Noble metals, despite their expensiveness, display irreplaceable roles in widespread fields. To acquire novel physicochemical properties and boost the performance-to-price ratio for practical applications, one core direction is to engineer noble metals into nanostructured porous networks. Noble metal foams (NMFs), featuring self-supported, 3D interconnected networks structured from noble-metal-based building blocks, have drawn tremendous attention in the last two decades. Inheriting structural traits of foams and physicochemical properties of noble metals, NMFs showcase a variety of interesting properties and impressive prospect in diverse fields, including electrocatalysis, heterogeneous catalysis, surface-enhanced Raman scattering, sensing and actuation, etc. A number of NMFs have been created and versatile synthetic approaches have been developed. However, because of the innate limitation of specific methods and the insufficient understanding of formation mechanisms, flexible manipulation of compositions, structures, and corresponding properties of NMFs are still challenging. Thus, the correlations between composition/structure and properties are seldom established, retarding material design/optimization for specific applications. This review is devoted to a comprehensive introduction of NMFs ranging from synthesis to applications, with an emphasis on electrocatalysis. Challenges and opportunities are also included to guide possible research directions in this field and promote the interest of interdisciplinary scientists.

1. Introduction

Noble metals are a group of oxidation-resistant transition metals, which are usually considered to consist of gold (Au), silver (Ag), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). They are quite expensive (≈15 USD per ounce for Ag; 200–400 USD per ounce for Ru, Os; 800–1500 USD per ounce for Pt, Au, Pd, Ir; ≈3000 USD per ounce for rhodium. Data are acquired on May 12, 2019[1,2] owing to their low mass abundance in the earth’s crust (0.001–2 ppm)[2]. Despite their inertness in bulk, noble metals become extremely active when the feature size reaches the nanoscale.[3] With the onset and advance of nanotechnology, they have exhibited irreplaceable functions in widespread fields, including electrocatalysis, heterogeneous catalysis, plasmonics, biology, etc.[4–6] Especially, exceptional performance is found in quite a few energy- and environment-related heterocatalytic and electrocatalytic reactions. Thus, many noble-metal-based materials, in spite of their high cost, have been commercialized in market, such as for catalysis and astronautics.

However, several issues exist in the development and practical use of noble metal nanomaterials. First, the melting point of noble metals considerably decreases with reduced feature size, which can incur and aggravate the aggregation and performance decline of noble metal nanoparticles (NPs) during storage or application. Second, certain strategies for suppressing aggregation (e.g., introduction of ligands or supporting substrates) work well in some cases, while the existence of additional components can affect the long-term stability and the unbiased evaluation of the true performance of noble metals. Third, to improve the performance-to-price ratio, both the increase of the utilization efficiency of noble metals and the search for their replacements[7,8] need to be explored. Because of certain unique physicochemical properties of noble metals which cannot be realized by other materials (e.g., electronic structures and plasmonic effects), under certain circumstances, improving the utilization efficiency and fully releasing the innate potential of noble metals are particularly favorable. Bearing the above concerns in mind, the engineering of noble metals into self-supported, nanostructured solid foams, i.e., noble metal foams (NMFs), serves as a promising solution.
that not only provides a structurally/chemically stable nanostructured network that considerably suppresses NPs aggregation and increases the utilization efficiency, but also expands the application space of noble metals (Figure 1a). In addition, because of negligible foreign components, they also offer opportunities to study the intrinsic electrocatalytic properties of nanosized noble metals.

Before further discussion, it is necessary to clarify certain terms and definitions. According to the International Union of Pure and Applied Chemistry (IUPAC), a foam is a dispersion in which a large proportion of gas by volume in the form of gas bubbles, is dispersed in a liquid, solid or gel. Hence, foams can be either open-cell-structured or close-cell-structured porous materials in either wet or dry state, regardless of the preparation methods and physical properties. In this manuscript, concerning industrial relevance and research mainstream, the scope of NMFs will be restricted to 3D noble-metal-based, self-supported, open-cell-structured solid foams. Notably, the majority of NMFs are fabricated via a sol–gel process followed by a special drying process (critical-point drying or freeze-drying). On these occasions, the term “noble metal aerogels (NMAs)” is adopted to comply with the definition of aerogels, where a sol–gel process is involved during material fabrication. It should be noted that in this context, NMAs are a kind of NMFs, both of which share similar structures and differ mainly in fabrication routes.

Inheriting the features of foams (e.g., 3D interconnected networks, high porosity, large specific surface areas (SSAs), and monolithic architecture) and the unique physicochemical properties of noble metals (e.g., high electrical/thermal conductivity, catalytic activities, and special plasmonic properties), NMFs showcase a variety of interesting properties and impressive prospects in a wide spectrum of fields, including electrocatalysis, heterogeneous catalysis, surface-enhanced Raman scattering (SERS), sensing, etc. The history of NMFs can be dated back to about half a century ago, where chemical or electrochemical dealloying approaches were applied to fabricate the porous gold foam from an alloy film. However, NMFs have drawn tremendously growing attention only since this century, when a widely accepted model for the morphology evolution during dealloying process was proposed by Erlebacher et al. Following this work, a vast number of NMFs have been reported and versatile strategies, including templating and combustion synthesis, have been developed. In the year 2009, our group pioneered introducing the sol–gel process in NMF fabrication, where an array of noble metal foams, to be precise, macroscopic self-supported noble metal aerogels including Au, Ag, Pt, Au–Ag, and Ag–Pt have been obtained, most of which displayed 3D

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**Figure 1.** a) The schematic structure of noble metal foams and their chemical compositions. b) The number of publication about noble metal foams in last two decades. The data were acquired from Web of Science on April 16th, 2019.
networks constructed by fused nanowires (NWs). Because of the mild reaction conditions and enormous potential in versatile nanoscale modulation, the sol–gel method has quickly become the dominating strategy for NMF fabrication, stimulating extensive investigation of NMFs for diverse applications.

So far, the most widely studied application of NMFs is electrocatalysis, which is largely related to the energy conversion and storage process that are profound for sustainable development of society. Combining the chemical nature of noble metals and the structural features of foams, NMFs provide an ideal platform for devising superior catalysts for a wealth of electrocatalytic reactions, such as alcohol oxidation reaction (AOR), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and carbon dioxide reduction reaction (CO2-RR), which are crucial for energy-related processes including fuel cells, lithium–air batteries, and the production of chemical fuels. Despite substantial efforts in searching for noble-metal-free and even metal-free electrocatalysts, NMFs play irreplaceable roles, because they not only inherit the unparalleled stability and activity of noble metals in acid medium, excelling most noble-metal-free catalysts, but also deliver substantially improved performance compared to unsupported or carbon-supported noble metals.[21] In addition to electrocatalysis, NMFs have also been characterized as outstanding candidates for heterogeneous catalysis, SERS substrates, sensors, self-propulsion devices, etc.[4,22–24]

To optimize the performance of NMFs for specific applications, a key point is to explore the guideline for material design by establishing the correlations between composition/structure and property/performance. In this regard, the development of effective fabrication strategies capable of flexibly tailoring composition/structure of materials is of utmost importance. Controlled engineering of noble metal nanocrystals with tailored size, dimensions, shapes, facets, and compositions has been intensively studied and realized for years.[25] However, the transformation of these merits to their macroscopic counterparts, i.e., nanostructured NMFs, is highly challenging. In fact, most existing synthetic approaches for NMFs only show certain modulation ability and always fall short in fine structure manipulation down to nanoscale. Even for the most promising sol–gel method, the ambiguous gelation mechanism originating from a complicated reaction environment (involving reductants, ligands, metal precursors, initiators, etc.) strongly challenges NMF design and optimization. Therefore, although a library of high-performance NMFs have been reported, clear guidelines for on-target design and optimization of NMFs for specific applications are rarely unveiled, which largely retards their development for practical use.

In light of the vast unexplored potential of NMFs, in recent years, an increasing number of studies arose and multidisciplinary researchers, including chemists, physicists, biologists, and material scientists, became involved in this field (Figure 1b). Several excellent review articles containing certain introduction to NMFs have been published previously,[19,26–29] and the development of NMFs and NMAs on certain aspects is presented in a few focused review articles.[31] However, a comprehensive overview of state-of-the-art progress of NMFs is missing, especially concerning the synthetic strategies and (electro)catalytic applications. Therefore, this review devotes to providing a systematic introduction of NMFs, discussing as-developed synthetic methods as well as highlighting state-of-the-art applications, including diverse important electrocatalytic reactions and beyond. Specifically, the manuscript begins with an overview of essential characterization techniques employed for NMFs, followed by their fabrication strategies and corresponding formation mechanisms. After a comprehensive showcase of the application fields with the emphasis on electrocatalysis, the challenges and opportunities of NMFs are concluded to direct future research. Because of the predominant advantages and studies of NMAs overwhelming other NMFs, a special attention will be paid on the former ones throughout the manuscript.

2. Characterization

NMFs are 3D self-supported, highly porous materials structured from noble metals. To gain a comprehensive understanding of NMFs, it is necessary to probe them from different aspects. This section aims to shed light on frequently used techniques for characterizing the fundamental physicochemical properties and formation process of NMFs.

2.1. Density, Pore Structure, and Surface Area

For self-supported light materials, the apparent density ($\rho_a$) is an important parameter to evaluate their potential application performance, such as the capacity of oil uptake for water remediation.[31,32] In addition, it can be used to estimate the porosity ($\phi$) of materials from all-sized pores by the following equation[31,33]

$$\phi = (1 - \rho_a / \rho_b) \times 100\%$$  

(1)

where $\rho_a$ represents the density of the bulk material constituting the foam. The bulk material density $\rho_b$ (g cm$^{-3}$) is usually known from the reference (19.30 for Au, 10.49 for Ag, 12.45 for Ru, 12.41 for Rh, 12.02 for Pd, 22.61 for Os, 22.65 for Ir, and 21.09 for Pt),[34] while $\rho_b$ can be calculated by dividing the NMF mass by its volume (1.3–773 mg cm$^{-3}$).[35] For NMAs, their extreme fragileness often poses difficulties in obtaining a regular shape, resulting in only a rough estimation of volumes and thus the corresponding densities. It is worth mentioning that certain work used tapped-like density to characterize $\rho_a$, where the volume of the aerogel is determined by inserting aerogel pieces into regular-shaped vials.[37] However, since significant unoccupied spaces could be generated due to imperfect stacking of those pieces, the volume can be largely overestimated. Thus far, the density estimation needs special care and is more convincing when measuring a monolithic aerogel with a relatively regular shape.

Attributing to their nanosized structure with ample interconnected pores, NMFs usually feature hierarchically porous structures and large specific surface areas, which are commonly characterized by the nitrogen adsorption test. By using nitrogen molecules as probes and measuring pressure changes during their adsorption/desorption on foams, adsorption isotherms will be obtained and abundant information, including SSAs, pore...
size distribution (PSD), and pore volumes, can be derived on the basis of various models. Generally, with dominant mesopores in NMFs, the Brunauer–Emmett–Teller (BET) method, which complies with a multilayer gas adsorption model, is prone to be adopted, where the SSA is commonly obtained by fitting adsorption data in a relative pressure range \( p/p_0 \) of 0.1 to 0.3 (\( p_0 \) denotes the saturated vapor pressure of the probe molecules). For certain low-SSA NMFs,\(^{[24]}\) krypton molecules are used as probes, due to their lower saturation pressure (~2.63 Torr for supercooled liquid krypton at 77K) compared to that of nitrogen molecules (~760 Torr at 77K), thus allowing to acquire a much more accurate result ascribed to a large relative pressure change with a small amount of gas adsorption/desorption. Depending on composition and structure, SSAs ranging from 0.1 to 269 m\(^2\) g\(^{-1}\) have been reported for NMFs.\(^{[16,38]}\) Since significantly large atomic weight of noble metals lead to quite low mass-normalized SSAs compared to that of other materials like silica aerogels and nanocarbon foams, SSAs normalized by molar quantity have also been adopted, which are typically located in the range between 100 to 20 000 m\(^2\) mol\(^{-1}\). For example, a mass-normalized SSA of 100 m\(^2\) g\(^{-1}\) converts to a molar quantity normalized SSA for a Pd aerogel of about 1.1 × 10\(^4\) and for a carbon aerogel of about 1.2 × 10\(^3\) m\(^2\) mol\(^{-1}\), respectively. However, to directly compare with the values for other materials, the report of mass-normalized SSAs is more preferred.

Regarding PSD, density functional theory (DFT) related models depict more accurate distribution profiles of micro- and mesopores than that of the Barrett–Joyner–Halenda (BJH) model.\(^{[39,40]}\) In general, the former models are more suitable for describing pore structures of NMFs, since the information obtained by them is closely related to material performance for catalysis and other applications. The pore volume, which is normalized by mass, is usually calculated by either the BJH model or the single-point pore volume at \( p/p_0 \) of 0.98 or 0.99, which corresponds to the total volume of measured pores (these pores are usually with the size less than 200 nm). For the volume from all-size pores \( V_{\text{tot}} \), it can be calculated by

\[
V_{\text{tot}} = \frac{1}{\rho_s} - \frac{1}{\rho_a}
\]

\( V_{\text{tot}} \) is usually much larger than the value obtained by the nitrogen adsorption test, because larger pores that are not included in gas adsorption calculations can considerably contribute to the pore volume. However, in most cases, information given by the nitrogen adsorption test is sufficient enough to evaluate the properties and performance of NMFs, because usually micropores and mesopores govern the SSA and most concerned physicochemical processes (e.g., in electrocatalysis).

