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Review

Methods to Generate Structurally Hierarchical Architectures in Nanoporous Coinage Metals

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Abstract: The fundamental essence of material design towards creating functional materials lies in bringing together the competing aspects of a large specific surface area and rapid transport pathways. The generation of structural hierarchy on distinct and well-defined length scales has successfully solved many problems in porous materials. Important applications of these hierarchical materials in the fields of catalysis and electrochemistry are briefly discussed. This review summarizes the recent advances in the strategies to create a hierarchical bicontinuous morphology in porous metals, focusing mainly on the hierarchical architectures in nanoporous gold. Starting from the traditional dealloying method and subsequently moving to other non-traditional top-down and bottom-up manufacturing processes including templating, 3D printing, and electrodeposition, this review will thoroughly examine the chemistry of creating hierarchical nanoporous gold and other coinage metals. Finally, we conclude with a discussion about the future opportunities for the advancement in the methodologies to create bimodal structures with enhanced sensitivity.

Keywords: hierarchically porous materials; dealloying; templating; pores and ligaments

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1. Introduction

The study of the corrosion properties of alloys has added substantial value in the field of scientific study that deals with the aspects of electrochemical kinetics with morphological evolution of surfaces along with the contributions from ancient history on depletion gilding. Depletion Gilding or *Mise en Couleur* is the technique of changing the surface composition of an alloy by the removal of the less noble metal from the surface layer giving rise to a surface-enriched product. The pre-Columbian populations of South America mastered the art of "Depletion Gilding" on an alloy of gold (Au) and copper (Cu) by selective corrosion of copper in acid media. It is pertinent to review the historical evidence of this 2000-year-old process used for surface enrichment due to its relevance to some of the more modern processes that will be discussed in the later sections [1–4]. The 1980s marked the beginning of an era when considerable insight was put into understanding the micromorphological changes occurring near the surface after alloy corrosion. Corrosion tunnels in Au-Cu alloys were seen for the first time by Pickering and Swann using transmission electron microscopy. It was found that closely spaced pits or tunnels appeared to be the dominant features that were dependent on the alloy composition and the nature of the corroding reagent [5]. Through the pioneering work by Forty and Pickering, the process of dealloying and the unusual appearance of an open bicontinuous nanoporous microstructure was understood. Recently, Erlebacher et al. explained the atomistic details regarding the generation of porosity during dealloying. His model was based on "interfacial phase separation" in which he explained the formation of clusters and islands of gold rather than uniform spreading over the surface, which in turn passivated the interface and stopped further etching. Combining the knowledge gained from the historical connection between dealloying and depletion gilding, he fabricated ultra-thin nanoporous gold membranes having a large surface area [6].

Nanoporous metals have attracted much attention owing to their extraordinary electrical and optical properties due to the unique bicontinuous interpenetrating ligaments and open pores present in their structural architecture [7]. Two different nanofabrication methods for creating novel functional materials are classified as bottom-up and top-down approaches. Specifically, top-down approaches create nanoscale structures by the controlled removal of materials from bulk solid or by adding patterns on a blank canvas of the bulk sample. In contrast, the bottom-up approach involves the self-assembly of precursors into the final structure of the desired arrangement. Fine-tuning of features at the microscale and larger length scales in an arbitrary fashion can be achieved using top-down approaches while researchers can modulate molecular-scale lengths using bottom-up methods of synthesis [8]. Using various dealloying techniques, many nanoporous metals have been fabricated and among these materials, nanoporous gold (NPG) is the most widely studied prototype as it combines the advantages of nanoporous and metallic materials. Due to the excellent structural stability, high conductivity, tunable structural features, remarkable biocompatibility, and electrochemical catalytic activities, NPG has promising application potentials in the fields of catalysis, biosensing, energy storage, and biomedicine [9,10]. However, despite these advantages, bulk nanoporous metals suffer from transport limitations where diffusion-based mass transport is slow through the bicontinuous network. This limits their benefits in the field of catalysis, sensors, actuators, and chemical separations. To resolve the aforementioned issue, the best approach will be the addition of a structural hierarchy incorporating microporous transport in the entire structure, which also ensures the accessibility to the large surface area of the porous structure [11].

Hierarchical organization is most evident in biological systems such as the porous network seen in bones and trees, wherein the ordered hierarchy reduces the density of the structure, provides channels for easy flow of fluids and nutrients, and enhances mechanical properties. To mimic such advanced systems where structural elements themselves have a structure on a smaller scale requires the appropriate preparation procedures along with the impact of introducing such hierarchy on the functional aspect of the material [12]. Over the last decade, a range of strategies has been employed to fabricate hierarchically porous materials, which include surfactants as soft templates to create materials with dual mesoporous structures [13], hard template method [14], supercritical fluid technology [15], freeze-drying [16], self-assembly approach using metal alkoxides [17], etc.

There is widespread interest in the development of hierarchically porous materials owing to their diversity and performance. Hierarchically porous materials have been used as photoanodes for dye-sensitized solar cells due to their ability to increase the optical path length, thereby enhancing the adsorption of dye molecules. Moreover, due to improved diffusion pathways, they have been used in fuel cells improving the current density and conversion efficiency. Electrical energy storage, high performance in heterogeneous catalysis, potential adsorbents for gas and liquid separation, and in the removal of pollutants, drug delivery, and enzyme immobilization are some of the other significant areas where such materials due to their large surface area and facile mass transport greatly improve the sensitivity and response time [18]. Hierarchical materials, particularly traditional coinage metals, have large porosity channels with several smaller pores on channel walls that enhance the density of plasmonic hotspots, making it a suitable platform for surface-enhanced Raman spectroscopy (SERS) for ultrasensitive sensing applications as well as photocatalysis [19]. Figure 1 shows the major areas where hierarchically designed materials can be employed for better sensitivity and selectivity.

Due to the growing focus on the fabrication strategies to create hierarchy in nanoporous metals, it is of great importance to review the recent progress in the synthesis of hierarchically nanostructured metals. In this review, we will describe some of the most prominent approaches used to create structural hierarchy in nanoporous gold along with some other coinage metals. We hope that with this review the reader will gain in-depth knowledge of designing and controlling a specific pore structure along with the prospects associated with such materials.

