterparts. The electrocatalytic activities of the porous films depend on the roughness factor and the existence of special binding sites on the surface. NPG films possess higher roughness and better electron transport leading to its distinguished performance in the field of catalysis [89]. Studies have shown that NPG is active towards catalyzing low-temperature CO oxidation which is attributed to the peculiar structure of NPG and the prevalence of step and kink sites on the surface of the material [90]. Nanoporous metals have recently attracted considerable attention fueled by their potential use in the filed od catalysis, sensor, and actuator applications by increasing the activity drastically via thick oxide film deposition to stabilize the nanoscale morphology [91]. The potential of nanostructured metallic surfaces has also been seen in optical applications and has been demonstrated for biosensing applications, SERS, guiding and manipulating light, and trapping of micro-sized particles [92]. The electrodeposition approach has been used for depositing a thin layer of AuNPs from 10 mM $HAuCl_4$ for 20 s at -0.2 V (vs. Ag/AgCl) yielding oblate particles of 200 nm average diameter that immobilized an aptamer specific for LPS detection achieving a linear range of 0.1–10.24 ng mL^{-1} [93]. Thin nanoporous membranes of gold are best suited to the examination of surface plasmons as the analyte can get into the pores of NPG and can modify their dielectric atmosphere are detectable via absorption peaks in SPR
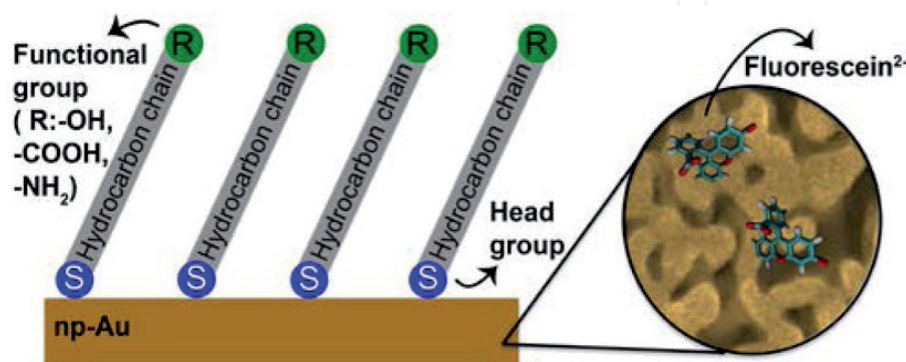

Figure 7.
Depiction of surface engineering of NPG film via immobilizing alkanethiols with varying functional groups and chain lengths to enhance the drug delivery performance monitored via fluorescein release signal. Reproduced with permission from reference [88], Copyright 2016, American Chemical Society.

whereas the species that adsorb onto the geometric surface of the pores of the film are equally detected by SPR measurements [94].

5. Conclusion

The electrodeposition of noble metals on support provides a unique possibility to obtain films of varying thickness and roughness. Many advanced electrodeposition techniques are known so far, and the field is actively developing with specific controllable nanostructural features leading to an increased number of grain boundaries for high catalytic performance [95]. It is interesting to see how the porous gold nanostructures can be electrodeposited on a solid support and the impact of electrodeposition parameters namely, potential and time of deposition, on the morphology and thickness of the film so formed. Detailed investigation on NPG surface pore size and the correlation with electrocatalytic activity has aimed to understand the growth mechanism of NPG [13]. The experimental results from the electrodeposition techniques have highlighted that the formation of a well-organized NPG film requires the appropriate electrochemistry and physics/mechanics interactions between the substrate and the deposits [96]. NPG morphology evolution is highly influenced by the topography of the substrate emphasizing the structure–property relationship and opening doors for such high-throughput combinatorial studies [46]. An exciting new field of research within the domain is the electrodeposition of hybrid thin films which has opened the gate to an unlimited number of new materials [97]. Electrodeposition, therefore, is a promising fabrication technique that has the potential of producing thin NPG films for effective drug delivery systems as precise control of the NPG pore and ligament dimensions can be achieved which in turn control the drug loading and release performance inside the body [98]. Electrodeposition is a distinct form of grain boundary engineering by which a material's property can be enhanced to synthesize advanced materials both in bulk form and as thin films. It is a technologically viable production method for upgrading the mechanical, electrical, magnetic, and corrosion properties exhibited by metals [99].

Conflict of interest

The authors declare no conflict of interest.

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