### 2.2. Composition

Composition analysis can provide information about not only the proportion of different noble metals in alloy NMFs, but also the purity of products. For a rough analysis, thermogravimetric analysis (TGA) is used to quantify the amount of non-metal impurities (e.g., ligands, initiators, reductants), and infrared (IR) spectroscopy is adopted to analyze impurities with polar chemical bonds (e.g., ligands with C=H, O=H, and N=H bonds).\(^{[24]}\)

To accurately determine the element composition, inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP mass spectroscopy (ICP-MS) are powerful tools. They can provide information of almost all metal elements and certain nonmetal elements with a detection limit down to ppb level. X-ray photoelectron spectroscopy (XPS) is another prevalently used technique for element analysis for NMFs.\(^{[28]}\) With a detection limit of ~0.1 at%, it is capable of giving surface information about chemical composition and chemical environment of all elements except for hydrogen and helium. Notably, results from the aforementioned techniques can vary considerably for NMFs with special architectures, e.g., core–shell structures, where the content of the shell element could be much higher once determined by a surface analysis technique (e.g., XPS) than that determined by a bulk analysis technique (e.g., ICP-OES and ICP-MS).\(^{[24]}\) In comparison with the above techniques, X-ray absorption near-edge structure (XANES) analysis can afford in situ quantitative characterization of electronic structure and chemical environment changes during either synthesis or application scenarios, while it is rarely used for NMFs.

Combining analytical methods (e.g., energy-dispersive X-ray spectroscopy (EDXS) and electron energy-loss spectroscopy (EELS)) with imaging techniques (e.g., scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) bring the additional advantage to investigate the spatially resolved chemical composition from micrometer down to nanometer scale. Especially, spectrum imaging analysis based on EDXS or EELS in scanning transmission electron microscopy (STEM) delivers 2D element distributions, where it is possible to unveil fine details of certain nanoscale architectures, e.g., core–shell structures, at a very high resolution.\(^{[24,28,41]}\) This is extremely useful to unravel mechanisms regarding synthesis and structure–property correlations, thus significantly promoting the understanding for both material design and performance optimization.

### 2.3. Morphology

Due to the simple sample preparation and operation process, SEM is often adopted to get a primary impression of the NMF morphologies. To see the fine structure, especially for NMFs with small feature sizes (e.g., <10 nm), TEM is indispensable to unambiguously identify and acquire nanoscale information, including ligament sizes, crystalline structures, the connection form between building blocks, etc. To bridge the observation length scale ranges between electron microscopy (10\(^{-10}\)–10\(^{-5}\) m) and naked eyes (10\(^{-3}\)–1 m), we have recently introduced optical microscopy in this field.\(^{[24]}\) It can not only fill the length scale gap (10\(^{-5}\)–10\(^{-3}\) m) left by the above-mentioned techniques, but also give the possibility for in situ visualizing the formation process of NMFs.

### 2.4. Crystalline Structure

Almost all reported NMFs are polycrystalline, hence powder X-ray diffraction (PXRD) is employed as the typical technique to identify the phase structures and alloying behavior of NMFs. For single-metal NMFs, the crystallite size can be easily
estimated from the full width at half maximum (FWHM) of the diffraction peaks by using the Scherrer equation,\(^\text{[42]}\) which somehow reflects the feature size of the materials. Special attention needs to be paid when dealing with alloy systems, especially those containing various crystalline phases leading to close peak positions, because then the peak widths can be affected by multiple components. As complementary techniques, diffraction methods in the TEM, such as selected-area electron diffraction (SAED) or nano-beam diffraction, can be used to probe the micro- and nanoarea crystallinity and calculate the corresponding lattice parameters. Alternatively, evaluating high-resolution TEM micrographs by performing Fourier transform analysis can also be employed to unravel the nanoscale phase structure of NMFs. Very recently, extended X-ray-absorption fine structure (EXAFS) spectroscopy, owing to its capacity to in situ probe local structures and achieve sub-nanometer resolution for either long-range ordered or non-ordered materials, was also adopted to analyze the alloying structure of NMFs.\(^\text{[41]}\) It lays the foundation for revealing detailed microstructures of NMFs for a deep understanding of either the fabrication process or the structure–performance correlation for certain applications.

### 2.5. Physical Properties

Fundamental physical properties, such as electrical conductivity and mechanical properties, are important factors that can largely govern the application performance and potential application space of NMFs. Generally, a regular shape and sufficiently high mechanical strength are a premise to perform these measurements via commonly used techniques, such as the electrical conductivity as obtained by I–V curves from four-point probe tests, the mechanical modulus as characterized by dynamic mechanical analysis, etc. Although these properties have been investigated in certain NMF systems, such as silver foams obtained by freeze-casting\(^\text{[17,43]}\) and gold foams derived from dealloying,\(^\text{[44]}\) vital challenges exist to obtain reliable data, particularly for NMA systems because of their extreme fragileness.

### 2.6. Time-Lapse Techniques

Time-lapse techniques, either ex situ or in situ, are of paramount significance to understand the formation mechanisms of NMFs and underlying mechanisms for specific applications. Time-lapse ultraviolet–visible (UV–vis) absorption spectroscopy is the simplest way to in situ monitoring system evolution during synthesis, especially for the sol–gel process. However, despite its convenience, it only qualitatively reflects the structure change in systems which displays characteristic plasma absorption (e.g., Au, Ag).\(^\text{[43]}\) As a complementary approach, time-lapse ex situ TEM imaging has been employed, “seeing” the evolution of both gel networks and ligament size.\(^\text{[24,46]}\) Recently, our group developed time-lapse in situ optical microscopy imaging and in situ dynamical light scattering (DLS) techniques to probe the gelation process of gold nanoparticles (Au NPs), providing real-time information on the micrometer-scale growing process and the size evolution of aggregates, respectively.\(^\text{[24]}\) However, more time-lapse techniques that can provide NMF evolution information from different aspects (e.g., morphology, crystallinity, composition, and element distribution) are highly desired. Additionally, the employment of those approaches to study the reaction pathway for specific applications of NMFs is still missing, which calls for further endeavors.

### 3. Fabrication Strategies

A wide range of fabrication strategies have been developed in the last two decades, mainly including selective dissolution, templating, combustion, and the sol–gel method. Among them, selective dissolution by dealloying of a gold–silver bulk alloy is the first reported method,\(^\text{[12,13]}\) which can produce mechanically strong gold foams for versatile heterogeneous catalysis. The sol–gel method was newly developed in 2009,\(^\text{[20]}\) manifesting evident advantages in realizing chemical diversity and manipulating nanostructures of NMFs at mild conditions, thus drawing the most attention in this field. However, for all kinds of methods, a flexible modulation of composition/structure is still a challengeable task remaining to be addressed, which is ascribed to either the intrinsic restriction of the methods or the ambiguous understanding of the synthesis mechanisms. In this section, approaches for NMF fabrication are comprehensively reviewed, highlighting the underlying mechanisms as well as the pros and cons. To facilitate comparison, the fabrication strategies, physicochemical parameters, and application scopes of various NMFs are summarized in Table 1.

#### 3.1. Selective Dissolution

The core of the selective dissolution method lies in selective etching of one component from a bulk alloy, thus leaving behind porous and interconnected noble metal networks. Herein, the key point is to design and utilize the difference between dissolved and remaining components.

##### 3.1.1. Dealloying

As the most ancient and widely studied means to create NMFs, the appearance of the dealloying method can be dated back to the 1960s, when both chemical and electrochemical corrosion of copper–gold alloys were studied.\(^\text{[12,13]}\) Here, the selective dissolution of less-noble copper from alloys is based on the redox potential difference between copper and gold, where copper was etched by either chemical or anodic oxidation. Afterwards, a few studies were presented and ligament sizes of as-resulted gold foams were roughly modulated from 10 to 1000 nm by devising the corrosion conditions or performing postannealing (Figure 2a).\(^\text{[14,44,47]}\) However, this method has become well known only since the year 2001, when Erlebacher et al.,\(^\text{[15]}\) proposed a continuum model to describe the underlying mechanism for the structure evolution during corrosion. In brief, during the dealloying process of a bimetallic alloy, the less-noble metal is etched, while the more-noble
Table 1. Summary of fabrication strategies, physical properties, and applications of various NMFs.

| Metals | Methods | Gelation time | Density [mg cm$^{-3}$] | Size [nm] | Surface area [m$^2$ g$^{-1}$] | Applications | Refs. |
|--------|---------|---------------|------------------------|----------|-------------------------------|--------------|-------|
| Au     | Electrochemical dealloying under HClO$_4$ | / | / | 20–40$^d$ | 2 | / | [15] |
| Au     | Chemical dealloying with HNO$_3$ | / | / | 20–40$^d$ | 3.7 | CO oxidation | [4] |
| Au     | Chemical dealloying with HNO$_3$ | / | / | 10–50$^d$ | / | / | [14] |
| Au     | Chemical dealloying with HNO$_3$ | / | / | 30 | / | Semihydrogenation of alkynes | [104] |
| Au     | Chemical dealloying with HNO$_3$ | / | / | 10–50 | / | Oxidative coupling of methanol | [100] |
| Au     | Chemical dealloying with HNO$_3$ | / | / | 10–50$^d$ | / | Organosilane oxidation | [103] |
| Au     | Chemical dealloying with HNO$_3$ | / | / | 10–60$^d$ | / | Hydrogenation | [48] |
| Au     | Chemical and electrochemical dealloying, annealing | / | 386–773 | 5–1000 | / | / | [36] |
| Au     | Electrochemical dealloying under HClO$_4$ | / | / | 30–50$^d$ | / | / | [47] |
| Au     | Electrochemical dealloying under HClO$_4$ | / | / | 20–40$^d$ | 10–15 | Actuation | [107] |
| Au     | Electrochemical dealloying under HClO$_4$, annealing | / | / | 10–1000$^d$ | / | / | [44] |
| Au     | Electrochemical dealloying under HNO$_3$ | / | / | <6 | / | CO oxidation | [49] |
| Ag     | Reduction-induced decomposition | / | / | 72–213 | 1.9–7.6 | Ag/Ag$_2$O electrode | [50] |
| Au, Pd, Ag | Combustion of metal-BTA | / | 57 | 10–100 | 10.9 | CNT growth | [19] |
| Au     | Combustion of metal-BTA | / | 10–20 | 36.5 | H$_2$ storage | / | / |
| Ag     | Combustion of metal-BTA | / | 100–1000 | / | / | / | / |
| Templatining | | | | | | | |
| Au     | PS templating, dealloying | / | >280 | =50$^d$ | 1.48 | / | [54] |
| Au     | PS templating, dealloying | / | 450 | =40$^d$ | 21–24 | / | [55] |
| Ag     | Dextran templating | / | / | =4000 | 0.1–0.5 | / | [16] |
| Ag     | Triton X-114 templating | / | / | 50–100 | 0.7–1.9 | / | [52] |
| Ag     | Melamine foam templating | / | >18.7 | =3000$^d$ | / | / | [53] |
| Au-amyloid | Amyloid templating | 1.7–29.6 | =10.8 for NPs, =4600 for sheets$^t$ | 325 | Pressure sensor; p-nitrophenol reduction | [58] |
| Au, Ag, Pt | Silica aerogel templating | / | / | 10–100 | / | Rhodamine B degradation | [56] |
| Ag     | Freeze-casting | / | >4.8 | 50–100 | / | / | [43] |
| Ag     | Freeze casting | / | 25 | / | / | Conductor | [17] |
| Pd     | Freeze-casting | / | 12–135 | =200 | 6.9 | H$_2$ storage | [51] |
| Ag     | Freeze-substitution | / | 2.6–27.0 | =28 | / | / | [62] |
| Au     | Conc$^{c,1}$, direct freeze drying | / | 20–60 | 200–500 | / | / | [64] |
| Ag     | Conc$^{c,1}$, direct freeze drying | / | 10–50 | 15 | / | / | [64] |
| Pd     | Conc$^{c,1}$, direct freeze drying | / | 3–7 | 15 | / | / | [64] |
| Pt     | Conc$^{c,1}$, direct freeze drying | / | 3–10 | 33 | / | / | [64] |
| Metals | Methods | Gelation time | Density [mg cm\(^{-3}\)] | Size [nm] | Surface area [m\(^2\) g\(^{-1}\)] | Applications | Refs. |
|--------|---------|---------------|--------------------------|----------|-------------------------------|--------------|------|
| Ag     | Freeze casting & 3D printing | / | 1.3–12.6 | 25 | / | / | [35] |
| Au     | Dealloying & 3D printing | / | 25 | / | / | Methanol oxidation, flow cells | [65] |