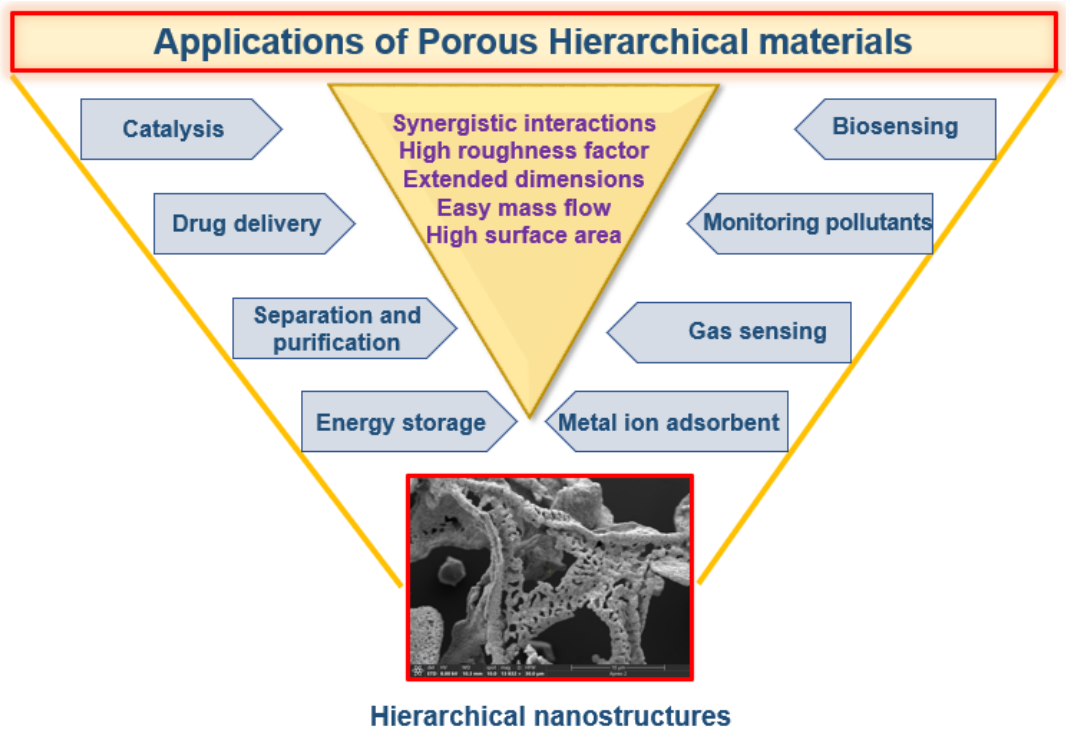

Figure 1. Schematic showing the wide-ranging areas involving the use of porous hierarchical materials.

2. Methods to Generate the Hierarchy

There have been tremendous efforts devoted to developing new approaches to functional hierarchical nanostructures, which are of both scientific and technological importance. The simple dealloying method has been known for years for creating functional nanoporous metals with tunable structural features. In particular, NPG prepared using alloy corrosion exhibits a series of intriguing properties to be used successfully in catalysis, sensing, and surface plasmon resonance. Considering the great success of the method that has been traditionally regarded as a destructive process, research efforts are focused on extending the dealloying methodology encompassing other advanced technologies [20]. This paper will summarize some of the general approaches in developing a hierarchical material at various length scales. Figure 2 depicts the top-down and bottom-up approaches in creating hierarchy in material design.

2.1. Multiple Annealing and Dealloying

Researchers have long endeavored to create hierarchical porous metallic materials using dealloying with or without their combination with other manufacturing processes. It has been seen that the dealloying method has the potential to create a structural hierarchy for promising applications [21,22]. Hierarchical nanoporous materials provide a large surface area and a structure rich in pore channels. They can be created by utilizing the dealloying approach that depends on the chemical stability difference of the constituent elements in the starting alloy material [23]. One-step dealloying is an attractive route to fabricate hierarchical nanoporous structures. Hierarchical nanoporous Cu@Cu_2O composite was easily fabricated using dealloying of CuAl thin foils in dilute NaOH solution until no hydrogen bubbles were generated. Selective dissolution of Al from CuAl alloy gave rise to a sponge-like structure with multimodal pore size distributions. The catalyst prepared in this way has shown advanced performance towards one-pot transfer hydrogenation reactions of diverse nitroarenes to anilines [24]. NPG with a bimodal pore size distribution has been created using a multistep process involving corrosion-coarsening-Ag plating-realloying-corrosion. The selective dissolution of silver from silver/gold alloy was

done by immersing it in nitric acid for 1 h. The remaining gold rearranges into the 3D porous network, which was annealed at an elevated temperature of 400 °C for 8 h for expanding the pore size to create an upper hierarchy. Pores of this annealed membrane were filled with silver using the gas-phase electroless plating technique and the second annealing step was performed to rehomogenize the material. The second dealloying step dissolved the remaining silver generating a hierarchical porous network. This diffusion-based process was applied to 100 nm thin, porous membranes leading to large porosity channels and small porosity channel walls with tunable pore size [25]. Hierarchically porous Au-Cu alloy film was created following a similar series of alloying/dealloying processes. The fabrication process involved electrodeposition of copper on a substrate followed by annealing and selective dissolution of copper from the alloy. The resulting architecture is comprised of micrometer-sized ligament channels and small ligament pores in the nanometer range. The catalytic activity for methanol electro-oxidation in alkaline solution using such materials has shown their remarkable performance in the field of catalysis and sensing [26]. Recently, an electrochemical dealloying strategy has been used to create "nested-network" nanoporous gold (N^3PG) bulk samples. Dilute alloys of Au in Ag were arc melted and homogenized at 850 °C. Cuboid samples created from the ingots were dealloyed under 300 mV potential control. An alloy sample with high silver content was used to ensure enough silver content is remaining for a second dealloying step. The first dealloying step created a ligament size of ~16 nm, which upon annealing at 300 °C for 3 h coarsened to ~200 nm. A second dealloying at 750 mV created an architecture consisting of a fine network of nanoscale ligaments nested within the upper hierarchy network [27]. Figure 3 shows the alloying-dealloying-annealing-dealloying approach used by many research groups to create hierarchy in porous materials.