### Sol–gel process

| Metals | Methods | Gelation time | Density [mg cm\(^{-3}\)] | Size [nm] | Surface area [m\(^2\) g\(^{-1}\)] | Applications | Refs. |
|--------|---------|---------------|--------------------------|----------|-------------------------------|--------------|------|
| Au     | Dippamaine | 6–72 h | 40–43 | 5–6 | up to 50.1 | Glucose oxidation | [45] |
| Au     | Glucose | / | / | >9 | 1.8–11.9 | / | [77] |
| Ag     | Evaporation at 313 K | / | 88 | 113 | 5.5 | / | [63] |
| Ag     | Conc. (C(NO\(_2\))\(_4\)) | 4–12 h | 37–41 | 5–11\(^{10}\) | 43–160 | / | [69] |
| Ag-carbon | HTR & annealing | / | 3.82 | >70 | 37.1–44.6 | Electromagnetic shielding | [109] |
| Pd     | Precursor \(=6.6 \times 10^{-3} \mu\), in acetic acid, CO & 313 K | 5 h | 11 | 50–100\(^{10}\) | / | EOR | [76] |
| Pd     | Glyoxalic acid, sodium carbonate & \(=338\) K | / | 1 h | 3–8\(^{a}\) | 50.1 | EOR | [92] |
| Au     | Precursor 12–24 \(=10^{-3}\) M | 190–200 | 3–8 | 30–40 | / | Hydrogenation of \(\alpha\)-keto esters | [37] |
| Pd     | Precursor 0.02–2 \(=10^{-3}\) M | 2–48 h | 83.0–212.8 | 6.9–113.7 | 2.5–29.7 | EOR; MOR; self-propulsion devices | [24] |
| Ag     | Conc. (C(NO\(_2\))\(_4\)) | / | / | 100–500 | / | / | [20] |
| Pt     | Conc.  \(=15 \times 10^{-3}\) M, N\(_2\)H\(_4\) (in hexane) | 1–5 h | 190–200 | 3–8 | 30–40 | / | [37] |
| Pd     | Precursor 5–100 \(=10^{-3}\) M | A few minutes | 540 | 18–280 | 3.1 | / | [84] |
| Au     | Precursor 15 \(=10^{-3}\) M, Na\(_2\)H\(_4\), or dimethylamine borane | 65 | 12–65 | 15.4 | / | / | [70] |
| Pt     | Conc. rotary evaporation or NaCl | 8–15 d | 55 | 13–60 | 20.6 | / | [24] |
| Au, Ag, Pt, Ag–Pt | Precursor 12–24 \(=10^{-3}\) M, Hydrazine, 333 K | Several hours | / | 12–50 | 14–96 | Congo red degradation, FOR\(^{f}\), SERS | [22] |
| Au–Ag, Ag–Au, Pt–Pd, Pd–Pt, Ag–Au–Pd | Conc. H\(_2\)O\(_2\) | / | / | 100–500 | / | / | [20] |
| Au     | Conc. H\(_2\)O\(_2\) | / | / | 50–100 | / | / | [20] |
| Pt     | Conc.  \(=15 \times 10^{-3}\) M, N\(_2\)H\(_4\) (in hexane) | 1–5 h | 190–200 | 3–8 | 30–40 | / | [37] |
| Pd     | Precursor 0.02–2 \(=10^{-3}\) M | 2–48 h | 83.0–212.8 | 6.9–113.7 | 2.5–29.7 | EOR; MOR; self-propulsion devices | [24] |
| Ag     | Precursor 5–100 \(=10^{-3}\) M | A few minutes | 540 | 18–280 | 3.1 | / | [84] |
| Pt     | Precursor 0.02–2 \(=10^{-3}\) M | 2–48 h | 83.0–212.8 | 6.9–113.7 | 2.5–29.7 | EOR; MOR; self-propulsion devices | [24] |
| Au     | Precursor 0.02–2 \(=10^{-3}\) M | 2–48 h | 83.0–212.8 | 6.9–113.7 | 2.5–29.7 | EOR; MOR; self-propulsion devices | [24] |

### References

[35], [63], [65], [69], [76], [77], [78], [79], [81], [82], [84], [92], [109]
Table 1. Continued.

| Metals                  | Methods                  | Gelation time | Density [mg cm\(^{-3}\)] | Size [nm] | Surface area [m\(^2\) g\(^{-1}\)] | Applications          | Refs. |
|-------------------------|--------------------------|---------------|---------------------------|-----------|-----------------------------------|------------------------|-------|
| Pt–Ni                   | NaBH\(_4\)              | 4 d           | /                         | 5         | 35                                | ORR                    | [80]  |
| Ir\(_x\)Cu             | NaBH\(_4\), 343 K       | 2–3 h         | /                         | 3–7       | 41.7                              | OER                    | [86]  |
| PdPb@Pd                | NaH\(_2\)PO\(_4\), 333 K| 4 h           | /                         | 5–40      | /                                 | Electrochemical ethylene glycol oxidation | [85]  |
| Pd–Cu                  | Glyoxylic acid, sodium carbonate & +333 K | 2–4 h         | /                         | /         | /                                 | FOR\(^{3}\)            | [94]  |
| Au\(_x\)Cu@Pd          | Post GRR\(^{4}\)         | /             | /                         | /         | 4.5                               | EOR                    | [88]  |
| Pd\(_x\)Au–Pt          | Post UPD\(^{5}\) & GRR   | /             | 45                        | 4–5       | 83–105                            | ORR                    | [41]  |

\(^{a}\)Estimated sizes from SEM or TEM images; \(^{b}\)The size of primary nanoparticles of aerogels; \(^{c}\)Conc. concentrating of NPs by ultracentrifugation, where the final concentration is \(\geq 10^{-3}\) M; \(^{d}\)The thickness of the shell of hollow structures; \(^{e}\)The lateral size of nanosheets; \(^{f}\)FOR, electro-oxidation of formic acid; \(^{g}\)BOR, electro-oxidation of borohydride; \(^{h}\)GRR, galvanic replacement reaction; \(^{i}\)UPD, underpotential deposition.

Figure 2. NMFs fabricated by the selective dissolution method. a) SEM images of dealloying-derived Au foams annealed at indicated temperatures. Adapted with permission.\(^{[44]}\) Copyright 1992, American Physical Society. b) The simulated evolution of artificial pits in Au–Ag (1/9) alloy with prolonging time. Cross-sections along the (1\(1\)1) plane defined by the yellow lines are shown below each plan view. Adapted with permission.\(^{[15]}\) Copyright 2001, Nature Publishing Group. c) Tunable structural hierarchy of Ag foams as fabricated by reduction-induced decomposition of Ag\(_{x}\)Na\(_{1-x}\)Cl, which is presented by SEM images and summarized hierarchical length scales. The scale bars in the SEM images are 1 \(\mu\)m. Adapted with permission.\(^{[50]}\) Copyright 2018, American Chemical Society.
metal adatoms are chemically driven to aggregate on the solid-electrolyte interface, accounting for the evolution of a 3D porous noble metal foam along with time lapse (Figure 2b).

Taking advantage of the self-supported nanosized framework, high mechanical strength, and the existence of a vast amount of low-coordinated atoms, Au NMFs have been extensively investigated due to the great potential in heterogeneous catalysis. The composition and the feature size have been modulated to investigate the corresponding performance. For instance, the amount of residual silver from dealloying of an Au–Ag foil, which was found to have a vast effect on the catalytic performance, was deliberately modulated from <1 to 10 at% by devising the concentration of nitric acid during corrosion, facilitating a systematic study of the composition effect. Another work delivered by Xu et al. reported gold foams with ultrathin ligament size, which was dramatically reduced from \( \approx 30 \) to \(<6\) nm by additionally applying an anodic potential at 1 V during the dealloying process by nitric acid. This can render a much larger SSA accompanying with enhanced catalytic performance.

Although the dealloying method has received tremendous attention, its viability is highly dependent on the fabrication of alloy precursors and the redox potential difference between the corresponding metals, which increases the production cost and restricts its success only in producing gold foams. In addition, low SSAs (typically \(<5\) m\(^2\) g\(^{-1}\)) and relatively large characteristic sizes (typically \(>10\) nm) further retard its high performance in applications, such as electrocatalysis.

### 3.1.2. Reduction-Induced Dissolution

As an innovated expansion of the dealloying approach, the reduction-induced dissolution method was recently developed (Figure 2c). In brief, AgCl was melted and then reduced by using NaBH\(_4\), thus eliminating chlorine and producing monolithic bicontinuous porous Ag foams with a feature sizes of 72–213 nm and a SSA of 7.6 m\(^2\) g\(^{-1}\). More interestingly, by enrolling NaCl in the AgCl precursor to obtain bulk Ag\(_x\)Na\(_{1-x}\)Cl, hierarchically structured Ag foams with different length scales were acquired via sequentially dissolving NaCl in water and reducing Cl\(^-\) in NaBH\(_4\) solutions. However, similar challenges as for the dealloying method, including nanoscale structure control, improvement of SSAs, and extension to more noble metals, are faced by the RID approach.

### 3.2. Combustion Synthesis

The combustion synthesis of monolithic metal foams was accidentally found during the characterization of combustion of energetic salts bistetrazolamine (BTA) and transition–metal complexes, where the iron BTA complex pellet was unexpectedly converted to an ultralow-density gray foam by decomposition under inert environments at certain pressures. As shown in Figure 3a, during decomposition of Fe-BTA, metal centers were liberated from the BTA complex, quickly converting to the zero valence state metal atoms and dynamically assembling to foams at the flame front. Herein, energetic ligands (i.e., BTA) provide both a blowing agent and heat on molecular level. More importantly, the steady burning behavior rather than denotation of energetic complexes ensures a relatively stable environment, which facilitates the formation of monolithic foams instead of disperse powders.

Afterwards, the method was extended to a number of metal systems, including noble metals such as Au, Ag, and Pd (Figure 3b–d). The silver foam was the densest material made, which is due to a high mass fraction of Ag in the complex compared to the other complexes, with only one BTA ligand for every two Ag atoms (Ag\(_2\)-BTA). In comparison, gold and palladium foams were acquired from [Au(BTA)\(_2\)-(NH\(_4\))(H\(_2\)O)]\( \cdot \)2H\(_2\)O (or Au(BTA))\(_3\)(NH\(_4\))\(_3\) and Pd-BTA, respectively, displaying high SSAs of up to 10.9 m\(^2\) g\(^{-1}\) for Au foams and 36.5 m\(^2\) g\(^{-1}\) for Pd foams. The feature sizes of the corresponding Au, Pd, and Ag foams are 10–100, 10–20, and 100–1000 nm, respectively.

Combustion synthesis can theoretically work with a wide spectrum of noble metals to spawn NMFs and provide a reasonable SSA. However, complicated procedures for producing energetic metal complex precursors and special equipment to implement combustion synthesis under...
controlled pressure may affect the wide studies of this method. In addition, the nanoscale structure control of resultant NMFs is quite difficult owing to the aggressive fabrication process.

3.3. Templating

Templating is an extensively used method to fabricate materials with finely controlled architectures, where precursors usually conformally deposit on as-selected templates and thus giving rise to well-defined structures. In the field of NMFs, templates can display more functions. Besides structure tailoring, a delicate selection of templates can also promote the reaction and/or support the monolithic feature of the resulting foams.

3.3.1. Sacrificial Templating

To evaluate the intrinsic properties of NMFs, templates are always removed after reaction. To tailor the structure of the building blocks, Gilbert et al.\cite{51} firstly created Pd nanowires (ligament size of ≈200 nm) via electrodeposition by templating anodized aluminum oxide (AAO) or track-etched polycarbonate membranes, then assembled the Pd NWs into the corresponding foam by direct freeze drying. Compared to this two-step process, most works adopt templates with freestanding 3D networks.\cite{16,52,53} For example, commercial melamine foams were used to support silver deposition by the silver mirror reaction, after which the template was removed by calcination, thus producing lightweight Ag foams with a density of 18.7 mg cm\(^{-3}\).\cite{53} In 2003, Walsh et al.\cite{16} demonstrated the dual function of dextran as both soft template and reductant. By mixing dextran with metal salt precursors in water and drying in air, the as-obtained paste was heated at desired temperatures (600–900 °C), thus producing corresponding silver or gold foams with controlled feature size of micrometer scale (Figure 4a). Owing to the high-temperature calcination for template removal, the resulting NMFs by these methods often suffer from large feature sizes (typically >100 nm) and low SSAs (<2 m\(^2\) g\(^{-1}\)).

Combining sacrificial templating with dealloying, hierarchically structured gold foams with different length scales were reported.\cite{54,55} As displayed in Figure 4b, polystyrene (PS) beads were used as sacrificial templates, on which gold and silver

![Figure 4. NMFs fabricated by the templating method. a) BET surface areas and SEM images of silver sponges prepared by heating AgNO\(_3\)–dextran composites at different temperatures. Adapted with permission.\cite{16} Copyright 2003, Nature Publishing Group. b) Synthesis of nanoporous gold shell monoliths by dealloying of PS-templated Au–Ag hollow spheres. Adapted with permission.\cite{54} Copyright 2007, American Chemical Society. c) Schematic fabrication of porous metallic networks by templating silica aerogels and the corresponding digital photo and SEM image of the as-obtained silver networks. Adapted with permission.\cite{56} Copyright 2016, Wiley-VCH. SEM images and digital photos (inset) of d) the gold nanoparticle amyloid aerogel and e) the gold crystal amyloid aerogel. Adapted with permission.\cite{58} Copyright 2015, Wiley-VCH. f) Schematic formation of silver foams by freeze casting. Adapted with permission.\cite{17} Copyright 2014, Wiley-VCH. g–j) Silver foams fabricated by freeze-casting coupled with post heat treatment, SEM image, digital photo (inset), and TEM images. Adapted with permission.\cite{43} Copyright 2017, American Chemical Society.](image-url)
were sequentially deposited. These noble-metal-coated PS beads were then casted to form a monolith, followed by annealing in air to remove the PS as well as to alloy Au and Ag. After dealloying with nitric acid, a hierarchically structured gold foam was obtained with a SSA of about 1.5 m² g⁻¹. Although a following work has improved the SSA to 23.6 m² g⁻¹ the value is still relatively low. "Currently, this approach is only limited to the gold system, while theoretically it could be extended to other noble metal systems, given that a sufficient difference exists between the employed noble metals regarding their redox potential, or the resistance towards certain chemicals."

3.3.2. Silica Aerogel Templating

In sharp contrast with regular templating methods where materials conformally grow on the as-used templates, Salomon's group found a distinguishing phenomenon when a silica aerogel was applied as substrate. As illustrated in Figure 4c, after physical vapor deposition (PVD), a wide range of metals, including Au, Ag, Pt, and nonnoble metals (e.g., Fe, Al, Cu, Ti), formed macroscopic 3D networks on the surface of porous silica aerogels. These foams were usually micrometer-thick (up to 4 μm for gold) and showed an average ligament size of several tens of nanometers. It is believed that the combination of porous structure and surface charge states of the silica aerogel can generate an inhomogeneous electrostatic field, which drives the electron redistribution among the deposited metal particles and thereby continuously creating local electric fields. Such local electric fields play the central role in directing the growth of the metallic pillars and keeping them far away from the substrate, eventually producing 3D networks on the surfaces of silica aerogels.

Although the underlying mechanism has not been fully deciphered, the presented method fuels a brand-new perspective in understanding the functions and mechanisms of templates. In addition, its capacity in producing a wealth of NMFs validates broad application prospects. However, the separation of the template and the as-grown metal foam is not an easy task, since it is difficult to produce thick foams by PVD, considering the formation mechanism and the production costs. In addition, fine structure control of the building blocks and connection architectures of NMFs, especially below 10 nm, is still unsolved, which restrain a high SSA, thus discouraging certain applications, such as electrocatalysis.

3.3.3. Composites

To avoid the adverse effects incurred by the template removal process (e.g., collapse of the 3D network and increase of feature size) as well as to enhance the mechanical strength of NMFs, sometimes templates are deliberately remained in the final product.

For example, polyurethane (PU) sponges have been adopted to support gold foams by sequential copolymer coating, ion exchange, and electroleos deposition. In a recent work, Mezzenga's group demonstrated that amyloid fibrils can serve as a multifunctional template to in situ reduce gold precursor salts and scaffold corresponding nanostructures. By mixing chloroauric acid with water suspension of β-lactoglobulin amyloid fibrils with/without the existence of NaBH₄, followed by salting out with sodium chloride and critical point drying, free-standing composite foams loaded with either Au NPs (~10 nm) or micrometer-sized gold platelets were obtained. The morphology difference of loaded gold structures can be attributed to the impurity of nucelation sites and speed during reaction, which further determines their interactions with incident light, thus producing different colored foams (Figure 4d,e). By varying the reaction parameters, the density of the composite aerogels could be readily tuned from 1.7 to 29.6 mg cm⁻³.

Composite NMFs always hold excellent mechanical properties (flexibility, compressibility, high strength, etc.) and tailorable shapes. The reasonable combination of noble metals and desirable templates can also impart additional functions in the resulting materials. However, a uniform distribution of noble metals on the template and the fine control of their microstructure are hardly to be achieved. In addition, the physical properties (e.g., density, SSA, electrical conductivity) are contributed by all components of the composite NMFs, which hinders the investigation of the intrinsic features of the noble metal networks.

3.3.4. Ice Templating

Aside from the aforementioned templates, which either remain in the final foam or are needed to be removed under destructive conditions, ice is characterized as a multifunctional and eco-friendly template, which is frequently applied for NMF fabrication. Ice templating has been widely explored in widespread systems, including oxides, nanocarbons, and polymers. Taking advantage of the water phase transitions under mild conditions, usually it first acts as dispersant at its liquid state to disperse the metal nanoparticle precursors, then being freezed (liquid-solid transition) to serve as both a solid template and shaping agent for retaining the monolithic feature, and eventually being removed via sublimation (solid–gas transition) to produce solid foams. Especially, when a directional temperature gradient is deliberately applied, foams with aligned porous structures will be presented because of the anisotropic solidification behavior of water, in which case the method is termed freeze casting.

Among all noble metals, Ag is the first system engineered to NMFs by ice templating, which is pioneered by Yu's group in year 2014. By unidirectional freezing as-obtained concentrated Ag NW solutions, Ag foams with aligned macroporous (several micrometers to several tens of micrometers) were obtained (Figure 4f), displaying low densities of 10–40 mg cm⁻³ and high electrical conductivity up to 50 S cm⁻¹, Following similar procedures but imparting a post-thermal-sintering process, Qian et al. further reduced the density of Ag foams to as low as 4.8 mg cm⁻³ and increased the conductivity up to 510 S cm⁻¹ (Figure 4g–i). Combining AAO templating and ice templating, Pd–NW-based foams with densities of 12–135 mg cm⁻³ and SSAs of less than 10 m² g⁻¹ were also reported.

It is well known that the gelation capacity is highly dependent on the aspect ratio of NWs, which is inversely proportional to the volume fraction required for gelation. Hence, it is not surprising that large-aspect-ratio Ag NWs (typically > 200) were easier to form self-supported 3D monoliths by freezing, during
which process the suspension was dramatically concentrated. In 2016, Freytag et al.\textsuperscript{[64]} showed for the first time that isotropic noble metal NPs (i.e., aspect ratio is 1) can also be converted to free-standing foams by freezing–sublimation of highly concentrated solutions (several hundred $\times 10^{-3}$ m achieved by ultracentrifugation method), thus providing the possibility to prepare NMFs with compositions extending to Au, Ag, Pd, and Pt. The resulting NMFs are fragile, displaying densities of 20–60 mg cm$^{-3}$ and SSAs of less than 33 m$^2$ g$^{-1}$.

Ice-templating is one of the most facile strategies for producing NMFs and engineering their multiscale structures, capable of acquiring ultralight foams ($<10$ mg cm$^{-3}$) with regular shape and excellent mechanical and electrical properties. However, a very high precursor concentration ($10–500 \times 10^{-3}$ m) is required to ensure the monolithic feature, and stabilizers are frequently involved to ensure a stable dispersion prior to freezing. Therefore, NMFs with low SSAs (typically $<10$ m$^2$ g$^{-1}$) and considerable quantity of impurities are always produced by the ice-templating approach.

### 3.4. 3D Printing Method

3D printing, as an emerging technique in the last few years, has also found its application in fabricating NMFs with controllable macroscopic architectures. Yan et al.\textsuperscript{[35]} showed an interesting study by combining the 3D printing technique with freeze casting. An aqueous Ag NW suspension was printed drop by drop on a cold plate (30 °C), and as-printed patterns were post-freeze at $-70$ °C followed by sublimation. In this way, Ag foams with a density down to 1.3 mg cm$^{-3}$ and an electrical conductivity of up to 1.5 S cm$^{-1}$ were obtained. In another recent work, Zhu et al.\textsuperscript{[65]} presented a combined 3D printing with a dealloying approach. The initial thixotropic Au–Ag composite inks were prepared by mixing Ag clay, Au clay (metal powders, water, and organic binders), and an organic solvent, which were then printed to form a desired architecture. After annealing to remove binders and solvent, and dealloying to eliminate the Ag component, 3D hierarchical nanoporous gold foams with controlled macroscopic feature sizes of 30–500 nm and macroscopic length scales of 10–1000 µm were produced.

As the latest fabrication method developed, especially in conjunction with other processes, 3D printing provides a promising way to manipulate the architecture of NMFs at the length scale $>1$ µm, thus creating free-standing and mechanically robust materials with micron-scale-nonorder while large-scale-ordered structures. However, similar to other 3D printing systems, the efficient structure control at small length scales (e.g., $<1$ µm) is extremely difficult. Additionally, to ensure appropriate rheology properties, the introduction of impurities (e.g., binders) in the ink preparation process is unavoidable, causing difficulties in acquiring pure NMFs with small feature sizes.

### 3.5. Sol–Gel Method

The sol–gel method is the most prevalently adopted approach for NMF fabrication. Because of the encouraging potential in creating materials with highly tunable microstructures, large SSAs (up to 269 m$^2$ g$^{-1}$), and various compositions (Au, Ag, Pd, Pt, and diverse noble-metal-based alloys and mixtures) under ambient conditions, it facilitates both the mechanistic study of the formation process and the structure optimization for tailored applications. Strictly speaking, the sol–gel process refers to the process where the solution is destabilized to form the wet gel. To acquire the corresponding aerogel, an additional drying step by either freeze drying or critical point drying is required. Since the drying process, i.e., replacing the solvent inside the wet gel with air, causes only few composition/structure changes of the 3D gel network, the sol–gel step determines the structures/properties of the resulting NMAs. Here, only the gelation process for noble metal wet gels will be focused on in this section. Since the majority of syntheses are performed in aqueous solutions, in this part, the solvent will be water if not otherwise specified.

Three main branches of the sol–gel method are summarized in Figure 5, i.e., 1) the two-step method following the conversion from metal salts to metal NPs, and further to metal gels, 2) the one-step method following the conversion directly from metal salts to metal gels, and 3) a posttreatment of the as-obtained metal gels. In this section, these three processes will be sequentially and comprehensively reviewed, highlighting the designing ideas as well as the pros and cons. Finally, a separate portion on

![Figure 5.](image-url)

**Figure 5.** a) A summary of the sol–gel method for the fabrication of noble metal wet gels. b) Schematic illustration of NMA preparation from corresponding wet gels via freeze-drying or critical-point drying.
the investigation of the gelation mechanism will be presented, highlighting the unique phenomena in noble metal systems and possible physical pictures accounting for the gelation process.

3.5.1. Two-Step Method

The two-step method is the earliest applied sol–gel approach to obtain NMAs, where the NPs were presynthesized before conducting gelation. The decoupling of the above two processes allows to separately devise and optimize the NPs and the gels, offering unprecedented opportunities in manipulating composition/structure of NMAs and understanding the gelation mechanism. However, the two-step method is always time-/cost-consuming because of multiple steps, including NP synthesis, NP processing (e.g., purification and concentration), and gelation. This section will consist of two main parts, i.e., the synthesis strategies and the structure modulation.

**Synthesis Strategies:** The first NMA was reported by our group in 2009, which is following a two-step process. Briefly, dilute NP solutions ($\approx 0.2 \times 10^{-3}$ m) were obtained from the metal salt precursors used in the synthesis by assuming 100% conversion from salts to NPs) were fabricated and then concentrated to a higher concentration of $\approx 10 \times 10^{-3}$ m by ultracentrifugation. After destabilization by hydrogen peroxide or ethanol, gels formed in 1–4 weeks after grounding. The resulting gels often feature 3D networks built up from NP-fused branched nanowires, where the feature size ranges from 3 to 100 nm depending on the size of the starting material and chemical composition. However, several crucial issues remain, including ultralong gelation time, the highly costly concentration process by ultracentrifugation, limited control of the microstructure/composition of NMAs (especially for gold aerogels), and the relatively low SSAs (46–48 m$^2$ g$^{-1}$ for alloy NMAs). To address the above issues, a wide spectrum of approaches on the basis of the two-step gelation process have been developed, which mainly focus on the type of the destabilization method, such as heating ($313–363$ K),

oxidative ligand removal by $\text{C(NO}_2\text{)}_4$, salting-out,

electrostatic crosslinking, or dopamine-induced destabilization.