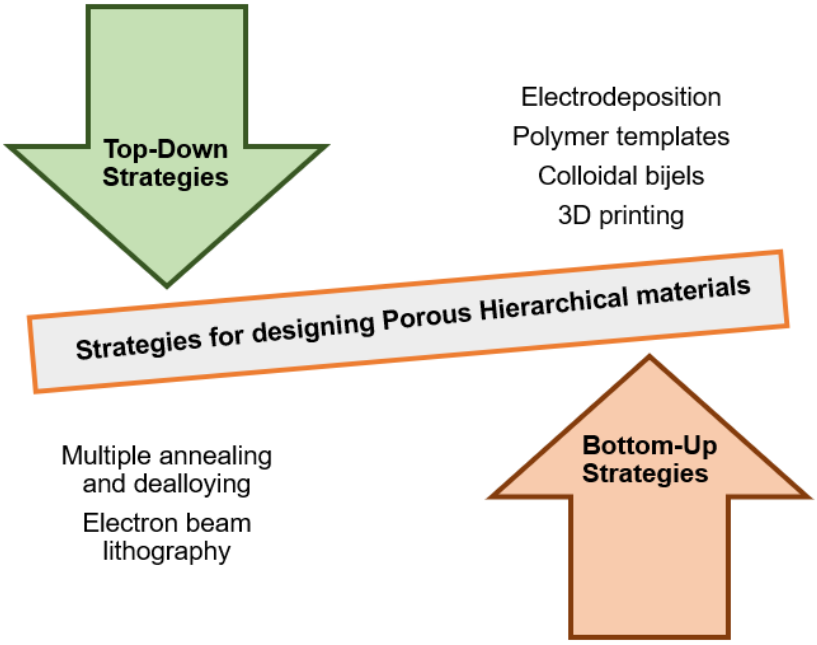

Figure 2. Diagram showing the common methodologies under the top-down and bottom-up approaches.

Ternary alloys have been used in the past to create bimodal ligament/pore size distributions. The hierarchical nanoporous-AuAg alloy has been fabricated by the selective removal of Al and redealloying of Ag from the AuAgAl source alloy combined with annealing operation. The presence of two order ligament/ pore size distributions around 100 and 10 nm in the material have shown high electrochemical sensing towards dopamine and uric acid [28]. Another such ternary alloy of AgAuPt has been electrochemically dealloyed under potential control in $HClO_4$ to generate hierarchical nested-network nanoporous

gold [29]. A two-step liquid metal dealloying to generate a hierarchical porous metal is another technique that came into use very recently. Hierarchically porous Fe-rich alloy with bimodal pore size distribution has been prepared using this technique for the first time. The precursor alloy (Fe-Cr-Mn-Ni) was first immersed in Mg melt, wherein Ni was leached out and the material formed has a coarsened porous structure. Subsequent immersion was done for a shorter time in a Bi melt, wherein Mn was leached out to generate a fine porous structure within the ligaments of the original structure giving rise to a hierarchical morphology [30].

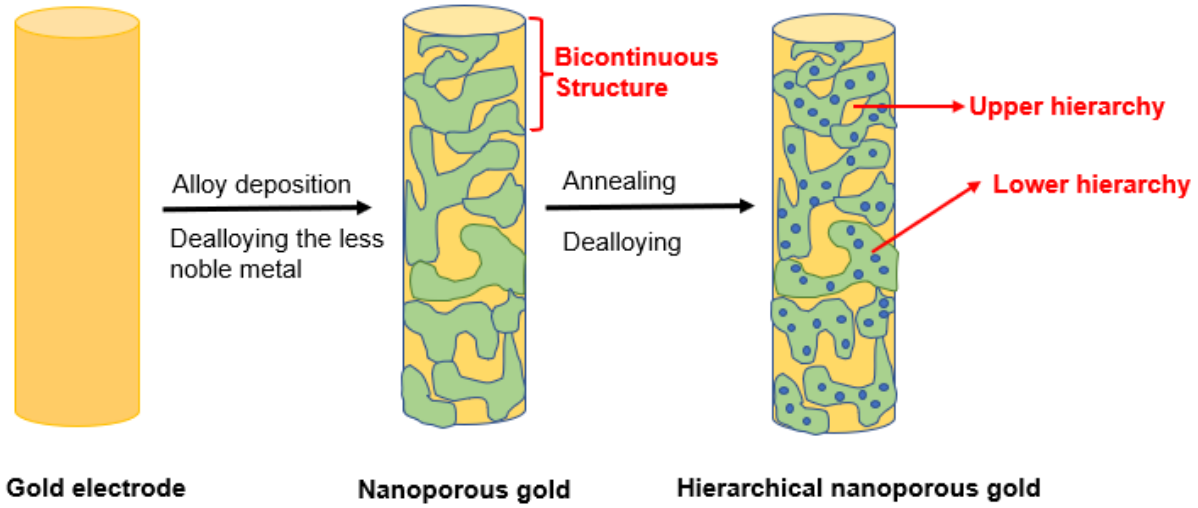

Figure 3. Depiction of the common route used to create upper and lower hierarchy in a material.