To address the time-consuming fabrication process, Wen et al. reduced the gelation time to as short as 5 min. by electrostatically linking negatively charged citrate-capped Pd NPs by $\text{Ca}^{2+}$ ions, producing aerogels with much higher surface areas (40–108 m$^2$ g$^{-1}$) as compared to Pd-based foams obtained from non-sol–gel methods. Tang et al. found an increase of the noble metal salt precursor concentrations to 12–24 $\times 10^{-3}$ m, resulted in a wide range of spongy solids after hydrazine reduction and subsequent ethanol destabilization. Instead of introducing chemical initiators, Jung et al. straightforwardly assembled Ag NWs into 3D hydrogels in a few days by evaporation of the corresponding colloidal solutions at slightly elevated temperature (313 K). During this process, the continuous concentration of the solutions increases the chance for interlinking of the NWs, inducing a transition from the semi-dilute to the isotropic concentrated regime and thereby generating free-standing networks with a low density (88 mg cm$^{-3}$) and high electrical conductivity ($3 \times 10^4$ S cm$^{-1}$). However, a highly concentrated precursor solution ($>15 \times 10^{-3}$ m) is a premise for this work, which inevitably involves either costly ultracentrifugation or a considerable amount of stabilizers.

To cut down the concentration threshold for gelation, dopamine, which is known as highly sticky molecule due to its functionalities (catechol and amine moieties) and the self-polymerization reaction, was elegantly applied as an initiator. As shown in Figure 6a,b, 3D nanowire-fused gold aerogels were directly obtained from dilute gold NP solutions ($\approx 0.2 \times 10^{-3}$ m), displaying ultrathin ligament sizes (5–6 nm) and record-high SSAs (up to 50.1 m$^2$ g$^{-1}$ for $\beta$-cyclodextrin ($\beta$-CD) capped aerogels). The gelation process was investigated by in situ UV–vis spectra, as shown in Figure 6c, where the surface plasmon resonance (SPR) absorption was broadened and red-shifted upon addition of dopamine, suggesting the formation of multiscale nanostructures. This milestone work for the first time cut down the ligament size of gold aerogels below 10 nm, leading to quite a few follow-up works. However, the detailed interactions between the multiple species and the exact role played by dopamine are still unknown. In addition, a large amount of 18 wt% of $\beta$-CD, which serves as a stabilizer, remained in the final product, suppressing the investigation of the intrinsic properties of gold aerogels.

**Structure Modulation:** The efficient structure control is another challenge encountered in the NMA preparation, which is of paramount significance for structure-property correlation investigations and material optimization for specific applications. On the one hand, 3D networks structured from fused NWs were frequently observed for NMAs. The ligament sizes of those NWs, being seemingly independent on the synthetic methods, are often located in a certain range and rely strongly on their chemical compositions. Despite a few exceptions, usually ligament sizes of several tens to several hundreds of nanometers were found for Au and Ag gels, while less than 10 nm were observed for Pd, Pt, and alloy gels. On the other hand, with solely fused NWs as underlying structures, multiscale architectures are always missing in NMAs. The lack of structural diversity can block the activation of synergistic effects and the manipulation of their properties, which is unfavorable for both fundamental studies and practical applications. Notably, if two or more elements are incorporated, the spatial element distribution along the gel network invites an additional variable to the structure. Feasible strategies capable of introducing certain special morphologies, such as core–shell and yolk–shell architectures, into NMAs are highly desirable for pursuing novel properties and enhancing the performance toward specific applications.

Regarding the two-step sol–gel method, the innate decoupling of NP formation and gel development facilitates a precise engineering of the nanobuilding blocks, thus introducing additional structure levels into the gel network. Ramnath et al. pioneered the investigation of hierarchically structured NMAs by assembling pre-synthesized Au–Ag, Pd–Ag, and Pt–Ag alloy nanoshells via salting-out (Figure 6d). Aside from the resulting multilevel structured NMAs, the salting-out effect was proposed for the first time to spark gelation, which was realized by either rotary evaporation or the addition of sodium chloride. One year later, tetranitromethane ($\text{C(NO}_2\text{)}_4$) was introduced as a new type of initiator, which is capable of oxidatively removing thiolate ligands, thus linking Ag nanoshells into 3D gel networks.
Intriguingly, depending on the amount of oxidant, either small transparent Ag–NP-based gels or black Ag–nanoshell-based gels were prepared due to different degree of oxidative etching. Impressively, an ultrahigh specific surface area of up to 160 m$^2$ g$^{-1}$ was obtained for the resulting Ag–nanoshell-based aerogels, outperforming the SSAs of most NMFs. Several following studies further expanded the system to Au–Ag and Au–Ag–Pd aerogels.\cite{38,70} By engineering the composition of ternary Au–Ag–Pd alloy NPs by the stepwise galvanic replacement reaction (GRR) of l-glutathione-stabilized Ag NPs, Nahar et al.\cite{38} observed that spherical and anisotropic NPs were obtained with higher and lower Pd proportion, respectively, further resulting in gels with different microstructures. Impressively, a BET surface area of up to 269 m$^2$ g$^{-1}$ was obtained, setting the record for all kinds of NMF materials made so far. Recently, Cai et al.\cite{66,67} found that the gelation can be simply triggered at elevated temperature ($\approx$348 K) without chemical initiators. As shown in Figure 6e,f, they assembled predesigned Pd–Ni hollow nanospheres or Pd–Pt–Ni NPs into various hierarchically structured NMAs with low densities (35–50 mg cm$^{-3}$) and high SSAs (67.7–95.4 m$^2$ g$^{-1}$).

On the other hand, organic-phase synthesis holds great promise in directly producing highly concentrated noble metal NP solutions with tailored morphologies, probably due to a library of available and strong-coordinating ligands, which can be only applied in organic solvents. Taking advantage of this, Naskar et al.\cite{37} fabricated Pt nanopheres and nanocubes directly from highly concentrated metal salt solutions ($>30 \times 10^{-3}$ M), followed by assembling them into monolithic gels in hexane assisted by hydrazine. However, relatively low SSAs (30–40 m$^2$ g$^{-1}$) were observed by this manner, leaving large space for improvement.
Another interesting and counterintuitive work was delivered by Kühn et al.\[78\] They found that by mixing two kinds of presynthesized noble metal NPs (e.g., Au NPs and Pd NPs, or any other combination of two noble metals) and triggering gelation by heating, the resulting spatial element distributions of the as-obtained gels varied enormously depending on the initial composition of the NPs. A homogeneous distribution was found for the Au–Ag gel, a randomly discontinuous distribution was observed for the Pd–Pt gel, and an Au–Pd core–shell-like structure was acquired in the Au–Pd system. The result confirms the presence of diffusion and alloying processes for different NPs during gelation, while the mechanism behind remains unclear.

Very recently, our group presented well tunable NMAs by regulating the interactions between the NPs and ions.\[24\] Gold hydrogels were acquired directly from dilute NP aqueous solutions typically within 6 h at room temperature, where the threshold concentration for gelation was as low as 0.02 × 10^{-3} M, much lower than that of other reports (0.2 × 10^{-3} M to several hundreds of × 10^{-3} M). The specific ion effects validate widely tunable ligament sizes (6.9–113.7 nm) and chemical compositions (Ag, Pd, Pt, Au–Pd, Au–Pd–Pt, etc.), facilitating a broad physicochemical property manipulation (Figure 6g). More impressively, a dynamic shelling approach was further developed within the framework of this strategy (Figure 6h), by which core–shell structures were obtained by simply designing the feeding order of the reactants. Briefly, after initiating the gelation process of the “core” metal NPs, the “shell” metal salts were added a few minutes later. In this manner, to minimize the energy cost, the “shell” metal will in situ nucleate and grow on the as-formed gel fragments of the “core” metal, eventually producing well-defined core–shell-structured alloy NMAs. This approach not only realizes a straightforward design of the spatial element distribution across the gel networks without prolonging the fabrication time, but can also be extended to a wealth of core–shell-structured gels on the basis of Au–Ag, Au–Pd, Au–Pt, and Au–Pd–Pt.

3.5.2. One-Step Method

Involving separate NP synthesis and sometimes an additional concentration step, the two-step method typically suffers from a tedious and time-/cost-consuming synthesis process. In comparison, the one-step synthesis fuels a much more convenient route in which the NP and gel synthesis are merged together. However, the simplified protocol comes at the expense of poor structure control, limited number of available systems, and the difficulty of elucidating the gelation mechanisms. Similar to the last section, the synthesis strategies and structure modulation approaches will be separately elaborated for the one-step method.

**Synthesis Strategies:** To ensure gel formation, three approaches are typically applied, i.e., 1) the introduction of additional additives before reduction, 2) the increase of reaction temperatures, and 3) the increase of reactant concentrations. The first one may bring additional attractive interactions to assemble in situ formed NPs, while the latter two approaches can promote the gelation by enhancing the chances for effective collisions and shifting the reaction equilibrium toward the products.

Liu et al.\[46\] pioneered the one-step approach by reducing palladium salt solutions (0.2 × 10^{-3} M) with NaBH\(_4\) in the presence of CD molecules (Figure 7a,b). The molar ratio...
of reductant to metal salts \((R/M = 3/2)\) was slightly lower compared to a typical NP synthesis \((R/M = 4/1)\). After 3–10 d, nanostructured Pd gels with small ligament size \((=3.6 \text{ nm})\) and large SSA \((92 \text{ m}^2 \text{ g}^{-1})\) were acquired. The gelation mechanism was ascribed to the destabilization of in situ formed Pd NPs, which is initiated by the raise of the ionic strength from the in situ generated salts during the metal salt reduction. However, the amount of in situ produced salts was quite small \((<2 \times 10^{-3} \text{ m})\), which was insufficient to trigger gelation according to our experience in a recent work.\(^{[24]}\) Additionally, massive organic residuals \((\approx 44 \text{ wt\%})\) remain in the as-obtained aerogel, causing great difficulties in probing the intrinsic properties of the NMAs. The same authors found that high-SSA aerogels \((73 \text{ to } 168 \text{ m}^2 \text{ g}^{-1})\) can be also obtained for the Pd–Pt system without the introduction of additives, but a much longer time of 3–17 d was required to acquire hydrogels.\(^{[79]}\) Because of the extreme simplicity, this method has been widely adopted and extended to Au–Cu, Pd–Cu, and Pt–Ni systems.\(^{[80–82]}\)

To reduce the long gelation time required for the one-step method, Lin’s group addressed this issue in M–Cu \((M = \text{Pd, Pt, and Au})\) and Au–Pt systems by raising the reaction temperature (Figure 7c).\(^{[74,83]}\) Via one-pot reducing two metal salt precursors by NaBH\(_4\) at 333 K, monolithic hydrogels formed in 2–6 h, displaying moderate SSAs of 21.3–37.5 m\(^2\) g\(^{-1}\). On the other hand, an increase of the reactant concentrations was found to considerably accelerate the gelation process. As shown in Figure 7d,e, Au, Pd, and Pt gels were instantly produced by mixing highly concentrated solutions of reductants \((100 \times 10^{-3} \text{ m} \text{ NaBH}_4, \text{ NaH}_2\text{PO}_4, \text{ or dimethylamine borane})\) and metal salts \((5–100 \times 10^{-3} \text{ m})\).\(^{[84]}\) However, low SSAs of less than 20.6 m\(^2\) g\(^{-1}\) were obtained for all aerogels, presumably owing to the large ligament sizes resulting from the ultrafast reaction kinetics.

**Structure Modulation:** In spite of the grand difficulties in precise structure control of the one-step method, incessant efforts have been made in the last few years. Taking advantage of the redox potential difference between two metals, the in situ GRR was utilized for constructing Pd\(_3\)Pb\(_1–\)Pd core–shell gels by a NaHPO\(_4\)-assisted reduction of the corresponding metal salts (Figure 7f).\(^{[85]}\) Likewise, for the first time, iridium was introduced in NMAs with the assistance of copper by direct reduction at elevated temperature.\(^{[86]}\) Here, copper salts were reduced to form nanocrystals at first, which served as sacrificial templates for the following GRR with H\(_2\)IrCl\(_6\), thereby incorporating Ir and producing nanovoids. After the orientated attachment of these nanocrystals, 3D networks with an average ligament size of \(\approx 4.6 \text{ nm}\) were acquired. In another work, a gas-phase reductant, i.e., carbon monoxide, was used for the first time, where Pd gels were obtained by CO bubbling of Pd(acac)\(_2\) solutions in the presence of trioctylphosphine oxide in acetic acid.\(^{[76]}\) In sharp contrast with previous reports where the building blocks are either 0D particles or 1D NWs, the resulting aerogels were structured from 2D nanosheets (lateral sizes of 50–100 nm), which was ascribed to the strong interactions between CO and Pd (111) surfaces.

### 3.5.3. Posttreatment

Both the two-step and the one-step sol–gel process have been demonstrated to work with a number of noble metal systems and enabled structure modulation to some extent. However, they become feeble with certain complex architectures, especially when a good structural connectivity of 3D networks is required. In this scenario, a posttreatment of the as-obtained noble metal gels can provide an alternative solution. However, it is noteworthy that posttreatments bring about more steps as compared to either one-step or two-step methods as described above, thus substantially increasing the cost and elongating the fabrication period. In addition, certain posttreatment steps suffer from mass/thermal transfer issues or cause macroscopic structure collapse, which will lead to low yields and powder-like products.

As illustrated in Figure 8a,b, by partially substituting silver in an as-obtained Ag hydrogel with platinum by a post GRR, a hierarchically structured Pt–Ag nanotubular gel was obtained.\(^{[87]}\) It was found that the original building blocks, e.g., fused Ag NWs, were converted to interconnected nanotubes with a similar diameter (several tens of nanometers), which were made up of many thin NWs (diameter of \(\approx 2.6 \text{ nm}\)). This

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**Figure 8.** Hierarchically structured NMAs obtained by posttreatment. a,b) Synthesis process of Ag–Pt hierarchically structured gels by post GRR, and SEM and TEM images of the corresponding gel. Adapted with permission.\(^{[87]}\) Copyright 2016, American Chemical Society. c,d) Schematic illustration of Au–Cu gels before and after Pd anchoring, and the STEM-EELS mapping of a Pd-anchored gel. Adapted with permission.\(^{[88]}\) Copyright 2018, Elsevier.
special two-level structure considerably improves the SSA from 10.0 m² g⁻¹ for the original Ag aerogel to 83.4 m² g⁻¹ for the Pt–Ag nanotubular aerogel. A PdAu–Pt core–shell aerogel, presented by the same group,[86] was created by the sequential underpotential deposition of copper on an as-obtained Pd–Au hydrogel and the galvanic replacement of copper by platinum. Because the theoretical basis of the underpotential deposition is the strong interactions between the deposition metal and the substrate, only an ultrathin Pt shell was produced throughout the 3D gel network, allowing both an ultrahigh utilization of Pt atoms and the efficient modulation of strain in the Pt shell. The resulting PdAu–Pt core–shell aerogels displayed high SSAs of 83–105 m² g⁻¹. Another type of hierarchically structured aerogel was delivered by Shi et al.[88] where Pd ensembles were anchored on the surface of as-obtained AuCu gels by GRR between [PdCl₄]²⁻ and Cu (Figure 8c,d). Notably, an ice bath was adopted to generate a low temperature environment during GRR, because the retarded reaction kinetics is essential to produce Pd nanoclusters instead of thick Pd shells on the gel surfaces.

3.5.4. Gelation Mechanism Investigation

Presumably because of the complicated reaction environment, the underlying mechanism for gel formation is scarcely analyzed and a deep understanding of the sol–gel process in noble metal systems is missing. Notably, the gelation behavior of noble metal NPs is remarkably different from widely studied systems, such as nanocarbons or polymers.[33,39] First, the typical threshold concentration for gelating noble metals (e.g., 0.04 mg mL⁻¹) is significantly lower than that of other systems (≥1 mg mL⁻¹). Second, a thin gel film at the container bottom is frequently observed for noble metal systems (especially for gels obtained from dilute solutions), whereas a large gel with the volume resembling that of the original solution is often obtained for other systems. On this occasion, a deep interpretation of the formation mechanism of noble metal gels is particularly essential, which will greatly fertilize the NMA manipulation and the study of correlations between their composition/structure and property/performance. Due to the natural decoupling of the NP and gel formation processes, the two-step method considerably facilitates the gelation mechanism exploration. Hence, in this section, the discussion will be primarily based on the two-step sol-gel method.

The gelation is a process where the initially stable solution is destabilized and the dispersed building blocks are linked together extending into 3D space via certain covalent or nonvalent interactions, thus triggering the phase separation and the formation of porous networks. The gelation process is accompanied with a decreasing enthalpy change from covalent/noncovalent bonding of the building blocks and a decreasing entropy from the reduced degrees of freedom, where the former effect promotes the assembly and the latter effect retards it.[20,71] Since the change of Gibbs-free energy is governed by the above two effects, the gel will form when the enthalpy effect excels the entropy effect throughout the reaction process. For the two-step sol–gel process, the reaction system usually includes metal NPs, stabilizers (or ligands), solvents (usually water), initiators, and other components (e.g., unreacted reductants). To investigate the gelation mechanism, the mission is to figure out how these ligand-capped or ligand-free NPs assemble to a macroscopic 3D network in such a complex environment.

Instead of depicting the holistic gelation process, usually the driving force, i.e., the core of the NP assembling, is discussed. For example, oxidants, either H₂O₂ or C(NO₂)₄,[20,69] were applied to etch the surface ligands, thus inducing the fusion of the resulting bare NPs. This idea was first explored in producing semiconductor chalcogenide aerogels from the corresponding colloidal solutions,[89] and then transferred to noble metal systems without a clear proof for the underlying process. From the knowledge of colloidal chemistry, poor solvents (e.g., ethanol) or electrolytes (e.g., NaCl) have been used to destabilize the NP colloidal solutions by reducing the NP solubility and screening the interparticle electrostatic repulsion, respectively.[20,71] By further considering the specific ion effects, which are dictated by the Hofmeister series, our group demonstrated that salts can simultaneously trigger the gelation and tune the material structure.[24] Introducing opposite-charged multivalent ions, e.g., Ca²⁺ ions, is another way that can link electrostatically stabilized NPs,[71] which had been applied in other gel systems.[90] However, the underlying mechanism is elusive because no calcium was detected in the resulting aerogels, which doubts its role as crosslinker. For certain highly concentrated systems, the enhanced Brownian motion resulting from elevated temperatures (313–348 K) was proven to efficiently destabilize solutions and induce gelation without introducing extra chemicals.

To go a step further, quite a few studies tried to reveal the gelation process resorting to time-lapse techniques. Time-lapse ex situ TEM imaging has been well developed to monitor the network evolution during gelation, which is used to give a direct impression of the network development and ligament size changes at different stages.[45,46] On the other hand, in situ UV–vis spectroscopy has been applied to indirectly deduce the structure change during the reaction, where the red shift and broadening of the plasmon absorption from the metal nanostructures can qualitatively reflect real-time information regarding the ligament size growth as well as the network formation.[45] However, these time-lapse techniques, especially when used alone, give only limited insight in the gelation process, thus contributing only little understanding to the underlying mechanisms.

Therefore, despite quite a few efforts made as shown above, sufficient proofs have not been provided and some key questions regarding the assembling process remain open. For example, poor solvents and electrolytes do destabilize colloidal solutions, while there is no explanation of how the ligands leave the NP surfaces and thus inducing NP fusion. In this regard, the in-depth understanding of the corresponding gelation mechanism is far from satisfactory, discouraging the on-target structure control and material optimization toward specific applications. Hence, clear physical pictures and reasonable models for the gelation process are highly desired, which should explain not only the driving forces triggering the NP assembly but also the macroscopic phenomena featured by the noble metal systems.

Regarding the one-step gelation process, in spite of the grand difficulties, Lin’s group has proposed an orientated attachment
model for the gel formation by combining the knowledge from NW growth and time-lapse TEM observation.[83] The MCu (M = Pd, Pt, and Au) gels were fabricated as described above. From TEM imaging, it is deduced that both NPs and short fused NWs form at the initial reaction stage. With prolonged time, these capping-agent-free NPs/intermediates attach to each other and develop branched gel networks driven by their high surface energy.

For the underlying mechanism of the two-step sol–gel method, taking the salt-induced gelation system as a platform, our group recently made a primary attempt and presented a physical picture of the overall gelation process.[24] The gelation of noble metals is interpreted from two aspects, i.e., the macroscopic phenomenon and the nanoscale interactions. In the first place, from the observed phenomenon and the results of various time-lapse techniques, including UV–vis spectroscopy, dynamic light scattering, TEM imaging, and optical imaging, a general model for the gelation process in noble metal systems was concluded (Figure 9a,b). Upon the addition of initiators, noble metal salts or particles are immediately converted to primary aggregates, leading to a sharp decrease of the substance concentration. Driven by the combined force of gravity (G), buoyancy (f), and viscous drag (F), these heavy aggregates sedimentate and grow at the same time. With continuous sedimentation, the increasing concentration at the bottom enhances the chance for collisions and connections between the aggregates, eventually reaching the threshold concentration and producing a gel film. The aggregates were proven to maintain the reaction activity throughout the gelation process, which further verifies the feasibility of the proposed description. Compared to noble metals which feature high bulk densities (10–20 g cm$^{-3}$), other materials usually hold much lower densities (typically <3 g cm$^{-3}$) that lead to less pronounced sedimentation, thereby retarding the automatically concentrating of the building blocks at the bottom and confining the gel formation only to the bulk solutions. To this end, the differences in the macroscopic phenomena during the gelation process for noble metals and other material systems could be reasonably explained.

The nanoscale interactions, which are specific for the destabilization method by salts, were also analyzed (Figure 9c–f). Upon the addition of salts, citrate-capped Au NPs approach each other due to salting out effects. Afterwards, presumably due to electrostatic
attraction, negatively charged ligands are stripped away from the NP surfaces by positively charged salt cations. This is partially supported by combined experiments and calculations, where stronger cation–ligand interactions increase the isotropic attraction force between NPs, thus resulting in larger ligament sizes. The removal of ligands exposes the high-energy NP surfaces, leading to the fusion of uncapped NPs both axially and radially, where the growing extent along two directions is mainly determined by the relative ratio of the van der Waals attraction and the electrostatic repulsion. This mechanism provides the theoretical basis for the ligament size manipulation of NMAs by using different salts.

4. Applications

Featuring the unique optical and electronic properties of noble metals as well as the monolithic porous structure of foams, NMAs manifest many intriguing properties and have been applied in a wide range of fields. Because of the increasing energy crisis globally, important energy-related electrocatalytic reactions which are involved in fuel cells, water splitting, and batteries dominate the applications of NMAs. Therefore, this section comprises a number of important application fields of NMAs, including electrocatalysis, heterogeneous catalysis, SERS, sensors, hydrogen storage, etc., with particular emphasis on the first one. In each part, aside from the merits achieved by NMAs, the uniqueness and relevance of noble metals toward the corresponding applications will be analyzed. In addition, the current challenges and future opportunities using NMAs will be shortly discussed.

4.1. Electrocatalysis

In light of practical demands of society as well as the attributes of NMAs, electrocatalysis of important and industry-relevant electrode reactions is the most frequently explored application. NMAs feature highly efficient catalytic centers, excellent electrical conductivity, self-supported structures, extended surfaces, and interconnected pores, thus meriting countless accessible active sites, 3D mass/electron transfer expressways, and short reactant diffusion lengths. In addition, because of negligible foreign components, they also offer opportunities to study the intrinsic electrocatalytic properties of nanosized noble metals. As a type of emerging high-performance catalysts, NMAs excel not only most non-noble-metal catalysts due to the intrinsic high catalytic activities, but also the carbon-supported noble metal NPs owing to the elimination of corrodible supporting substrates.

Despite these merits, many crucial issues remain. The high production cost, insufficient microstructure control (e.g., ligament sizes and facets), and the ambiguous correlation between performance and physicochemical parameters of aerogels impede the practical use of NMAs. Additionally, the discrepancies in the preparation techniques of the catalyst ink, the calculation of the loading amount, and the estimation of the electrochemical surface area (ECSA) require special care, because these parameters can result in a large performance difference for the same commercial catalyst tested under similar conditions. Moreover, certain ECSA estimation methods have limitations, e.g., the calculation from the reduction charge of metal hydroxides may not be suitable for calculating the ECSA of a single metal in alloy systems, and the existence of Pd (showing a strong affinity to hydrogen) can interfere the ECSA quantification of Pt which is calculated by the charge of underpotential deposition of hydrogen. Under such circumstances, a mass-normalized activity is a more suitable and reliable index to evaluate the catalyst activities. Finally, certain important electrochemical reactions, such as the electrocatalytic HER, remain to be explored with NMAs.

NMAs, especially NMAs, have been explored in a wide range of electrochemically catalytic processes that are related to fuel cells, biofuel cells, batteries, water splitting, and so on. Relying on the chemical compositions of NMAs, the studied electrocatalytic reactions comprise the AOR, glucose oxidation reaction (GOR), OER, ORR, CO2-RR, etc. In this section, electrocatalysis will be presented in two classes, i.e., electrocatalytic oxidation reactions and electrocatalytic reduction reactions.

4.1.1. Electrocatalytic Oxidation Reactions

Alcohol Oxidation Reaction: AOR receives the most popularity among the studied electrocatalytic reactions for NMAs, which can serve as a model reaction to evaluate the potential of the corresponding catalysts. Moreover, AOR is the anodic reaction in a direct alcohol fuel cell, which is of vital industrial value. Within this framework, the methanol oxidation reaction (MOR), ethanol oxidation reaction (EOR), and ethylene glycol oxidation reaction have been investigated, in which the Pd and Pd-containing alloy aerogels are mostly involved due to the intrinsically high activity of palladium.