2.2. Electrochemical Approach

Electrodeposition is a powerful technique and a convenient tool to create nanostructures by controlling the growth rate via altering the deposition potential [31]. One such surfactant and template-free route to create hierarchical dendritic gold microstructures (HDGMs) with secondary and tertiary branches have been used in the past using constant potential electrolysis at −0.6 V in 0.1 M Na_2SO_4 and 30 mM $HAuCl_4$ serving as the electrolyte against indium tin oxide as the working electrode and platinum wire and saturated calomel electrode used as counter and reference electrode, respectively [32]. Another one-step electrochemical method to fabricate 3D hierarchical porous gold films (PGFs) was done using the methodology of the surface rebuilding of smooth gold substrates using square wave voltammetry. This is another template-free strategy with pure gold substrates involving repeated gold oxidation-reduction by square-wave potential pulse between 0.8 and −5.0 V at 50 Hz in NaOH solution at different times. The pulse potential applied at 0.8 V generates gold oxide accompanied by the weak release of oxygen gas. As the potential switches to −5 V, gold oxides reduce back to gold atoms forming clusters. The resulting morphologies are shown in Figure 4. Here, reduced gold atoms assemble under the influence of hydrogen bubbles. This is a green, convenient, and economical method used to build 3D micro/nanostructured PGFs, which exhibited high electrocatalytic activity towards the oxidation of ethanol, glucose, and ascorbic acid [33]. A novel hierarchical nanoporous gold film electrode has been fabricated by the multi-cyclic electrochemical co-alloying/dealloying process in $SnCl_2/ZnCl_2$/benzyl alcohol system. The process took place in a three-electrode cell consisting of a Zn plate as the auxiliary electrode, gold wire as working electrode, and Pt plate as a quasi-reference electrode. The multi-cyclic potential sweep was applied in the sequence of open circuit (−0.8 to 1.8 V) and the later cycles were from 1.8 to −0.8 V repeatedly. Primary results have shown that the hierarchical structure generated has excellent catalytic activity toward methanol oxidation, which is due to the special structure of the electrode providing more active sites for the adsorption of OH^- anions [34]. A facile two-step synthesis involving the combination of electrodepo-

sition with galvanic replacement has been used to develop cobalt oxide/Au hierarchically nanostructured electrodes for glucose sensing. Fluorine-doped tin-oxide-coated glass slide was modified using electrodeposition of $CoSO_4$ with H_3BO_3 as the buffering agent using cyclic voltammetry in the potential range of −0.2 to −1.2 V at 20 mV/s for 20 cycles. The modified strips were immersed in $HAuCl_4$ solution for 30 min resulting in the preparation of a hierarchically nanostructured material. The hierarchical design of the electrode has been exploited for the detection of glucose in human blood samples with a detection limit of 0.1 µM owing to the facile electron conductivity due to the large active surface area [35]. A benign route has been developed to fabricate NPG ribbons through electrochemical dealloying of melt-spun Al-Au alloy with 20–50 at.% Au in a 10 wt.% NaCl aqueous solution at the potential of 0.8–2.0 V. It was seen that the surface diffusion of Au atoms increases with increasing applied potential. Electrochemical dealloying in NaCl is interesting due to the self-acidifying effect involved in the formation process. It arises due to the dissolution and hydrolysis of Al^{3+}/Al assisted by the chloride ions in the electrolyte. The dissolution kinetics of Al at different potentials impact the dealloying process and hence the overall formation of the porous material [36].

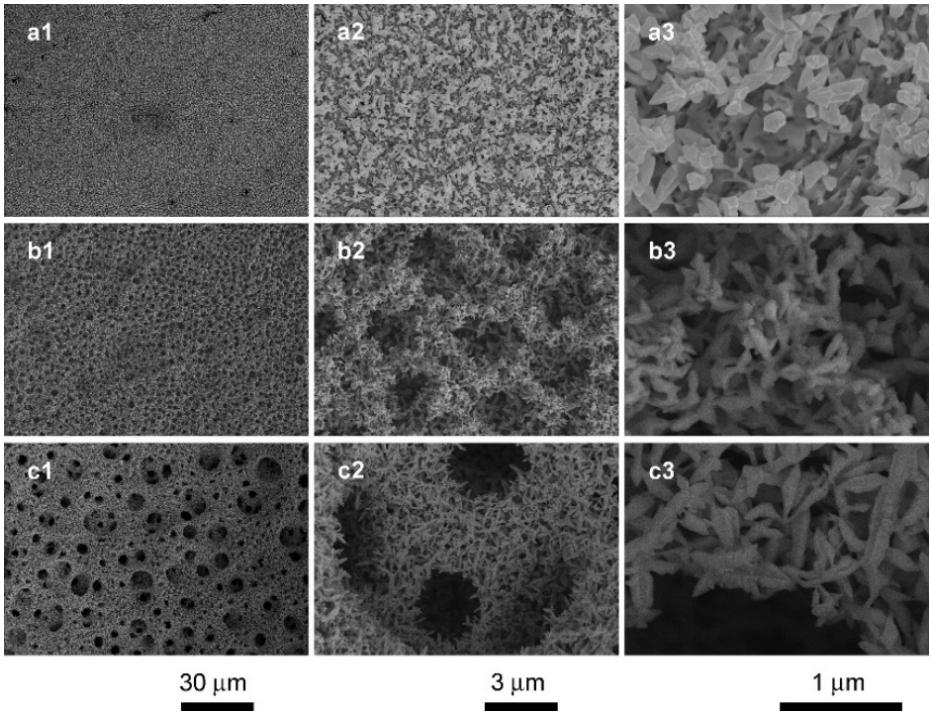

Figure 4. SEM images at different magnification scales for the PGF samples prepared using the technique of square-wave potential pulse in 2 M NaOH between the potential window of 0.8 and −5 V for different times: (**a1**–**a3**) 100 s, (**b1**–**b3**) 3000 s, and (**c1**–**c3**) 12,000 s (adapted with permission from [33], copyright 2009 American Chemical Society).

To generate structural hierarchy, nanoporous metals can be used as a coating on preexisting porous structures. Multimodal porosity is generated by sputtering or electrodeposition of a binary alloy on a 3D microporous template and then finally dealloying it to generate a nanoporous film [37]. Using this approach, an alloy film of Au-Sn has been galvanostatically electrodeposited on nickel foam in the alloy plating solution with a current density of 5 A dm^{-2} for 10 min. Selective etching of Sn was performed by immersing the sample into a 5 M NaOH and 1 M H_2O_2 solution for three days leading to the formation of 3D hierarchical porous NPG/Ni foam. The open and porous structure facilitates mass transport and charge transfer, which may hold great potential for its use in electrode material for electrocatalytic reduction of peroxide and other electrochemical reactions [38].

2.3. Synthetic and Natural Templates

Two approaches that can control the porosity within metals are dealloying and templating. Multimodal porous noble metals have been synthesized using a combination of techniques involving templating, slipcasting, and dealloying. Hierarchically porous gold monolith has been prepared using the dual approach of templating and dealloying on polystyrene (PS) beads working as the templates. Ag/Au PS core-shell particles were prepared using the electroless deposition approach with control over the sequence of metal deposition. The mole ratio of Au:Ag was adjusted during the plating process followed by casting the beads and heating them to remove the PS template. Hollow shells of Au/Ag alloy were placed in dilute nitric acid for dealloying [39]. Another route involving double-templating has also been used in the past to create highly ordered macro/mesoporous hierarchical metal architectures. It involves the electrodeposition of Au/Ag alloy within the void spaces of PS microspheres, which are closely packed within the micropores of a polycarbonate membrane. Dealloying and template dissolution gave rise to a highly regular 3D hierarchical gold structure with tunable morphology and porosity. The new double-templated electrodeposition approach is very attractive as the final material holds considerable promise for designing electrocatalytic surfaces for enhanced oxygen reduction reaction and hydrogen-peroxide detection [40]. Significant interest has been directed towards the fabrication of hierarchical templates with different shapes and sizes to generate bimodal macroporous gold electrodes with minimum diffusion restraints and increased surface area for chemical sensing, drug delivery, catalysis, and energy storage. In a recent study, amine (PS-NH_2, 80 or 10 nm diameter) and carboxyl (PS-COOH, 450 or 1500 nm diameter)-modified PS latex spheres were strategically coupled together based on the electrostatic force as seen in Figure 5. Each negatively charged PS-COOH was surrounded by positively charged PS-NH_2 spheres. The colloidal solution was made with the addition of EDC/NHS in the above mixture dissolved in buffer giving rise to the raspberry-like template. The hierarchical porous gold electrode was fabricated by electrodeposition (−0.65 V for 10 min) of gold around the colloidal crystal and finally removing the templating via soaking in chloroform. It is envisioned that the structure generated using this approach will be useful as platforms for chemical sensing, chromatography, and catalysis [41]. Liquid crystalline block copolymers (LCBCs) have gained great potential due to their inherent property of microphase separation and the presence of hierarchically assembled structures of liquid-crystalline polymers. Various micro/nano-patterned structures have been fabricated using light manipulation of photoresponsive LCBCs. LCBCs are utilized in the fields of optics, adhesives, and elastomers. Manipulation of such nanostructures may find its application as the future engineering plastics for functional materials [42]. Hierarchical nanostructures have been prepared using oblique angle deposition of Au with a patterned diblock copolymer template with varying molecular weights. Polystyrene-block-poly (methyl methacrylate) (PS-b-PMMA) films with different block ratios were prepared on a thoroughly cleaned silicon substrate. It was seen that the selective wetting behavior of Au affected the growth kinetics on the substrate giving rise to a hierarchical material that is of great interest for applications in organic photovoltaics and electronics [43].

Hierarchically porous gold structures have also been prepared by taking advantage of the unique structures, morphologies, composition, and spatial organization of biological materials. The bio-templated strategy is a unique way of creating nanostructures in an ordered array. Multiple hierarchies have been created using fine structures present in grapefruit exocarp [44], pollen and Lepidopteran wings [45], and butterfly wing scales [46]. One such novel route utilized calcium carbonate skeletal plates of sea urchins as the template creating pore diameters of 15 μm in the final structure. The material with a hierarchical structure was prepared by deposition of gold paint, wherein the paint was absorbed into the skeletal plates via capillary action. Gold-coated plates were then dissolved in acid solution to dissolve calcium carbonate followed by heating it using a hot air gun to burn off the organic matter left in the paint. The dipping/heating cycle was repeated ten times and was annealed finally at 400 °C for 36 h. The ordered architecture of the material

with pore dimensions comparable to optical wavelength could display unique optical properties [47]. Hierarchical porous gold networks (HPANs) have recently been prepared using a bio-inspired synthesis method in which the natural egg-shell membrane (ESM) was introduced as a template. As a natural biological material, ESM possesses an elaborate hierarchical network that cannot be imitated by artificial technology. The fabrication process involved immersing ESM into 1 mM $HAuCl_4$ for 5 min for the absorption of $[AuCl_4]^-$ ions on the macroporous network of ESM. Subsequently, the thoroughly washed membrane was immersed in NaOH for 12 h to reduce gold ions to metallic gold. After rinsing and drying the membrane was calcined at 600 °C for 3 h to produce the 3D HPANs with an unblocked macroporous network and an interwoven Au fiber structure. The material showed high catalytic activity towards glucose oxidization along with excellent stability and anti-interference performance [48].