The electrocatalytic performance of AOR is characterized by conducting cyclic voltammetry (CV) in the presence of the corresponding alcohol, where the forward peak (i.e., the anodic peak) represents the oxidation of freshly adsorbed alcohol, while the backward peak marks the removal of carbonaceous intermediates produced in the forward scan. Usually, a high mass-normalized peak current density of the forward scan (Ia) as well as a large ratio of the peak current densities of the forward/backward scans (Ia/Ib) is favored. The first work is reported on CD-capped Pd aerogels, in which the highest performance with an Ia/Ib of 1.28 and an Ib of about 2.3 times as high as that of Pd/C were obtained for EOR. Later on, composition and microstructure modulation of aerogels have been demonstrated to enhance the EOR performance. As displayed in Figure 10a–c, a stepwise GRR on Ag NPs followed by oxidant-induced gelation produced ternary alloy aerogels, displaying an Ib of about two times higher than that of Pd/C. By incorporating Cu and Au/Pd into palladium aerogels, Ib of about ~3 and 6.1 times higher than that of Pd/C for EOR were reported, respectively. The high performance was attributed to the synergy of electronic effects from the multimetallic alloys and geometric effects from structural features of aerogels. From the geometry modulation, Shi et al. further enhanced the activity by delicately decorating ultrathin Pd ensembles on Cu–Cu aerogels, acquiring a record-high Ib of 11.6 times higher than that of Pd black. This excellent performance was
ascribed to the large number of isolated Pd atoms on the aerogel surfaces, which remarkably boost the catalytic activity. Via simultaneously engineering the microstructure and composition, Cai et al.\[66,67\] reported hierarchically structured Ni–Pd\(_x\)Pt\(_y\) aerogels. As seen from Figure 10d,e, the morphology of the building blocks was tuned from hollow spheres to dendrite-like NPs by controlling the Pd/Pt ratio, and a homogeneous element distribution was observed. Ascribed to the synergy of regulated morphologies and multimetallic effects, the \(I_f\) of the optimized aerogel (Ni-Pd\(_{60}\)Pt\(_{40}\)) manifested an enhancement factor of 10.6 and 7.6 compared to commercial Pd/C and Pt/C catalysts, respectively (Figure 10f).

Aside from EOR, Lin’s group also investigated the performance of NMAs for other AOR. With optimized Au–Pt aerogels obtained by a NaBH\(_4\)-assisted synthesis at elevated temperatures, the AuPt\(_x\) aerogel was found to show a 2.5-fold enhancement of \(I_f\) compared to Pt/C (Figure 10g–k).\[74\] The same group further demonstrated PdPb@Pd aerogels prepared by a NaH\(_2\)PO\(_2\)-assisted synthesis, giving rise to a superior electrocatalyst towards the ethylene glycol oxidation which exhibits a mass activity of 5.8 times higher than that of Pd black.\[85\]

The electrocatalytic performance was mainly correlated to the number of active sites as reflected by ECSA. Generally, Pd-based aerogels display AOR activities being typically \(\approx\)2–12 times higher than that of commercial Pd black or Pd/C catalysts by reasonable devising the chemical compositions and microstructures, so as to activate both the electronic effects (ligand effects) and geometric effects. However, the \(I_f/I_b\) of aerogel catalysts often fall into the range between 1.0 and 1.5, displaying only slight differences compared to commercial catalysts. Additionally, the rapid performance decay for both NMF catalysts and commercial catalysts, despite recoverable, is another issue remaining to be tackled.

Glucose Oxidation Reaction: Glucose is an important class of biofuels for fuel cells, where the GOR serves as the anode reaction. In addition, the GOR is also critical for sugar sensing in human blood. Hence, devising materials for enhanced GOR electrocatalysis is of paramount practical relevance.\[73\] Taking advantage of the 3D electrically conductive networks with abundant pores in NMFs, Wen et al.\[73\] used Pd aerogels as electrode-enhancing material to boost the bioelectrocatalytic performance of glucose oxidase (GOD) toward glucose.
oxidation (Figure 11a). It was found that the anodic catalytic current of the GOR dramatically improved from 0.22 μA for a pure GOD to 11.96 μA for a GOD/Pd aerogel electrode, manifesting a remarkable enhancement effect of Pd aerogels. By further immobilizing bilirubin oxidase (BOD) to serve as the cathode, the same group assembled a BOD/Pd–Pt aerogel and a GOD/Pd aerogel into a membraneless glucose/O2 biofuel cell (Figure 11b,c), where the catalytic activity primarily originates from BOD and GOD, while the aerogels enhance the activity by offering highly conductive networks. The high selectivity of the enzymes retarded the crossover effect and eliminated the requirement of a selectively permeable membrane, which is advantageous compared to normal fuel cells. In comparison with the enhancement provided by Pd-based aerogels, Au aerogels were shown to directly electrochemically catalyze the GOR. The enhanced performance was found not only enabled by high SSA or ECSA, but also correlated to the capping ligands (e.g., β-CD) due to their interactions with glucose.

Oxygen Evolution Reaction: Due to a large overpotential (usually >300 mV), the OER is the half reaction, which determines the efficiency of electrochemical water splitting. Noble metals such as ruthenium, iridium, and their oxides are predominantly applied in this field due to their intrinsic high activity for OER catalysis. Gelating these noble metals should potentially enhance the performance for the OER due to the structural features of aerogels. However, compared to the Au and Pd counterparts, it is much more difficult to form Ru- and Ir-based aerogels. Very recently, Lin’s group pioneered introducing Ir into aerogels with the aid of copper and investigated the corresponding OER performance (Figure 11d–g). Ascribed to both the nanovoid microstructure and the coexistence of Ir and Cu, the optimized Ir3Cu aerogel showed an overpotential of 298 mV, a Tafel slope of 47.4 mV dec−1, as well as a surface-normalized specific activity ≈3.5 times higher than that of IrO2 NPs. Further DFT calculations depicted a volcano
curve by plotting the specific activity versus binding energy of adsorbed oxygen species (e.g., O\(^2\), OH\(^-\), and OOH\(^-\)), suggesting that an appropriate adsorption strength of oxygen species on electrode materials is crucial for the catalytic performance. Because of the significant practical importance, more efforts on creating Ru- and Ir-based NMFs are needed to obtain superior OER electrocatalysts.

Other Oxidation Reactions: Besides the aforementioned reactions, NMFs have also been sporadically explored in electrocatalysis of other oxidation reactions. For instance, the electrocatalytic borohydride oxidation was studied by Wang et al.\(^{[81]}\) over Au–Cu aerogels. As displayed in Figure 11h,i, despite similar rapid current decays, the Au\(_{52}\)Cu\(_{48}\) aerogel displayed the highest activity. This high activity was ascribed to a suitable d-band center level, which well balances the BH\(_4^-\) adsorption and the intermediate desorption, thereby allowing the highest activity sitting on the peak of the volcano curve of the activity versus Cu content.

Electrocatalytic formic oxidation (FOR) reaction, which can also serve as the anodic reaction in a fuel cell, has been studied over a library of NMAs on the basis of Pt–Ag, Pd–Cu, Ag–Au–Pt, etc.\(^{[22,87,94]}\) As illustrated in Figure 11j,k, Ag\(_{50}\)Au\(_{50}\)Pd\(_{30}\) sponges displayed high performance exceeding that of Ag\(_{50}\)Pd\(_{50}\) sponges, Pd sponges, and Pd NPs, which was claimed to root in the synergy provided by different metals such as alloying effects and increasing grain–grain interfaces.\(^{[22]}\) Similar to other electrocatalytic oxidation reactions, a rapid current decay was observed during long-term operation, which could be attributed to surface blocking by accumulated intermediates in situ generated during the reactions.

4.1.2. Electrocatalytic Reduction Reaction

Oxygen Reduction Reaction: In spite of the large number of studies spanning several decades and the applied electrocatalysts ranging from Pt-based, transition-metal-based, Fe–NC to metal-free materials, ORR is still the bottleneck cathodic reaction, which is indispensable in fuel cells and Li–O\(_2\) batteries. The advent of NMFs may bring about new hope to address this sluggish reaction. In addition to large SSAs and rich electron/mass transfer channels, their remarkably higher stability than carbon-supported Pt catalysts and higher activity compared to noble-metal-free catalysts have rendered them as superior candidates for ORR catalysis, especially in acid environment. Here, NMFs for ORR electrocatalysts are mostly based on Pt or Pt-based alloy aerogels. Liu et al.\(^{[79]}\) launched the ORR electrocatalysis study in 0.1 M HClO\(_4\) aqueous solution by using Pd–Pt bimetallic aerogels as unsupported catalyst. As shown in Figure 12a,b, a volcano curve was observed for the electrocatalytic performance as a function of the chemical composition, where the Pd\(_{20}\)Pt\(_{50}\) aerogel exhibited a maximal catalytic current which was well beyond that of commercial Pt/C. The remarkable activity of the Pd\(_{20}\)Pt\(_{50}\) aerogel was explained by its appropriate d-band center, which best balances the free energies of O\(_2\) adsorption and the surface coverage of intermediates. Following this work, different combinations of chemical composition, such as Pd–Ni and Au–Cu systems have been explored for the ORR, reaching slightly higher mass-specific activity than that of Pt/C when performing both in a three-electrode system or in membrane electrode assemblies.\(^{[80,81,95]}\) Impressively, an enhanced durability was frequently seen for NMAs compared to Pt/C, which could be ascribed to the elimination of corrodible carbon substrates.\(^{[79]}\)

In addition, multi-metallic Au–Pt/Pd or Pd–Au–Pt core–shell-structured aerogels have been also investigated, where the unique core–shell structure can not only boost the performance by both electronic and strain effects, but also increase the utilization efficiency of platinum.\(^{[41,96]}\) As seen from Figure 12c, a continuous Pt shell conformally grew on fused Au–Pd core NWs. A remarkably high Pt utilization efficiency was obtained on a Pd\(_{20}\)Au–Pt aerogel, which was 18.7 times higher than that of commercial Pt/C (Figure 12d).\(^{[41]}\) A delicate characterization suggested that the lattice parameter of the core substrate can serve as a new descriptor to predict the activity of ORR performance, by which a volcano curve was derived as shown in Figure 12e. The mechanism behind could be attributed to exerted strain on the Pt shell originating from the lattice mismatch with the core substrate.

CO\(_2\) Reduction Reaction: The electrochemical reduction of CO\(_2\), the most significant greenhouse gas, can not only address environment-related issues, such as global warming, by closing the anthropogenic carbon cycle, but also produce high value-added fuels by using the intermittent electricity generated from renewable energy sources (solar energy, wind energy, tidal energy, etc.). Very recently, Lu et al.\(^{[80]}\) initiated the studies of CO\(_2\)-RR on NMAs. In their work, palladium was paired with copper to produce bimetallic Pd–Cu aerogels, so as to address the low selectivity (i.e., Faradic efficiency) of CH\(_4\)OH production. Instead of a Pd–Cu alloy, crystallized Pd and amorphous Cu were observed along the gel network. As illustrated in Figure 12f, the methanol selectivity strongly correlates with the aerogel composition and reaches a maximum for Pd\(_{83}\)Cu\(_{17}\) over a wide potential range. According to XPS analysis, a high proportion of low-valence-state metal species (Pd\(^0\), Cu\(^0\), and Cu\(^1\)) may account for the high selectivity of Pd\(_{83}\)Cu\(_{17}\) (Figure 12g,h).

4.2. Heterogeneous Catalysis

Heterogeneous catalysis, where the catalyst and the reactant inhabit in different phases, features extraordinary merits in selectively catalyzing a wide range of reactions, where the catalysts can be easily separated and recycled, thus reducing production costs and facilitating continuous operation. In this light, chemical and energy industries, such as ammonia synthesis (Haber-Basch process) or hydrogen production by steam reforming, rely heavily on heterogeneous catalytic reactions. In this manuscript, “heterogeneous catalysis” only refers to the processes without applying external potentials, so as to differentiate it from electrocatalysis as discussed in the last section.

Heterogeneous catalysis is usually performed on solid catalysts, where active nanoparticles (typically 1–20 nm) are dispersed on a large-surface-area support.\(^{[97]}\) As one kind of the most promising and widely used heterocatalysts, noble metals have been employed not only in fundamental synthetic organic chemistry (e.g., C–C coupling reactions and hydrogenation), but also in practical use (e.g., automotive converters and environment
pollution remediation).\textsuperscript{[97–99]} The advent of unsupported noble metal catalysts with nanostructured monolithic skeleton (i.e., NMFs) marked a landmark progress, which provides an extended surface with a large fraction of low-coordinated surface atoms and good structure stability.\textsuperscript{[99]} These combined features considerably promote the catalytic activities/stabilities. In comparison with electrocatalysis where Pd- and Pt-based NMFs are prevalently applied, gold foams are almost exclusively used for heterogeneous catalysis, presumably due to its mature synthesis technique, excellent mechanical strength for easy recycling, nontoxic nature, and high selectivity for a library of catalytic reactions at low temperatures.\textsuperscript{[49,99,100]} In this section, the discussion will be divided into three parts, i.e., gas-phase catalysis, liquid-phase catalysis, and catalytic growth of carbon materials.