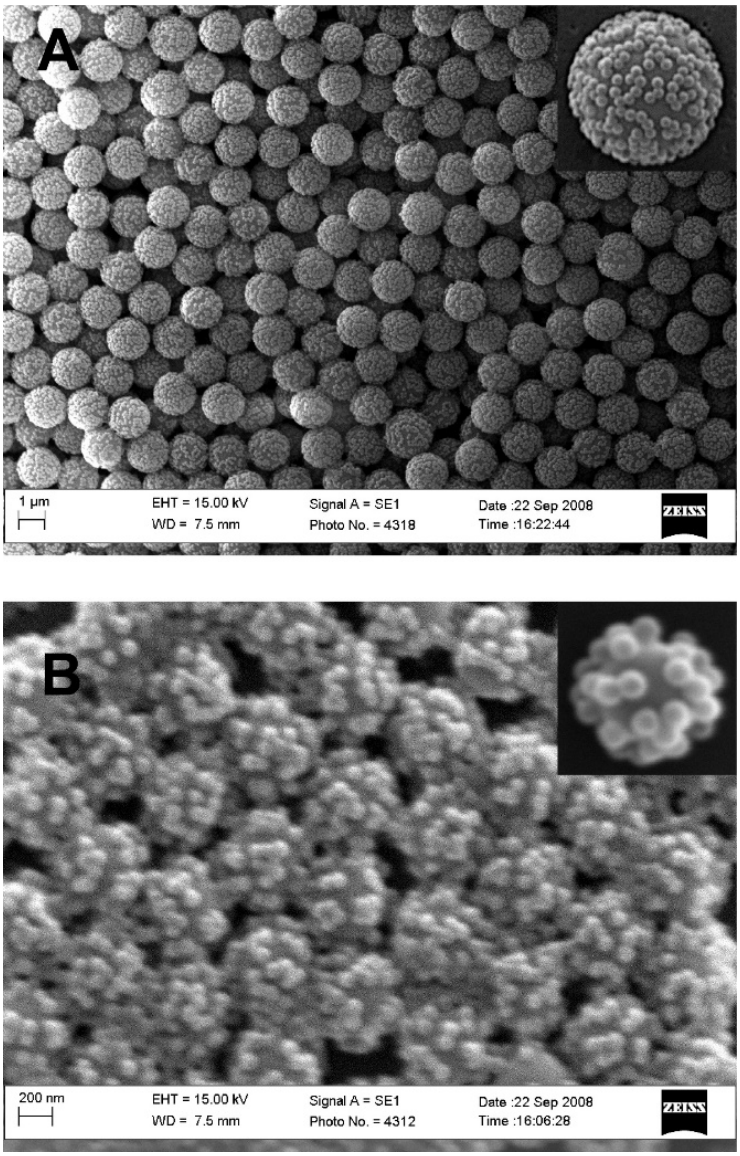

Figure 5. SEM images showing raspberry-like hierarchical templates prepared via coupling PS-COOH spheres with PH-NH_2. Templates with (**A**) 1500/110 nm and (**B**) 450/80 nm core/satellite were prepared (reproduced with permission from [41], copyright 2010 American Chemical Society).

A relatively new class of soft materials known as bicontinuous interfacially jammed emulsion gels or bijels have been used in material synthesis platforms to fabricate next-

generation gold electrodes. Bijels are complex fluids in which interpenetrating, continuous domains of two immiscible liquids are maintained by the colloidal particles that sequester to the fluid interface [49]. A novel synthetic route to fabricate bicontinuous hierarchical NPG monolith using colloidal bijel templates and a combination of nanocasting and chemical dealloying has been introduced very recently. The experimental design is simple without the use of sophisticated lab equipment. In this, bijels of 2,6-lutidine/water stabilized by colloidal silica microspheres were prepared. Further selective polymerization of lutidine-rich phase and draining of water-rich phase gave rise to continuous macropores along with textural pores of submicrometer scale within the cross-linked polymer phase. Polymerized bijels were then impregnated with silver and gold salt solutions and annealed to decompose the precursor, remove the polymer template, and create a homogeneous alloy system. The alloyed monolith created can be dealloyed traditionally using nitric acid to generate a hierarchical structure. It is believed that the use of bijels for creating hierarchically porous metal electrodes can offer enhanced performance for their use in supercapacitors, rechargeable batteries, and catalysis [50]. In contrast to the conventional particle-stabilized emulsions, bijels stabilized with catalytic nanoparticles enable the continuous mass transfer of reagents aiding in interfacial catalysis. Despite the advantages mentioned, bijels prepared by thermal quenching are limited to specific liquid pairs, formed in batch processes, and exhibit poor thermal stability. Therefore, asymmetric, and hierarchical bijels are produced continuously with a new technique based on solvent transfer-induced phase separation (STRIPS). This scalable approach requires rapid injection of a homogeneous mixture of three liquids in a continuous phase. Phase separation is induced by extracting solvent from the ternary mixture and the stabilization is provided by interfacial attachment of nanoparticles. The fast quenching of the ternary mixture by STRIPS allows the formation of hierarchical microstructures with submicron features [51].

2.4. Additive Manufacturing Techniques

Research interest in the field of additive manufacturing (AM) is growing rapidly due to the flexibility in complex and custom design that the technique offers. In contrast to the traditional subtractive fabrication strategies, AM builds 3D structures layer by layer, utilizing the necessary amount of material and scaffolding. Introduced by Charles Hull in 1986, the process of stereolithography helped to enhance the area of material fabrication [52]. Additive manufacturing is a collection of techniques for the fabrication of 3D materials by computer-controlled sequential release of energy and/or material to specified points in space. Currently, AM techniques for metals are paving the way to design complex geometries with tailored mechanical properties [53]. An exciting and rich space in material design chemistry lies in the current advances in the programmable synthesis of nanostructured materials. Among the various non-biological bottom-up fabrication methods, 3D printing is gaining much attention [54]. Recently, 3D printed hierarchical gold samples were prepared involving a multistep procedure of printing, annealing, and dealloying. In this, a viscous paste-like ink of Au: Ag (30:70 atomic ratio) was prepared by mixing silver and gold clay composed of organic binder into an organic solvent for 1 min in a centrifugal mixer. For printing, the ink was loaded in a syringe barrel affixed with a micronozzle, and 3D architectures were created under computer numerical control. To homogenize the as-printed structures, the assembly was annealed at 850 °C for 12 h in air. Thermal decomposition of the polymer binder created microscale porosity, whereas nanoscale pores were created by dealloying Ag by placing the annealed sample in concentrated nitric acid [11]. Another facile and cost-efficient route to fabricate hierarchical porous structures is through a photoresponsive ligand on an inorganic core (PLIC) scheme. This technique has opened a broad opportunity space in digital light processing and colloidal nanoscale materials. Also, this technique has the advantage of using light to spatially program the building blocks connection and generating complex geometries (Figure 6), which are not possible with the porous materials synthesized via solvothermal processes due to their weak mechanical strength. In the latest study, researchers formulated

the PLIC ink by dissolving zirconium isopropoxide in an excess of methacrylic acid, $Zr_6O_4(OH)_4$-MAA in the proper solvent (propylene glycol monomethyl ether acetate, PGMEA) with a UV-free radical initiator (diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide) [55]. A newly developed technique of 3D freeze assembling printing (3DFAP) by integrating drop on demand (DOD) inkjet printing and freeze casting is attracting interest amongst the research community. The procedure involved the dissolution of silver nanowires in polyvinyl alcohol to form a suspension. The Ag nanowire ink prepared was then loaded into syringe barrels attached by a drop-on-demand nozzle whose jetting and motion was computer programmable. The 3D-printed lattice was then transferred to a cryogenic environment. The hierarchical assembly was formed by subsequent sublimation for 48 h. This technique enables tuning of macro and microstructure by programmable 3D printing and freeze-casting. This technique successfully printed hierarchical metallic aerogels, enabling control over the density, electrical, and mechanical properties of the metal aerogel. These superior properties have paved their way in the fields of aerospace, biomedicine, defense, and smart structures [56].

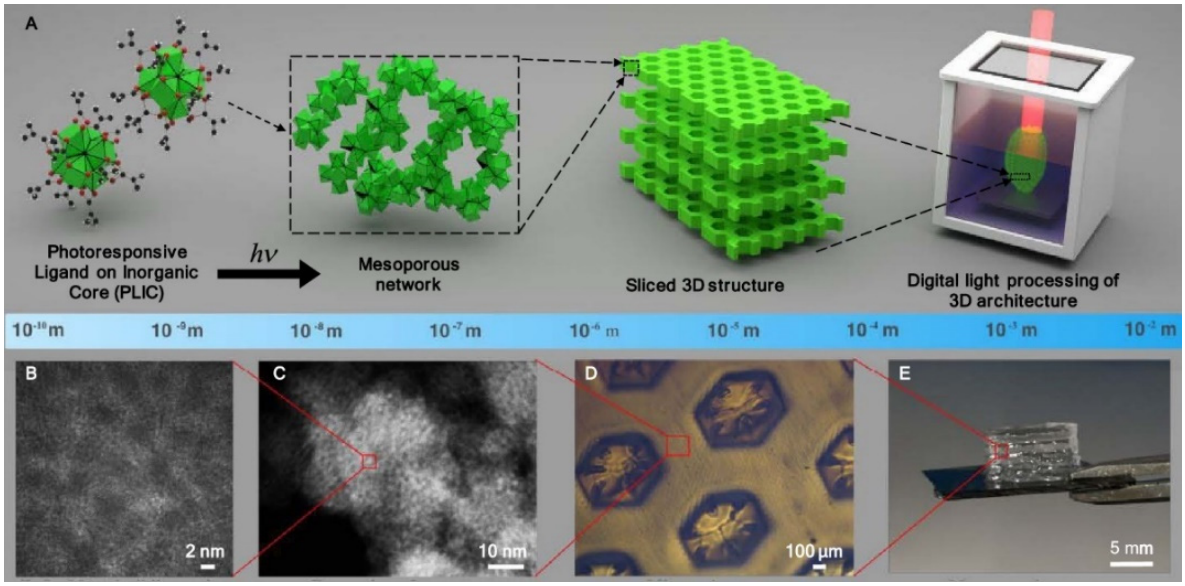

Figure 6. (**A**) Schematic representation of the printing process using photoresponsive ligand on the inorganic core (PLIC) as the building units and structured by a series of 2D UV images in the 3D printer. (**B**) Image showing zirconium oxide cluster with MAA surface ligands. (**C**) Pores were seen after the building blocks were connected. (**D**) Printed structure showing shape control for each layer. (**E**) Layer–by–layer stacking was seen in the structure in millimeter-scale (reproduced with permission from [55], copyright 2019 American Chemical Society).

3D hierarchically porous gold nanostructures with interconnected macroporous channels (200–300 nm) and nanopores of ~10 nm have been recently fabricated using the technique of Proximity-field nanoPatterning (PnP). The hierarchical structure produced using this optical lithography and electroplating techniques has been seen to significantly enhance electrocatalytic performance in CO_2 reduction. The fabrication process involved the deposition of a metal conductive layer consisting of Cr (5 nm) and Au (200 nm) on the SiO_2/Si wafer using an e-beam evaporator. 3D epoxy templates were fabricated using a photoresist of SU-8 with a thickness of 17 µm on the substrate using a spin coater. Resist-coated substrate undergoes a conformal phase mask containing square arrays with a cylindrical surface grating. Fabricated substrates treated by oxygen plasma were electroplated using Au-Ag alloy solution and finally soaked in nitric acid to remove the template and generate a 3D hierarchical structural design. The structural design is found to be useful for different energy applications, such as batteries and fuel cells [57].

Recently, a novel approach to fabricate sub-micron NPG disks and microscale NPG patterns by the combination of top-down lithography and bottom-up atomic dealloying has been used. The fabrication process involved the deposition of an adhesion layer consisting of 5 nm of Cr and 100 nm Au onto a silicon surface, followed by depositing a 90 nm alloy layer and a 20 nm Cr top layer. Patterning was done on poly (methyl methacrylate) (PMMA), which was spun onto the Cr top layer by exposing it to the SEM equipped with a nanopattern generation system. Pre-patterning of thin alloy films before time-controlled dealloying in nitric acid resulted in a hierarchical NPG structure. In situ patterning was achieved by restricting the reaction to only progress in-plane. The hierarchical NPG dot arrays generated via this methodology are effective for SERS and metal-enhanced fluorescence (MEF) techniques for highly sensitive molecular sensing [58].

2.5. Kirkendall Effect: Self Templated Methodology

The most widely used approaches to fabricate nanoporous hierarchical gold structures include dealloying, templating, and electrochemical synthesis. There is still scope to scale up the production of the fabricated material and eliminate the post-treatment steps leading to structural deformation, with more efficient and innovative procedures [59,60]. To overcome these limitations, a unique self-templated synthetic strategy based on the metallurgical concept of the Kirkendall effect has recently emerged, which explains the formation of voids at the interface of two metals due to their different interdiffusion rates. In nanochemistry, this effect is explained by the outward elemental diffusion leading to material flux across the interface and the formation of a series of void structures affected by reaction temperature and time [61]. The Kirkendall effect was first introduced in 1947 to generate pores in alloys. However, the methodology was not accepted by many due to the impairment of mechanical properties of the alloy [62,63]. Recently, synthesis of Kirkendall effect-based hollow 3D structures was achieved. In this work, investigations to use this effect systematically in the creation of 3D multilevel porous metal catalysts with tunable micropores ranging from 1.9–8.3 μm have been done. Synthesis was performed in a three-step strategy starting with controlled electrodeposition of Cu thin film at −1.8 V on 3D nickel foams using $CuSO_4$ and boracic acid as the electrolyte. The Ni-Cu composite foams generated were further annealed at 1000–1100 °C and were finally electrochemically etched at 0.6 V, giving rise to dense arrays of micropores uniformly distributed on the microstruts of the foam. An array of applications in energy storage and conversion devices can make use of the unique properties of such materials [64]. Chemists have exploited the Kirkendall effect to prepare nanomaterials of unusual morphologies. There are several interesting reports regarding the fabrication of hierarchical porous transition metal oxide films utilizing the Kirkendall effect. One such report explained the hierarchical architecture in porous iron oxide films through a hydrothermal reaction between an iron substrate and iodine solution. Different morphologies were seen in different solvents owing to different reaction-diffusion rates of iodine with iron [65]. A series of novel hierarchical nanoporous microstructures have been synthesized wherein the Kirkendall effect is believed to facilitate the formation of pores.

Different fabrication techniques offer unique structural features in the final porous material, and therefore, a comparison of the above-mentioned techniques is summarized in Table 1.

Table 1. Fabrication methods to generate hierarchical nanoporous gold are listed along with the advantages offered by each technique.

Method of Fabrication	Structural Features of Hierarchical NPG Created	Application of the Material	Advantages of the Methodology	Drawbacks	Reference
Multiple annealing and dealloying	Two hierarchy levels in a complimentary and geometrically similar pore channel structure with ~100 nm–2 μm upper hierarchy channels and ~5–25 nm lower hierarchy channels	Electrochemically or chemically driven actuators, varistors, microfluidic flow control, sensing, and catalysis	Bulk samples created with enhanced signal transport into the pore space by more than 2 orders of magnitude along with large specific surface area. Trimodal and higher-order architectures are possible by repeated cycles Independent tunability of pore sizes and topology	Annealing at an elevated temperature might result in the collapsing of ligaments starting at the grain boundaries on the surface forming cracks and making the material brittle.	[22,25,27,29]
Electrochemical approach	Morphological features vary according to the electrodeposition potential, time, and concentration of reactants.	Fuel cells, chemical sensors, biomedicine, surface-enhance Raman scattering (SERS), and self-cleaning functions.	Tailoring of pore size, thickness, and creating unique surface morphologies are possible by systematically changing the alloy composition, control on the deposition potential, and coarsening time	In electrodeposition, electrochemical species have a tendency towards non-conformal growth on non-planar surfaces	[31,32,37]
Templated synthesis	Interconnected porosity across widely separated length scales based on the type of template used	Supercapacitors, rechargeable batteries, renewable energy systems, and catalysis	Control pore sizes ranging from nanometer to the micron scale with more control over the structural design	Post-treatment required to get rid of the template, limited material flexibility	[39,50]
Additive manufacturing-3D printing and dealloying	Three distinct structural length scales ranging from a digitally controlled macroporous network of 10 to 1000 μm to nanoscale pore/ligament morphology within 30 to 500 nm	3D chemical reactors, advanced catalytic systems, flow batteries, and flow-through electrodes	Complex, multiscale architectures can be created with the combination of structural, mechanical, chemical, and thermal properties. A dramatic increase in electric-field-driven ion transport (up to 10×) and pressure-driven mass transport (up to 10^5×). Minimizing waste, cost-effective, and flexible design	Post-processing, design inaccuracies, and restricted build size	[11]
Self-templated approach	Pore size distribution controlled readily from micrometers to nanometers	Catalysis, photodetectors, electrochromic devices, sensors, and separation	Hierarchical hollow/porous metal oxides can be grown on metal surfaces without using any templates	Application of the Kirkendall effect at the micrometer scale is a difficult technical problem due to the slow diffusion	[63,65]

3. Conclusions and Outlook

Recent progress made in the fabrication of hierarchical nanoporous gold and other metals has been reviewed. Every synthetic method was unique in creating a structural hierarchy with different pore dimensions and structures. However, the designing of porous materials with controllable ordered pore structures, crystalline framework, and structural stability still needs to be resolved for their practical applications. More progress has been made in the templated synthesis strategies or in employing a porogen concept to create hierarchical metals and composites [66]. They are most popular due to their flexibility and ability to precisely control the structural features via directing reactions to a certain region. It is still a great challenge to explore a simple, green, and low-cost route to fabricate hierarchical gold nanoporous structures with a "clean" surface. The issue may be addressed in the future by taking inspiration from nature for the development of newer and greener strategies. Green design and technology can mitigate negative impacts on the environment. Promising green materials including plants, fungi, microorganisms, enzymes, and biopolymers could be used in the future for creating hierarchy in porous metals. Another interesting research direction involves the use of functionalized ionic liquids in aqueous solutions for the controlled synthesis of various gold hierarchical architectures.

The development of 3D printing technology in medicine is proceeding very rapidly. Additionally, in the era of the digital world, artificial intelligence is emerging as a game-changer in healthcare systems. To gain benefits in the mainstream clinical practice, 3D printing harnessing modern technology of AI could potentially increase the performance by reducing the risk of error, ensuring stringent quality control, reducing material wastage, and giving the benefit of automated production [67,68]. Recently, AI has been utilized in designing novel materials with complex architectures and unique material properties such as elasticity, plasticity, and wear performance. The key issues lie in the selection of proper methodology and the positioning of the functional elements in the resulting 3D structure. However, with the integration of AI and material design, the study of bioinspired hierarchical materials has been done by casting the natural process of evolution into a computational framework and thereby accelerating the material property prediction process [10,69]. In the near future, it will be interesting to link the field of artificial intelligence with 3D printing technology to discover new microstructural patterns leading to advanced materials in a vast design space.

It is reasonable to expect that further modifications in the synthesis scheme to control the individual porosities and intricate morphologies may open a new arena for these materials. It is expected that this work will provide useful ideas for the future synthesis of hierarchical nanoporous gold and other metals to be used in electrochemical applications.

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