4.2.1. Gas-Phase Catalysis

The exploration of gas-phase catalysis on NMFs is primarily focused on aerobic oxidation reactions (oxidation of CO and primary alcohols) on monolithic gold foams, which are obtained by dealloying Au–Ag alloys. Here, the bonding and activation of molecular oxygen are believed to be the basis for an effective catalysis.

\textbf{CO Oxidation Reaction:} The aerobic oxidation of CO is among the most studied gas phase catalytic reactions on gold foams, which displays significant industrial relevance in eliminating CO during exhaust gas treatment (e.g., in automotive converters) and in the purification of feed gas (e.g., H\textsubscript{2}) in fuel cells. Although Pt/Pd catalysts have been used for automotive converters in cars, they usually work at high temperatures, thereby causing CO pollution during the first several minutes after starting the engine. In contrast, rationally structured gold is able to oxidize CO at room temperature, thus providing the possibility of solving the pollution problem during the cold start-up period.

Bäumer’s group pioneered the research on CO oxidation on gold foams obtained by chemical dealloying with HNO\textsubscript{3}.\textsuperscript{[4]} They observed an unexpectedly high catalytic activity of gold foams at ambient pressure and a wide temperature range after...
activation at 50–75 °C, where an almost total conversion at –20 °C was found at CO concentrations up to 2 vol%. Besides the unique self-supported structure, the high activity was also ascribed to remaining silver segregating on the foam surfaces, which was determined as 4.4% by surface analysis (XPS) and 0.7% by bulk-phase analysis (atomic absorption spectroscopy). The mechanism for the silver-assisted activity improvement was explained by the promotion of either O₂ dissociation or O₂⁻ formation, thus enhancing the oxidation reaction.

In another milestone work reported by Ding’s group, an anodic potential was applied during the dealloying,[49] cutting down the ligament size of the gold foams to less than 6 nm, which is much smaller than that of foams obtained by the sole chemical dealloying process (20–40 nm). As shown in Figure 13a, without any preactivation step, a stable CO conversion rate (>99%) was observed over 20 h operation at 1 vol% CO across 0–30 °C with a turnover frequency (TOF) of about 0.034 s⁻¹. Even at –30 °C, gold foams retained a CO conversion rate of above 85% over 30 h.

**Alcohol Oxidation Reaction:** Another industry-relevant gas phase reaction is the aerobic oxidation of primary alcohols. Especially methanol is converted into its oxidation products on the order of millions of tons per year.[99] Gold has been proven for partial oxidation of alcohols, which is attributed to the delicate balance between its oxidation power and the relatively weak interaction with partially oxidized products. The first report was delivered by Wittstock and co-workers,[100] presenting the gas-phase oxidative coupling of methanol to methyl formate—a precursor for the formic acid synthesis—with high selectivities (>97%) and TOF (0.11–0.26 s⁻¹) below 80 °C. The proposed mechanism for selective oxidation is illustrated in Figure 13b. Methanol is activated...
by surface oxygen and bonded at the surface as methoxy, followed by the deprotonation to form aldehyde (rate-limiting step), and subsequently the fast coupling with another methoxy to produce methyl formate. The role of residual silver was also investigated, where Ag can promote the formation of reactive oxygen, thus favoring the total oxidation to CO$_2$ instead of the partial oxidation to methyl formate. Compared to previously adopted catalysts, gold foams feature a solvent- and base-free synthesis at ambient pressure and low temperatures, unlocking a green route for selective methanol oxidation. Later on, the gold foam was further extended to catalyze the oxidation of other primary alcohols (ethanol and n-butanol), providing an ideal platform for a predictable catalyst based on UHV model experiments.

4.2.2. Liquid-Phase Catalysis

A growing interest on heterogeneous catalysis of liquid-phase oxidation and reduction reactions has sparked during the last few years, which is favored for synthetic organic chemistry. Here, oxidation reactions, reduction reactions, and dye decomposition reactions will be sequentially narrated.

Oxidation Reactions: Besides the gas-phase oxidation of CO and primary alcohols, gold foams have also been applied for liquid-phase oxidation reactions. Oxidation of D-glucose was performed on gold foams by Ding’s group.[102] The size effect was studied on foams featuring tunable ligament sizes from 6 to 250 nm (Figure 13c), suggesting a superior activity for the smaller-sized foam due to its large surface-to-volume ratio as well as the abundant low-coordination vertex and edge atoms. It was found that the increasing amount of residual silver in the foams decreased the catalytic activity, which indicates the negligible role of silver for the glucose oxidation. In another work, the oxidation of organosilanes to the corresponding silanols was presented by Asao et al.,[103] in which manifold work, the oxidation of organosilanes to the corresponding negligible role of silver for the glucose oxidation. In another work, the oxidation of organosilanes to the corresponding silanols was presented by Asao et al.,[103] in which manifold organosilanes were catalytically oxidized to silanols with high yields (80–99%) and TOF ($\approx 3.0$ s$^{-1}$) under ambient pressure and temperature. More importantly, the activity of the catalysts remained unchanged for five cycles, indicating an excellent recyclability.

Reduction Reactions: Due to the limited ability of dissociating H$_2$, gold is unsuccessful for catalyzing hydrogenation. By using organosilanes and water as hydrogen sources as well as amines as additives, Yamamoto’s group demonstrated that gold foams can serve as efficient heterogeneous catalysts for selective semi-hydrogenation of alkynes (Figure 13d).[104] The amines were found to suppress the association of hydrogen atoms to hydrogen molecules, thus promoting the hydrogenation of alkynes with high yields and perfect enantioselectivity (>99%). The same group further reported the chemoselective hydrogenation of C=C, C=C, C=N, and C=O bonds under mild conditions (8 atm H$_2$ pressure, 90 °C) on gold foams.[105] By surveying a wide range of reactions, they found that a decreasing amount of silver residuals in foams showed better catalytic performance in hydrogenation reactions, which is on the contrary of the trend observed in oxidation reactions. Recently, an asymmetric catalytic hydrogenation was performed on Pt aerogels derived from organic-phase synthesis,[137] while a lower enantiomeric selectivity was observed compared to that catalyzed by commercial Pt/$\text{Al}_2\text{O}_3$ catalysts.

Dye Degradation: The degradation of dyes, which is also a liquid-phase heterocatalytic process, holds great promise in the remediation of industrially polluted water. As shown in Figure 13e, Ag$_{34}$Au$_{33}$Pd$_{33}$ can rapidly bleach Congo red in the presence of NaBH$_4$ with a rate constant of 74.8 x 10$^{-3}$ s$^{-1}$, increasing the reaction rate by more than a thousand times compared to decolorization in pure NaBH$_4$ solutions.[22]

4.2.3. Catalytic Growth of Carbon Materials

NMFs have also been applied to the catalytic growth of inorganic materials. Tappan et al.[19] reported that gold foams prepared by combustion synthesis were capable of growing carbon nanotubes (CNTs) and carbon nanofibers (CNFs) (Figure 13f,g). However, presumably because of the widely distributed sizes of the nanostructures in foams, both CNTs and CNFs were produced without a good controllability.

4.3. Surface-Enhanced Raman Scattering

One of the unique features of noble metal nanostructures is their extraordinary surface plasmon resonance falling into the visible light region, which is induced by the coupling of the incident light and the collective oscillation of the surface-free electrons.[106] Taking this advantage, a huge local electric field is produced surrounding the nanoparticles, dramatically enhancing the spectroscopic signal from adsorbed molecules by a factor that can be larger than 10$^{10}$.[106] In this light, the SERS technique that is used for ultrasensitive detection is developed primarily on metal nanostructures, especially for gold and silver. Compared to conventional SERS substrates where noble metal nanostructures are supported on a flat surface, NMFs provide a freestanding 3D substrate entirely made of SERS-active metal nanostructures, which may further enhance the signal intensity and enable the detection without the need for precise focusing exactly on a 2D surface.

Tang et al.[22] showed the first SERS study on NMFs, where a compressed Ag foam was used for the SERS detection of rhodamine B (Rhb). As shown in Figure 14a, b, the Ag foam manifested a significant enhancement compared to that on smooth silver and several other supported silver nanostructures, achieving a detection limit down to 10$^{-6}$–10$^{-7}$ μmol. In another work, the morphology effect on the optical fingerprint of NMA was investigated by assembling differently structured Au–Ag alloy NPs into corresponding gels.[70] It was found that the Raman signals of Rd 101 (the probe molecule) on aerogels were 10–80 times stronger than those of the corresponding NPs. In addition, the highest enhancement was observed on the gel with more interparticle gaps, which are believed to serve as hot spots in the 3D networks that considerably boost the signal intensities.

Despite certain progresses, the efforts in this fascinating direction are still very limited. Certain challenges, including the weak mechanical strength of the NMFs and the lack of a theoretical model to predict the enhancement with aerogels, remain to be addressed.
4.4. Actuation and Sensing

Combining the high SSA, 3D conductive networks, and the reaction activity on nanosized surfaces, NMFs have been applied for actuation and sensing. In light of the tunable surface chemistry, Biener et al. realized the actuation on a gold foam. The alternate exposure of the foam to O₃ and CO can change the gold surface to either an oxygen-covered state or a clean state ascribing to the surface reactions, thus causing reversible surface stress changes and the corresponding contraction/expansion of the foam (Figure 14c,d). Despite the small amplitudes achieved (0.05–0.5%), this work demonstrates the concept of the conversion of chemical energy from nanoscale reactions to macroscopically measurable mechanical energy.

Very recently, enzyme-based biosensors for the electrochemical detection of organophosphorus (OPs) compounds, which are among the toxic pesticides, were fabricated on the basis of Au–Pt hydrogels (Figure 14e,f). The toxicity of OPs can be reflected by the irreversible binding of acetylcholinesterase (AChE), thus inhibiting their hydrolyzing activity towards, e.g., acetylthiocholine (ATCh). Hence, by electrochemically monitoring the hydrolyzed products of ATCh (i.e., thiocholine (TCh)), the toxic OPs could be indirectly detected. On this basis, polydopamine-capped Au–Pt aerogels are applied for both immobilizing ATCh by polydopamine and amplifying electrochemical signals by the conductive gel networks. As a result, the as-fabricated biosensor displayed a wide linear region of 0.5–1000 ng L⁻¹ with a low detection limit (0.185 ng L⁻¹) for OPs.
4.5. Other Applications

Aside from the above mentioned examples, NMFs have been also sporadically explored in other fields, including hydrogen storage, capacitors, flexible conductors, solar steam generation, and electromagnetic interference shielding. A few examples are specified in this section.

4.5.1. Hydrogen Storage

In light of the considerable hydrogen affinity of palladium, the hydrogen storage behavior of Pd nanowire foams was studied in comparison to Pd micropowders, Pd foams demonstrated a faster hydrogen uptake kinetics and a lower onset absorption pressure. However, a reduced amount of the total H₂ absorption (15–50%) was observed in foams, which is similar to other nanosized Pd materials. Currently, this field is less explored by using NMFs. Further research, such as investigating the correlation between the structure (e.g., ligament size, morphologies) and absorption/desorption behavior (e.g., absorption kinetics, absorption capacity) of the Pd foams, and optimizing the absorption performance by tailoring the NMF composition might be rewardable directions for this application.

4.5.2. Self-Propulsion Devices

Most reported self-propulsion devices walk randomly on the water surface, which is driven by the liberated gases generated from the catalytic H₂O₂ decomposition by the corresponding materials (e.g., Pt, Ag, MnO₂). Combining the ductility and the catalytic properties of noble metals, our group has recently created a compressed heterostructured Au–Ag aerogel by simple manual pressing. As seen from Figure 15c, because of the inertness of gold and the reactivity of silver toward catalytic H₂O₂ decomposition, the resulting material exhibited an intriguing rotation behavior in 2 wt% H₂O₂ solution with an angular velocity of up to 168 rpm. The biggest challenge here is the mechanical fragileness of noble metal aerogels, which retards the fabrication of low-density and durable self-propulsion devices. In addition, the relationship between composition/structure and self-propulsion behavior remains to be clarified.

4.5.3. Flexible Conductors

Integrating highly conductive 3D networks with sufficiently high mechanical strength and flexibility, NMFs can serve as high-performance conductors for flexible electronic devices. However, the realization of such desirable mechanical properties is usually a profound challenge for NMFs. Yu’s group addressed this issue by infiltrating polydimethylsiloxane (PDMS) into Ag foams obtained by freeze-casting, where the PDMS elastomer imparted remarkable mechanical strength and flexibility. As shown in Figure 15d, ascribed to the unique hierarchical binary network architecture, the tensile strain applied to the network was shared by the 3D compartments, thus rendering a fascinating flexible conductor that can tolerate twisting, stretching, and bending without obvious defects.
The realization of these fascinating functions calls for well-tunable NMFs and a deep understanding of the correlations between application performance and material parameters. Among a number of reported fabrication approaches, the sol–gel method is currently the most popular strategy for its promising capacity for in situ monitoring the reaction process and manipulating multiscale structures, chemical compositions, and the corresponding physicochemical properties of NMFs under mild conditions. However, the understanding of the formation mechanism is still at its infant stage and the structure manipulation ability of NMFs is restrained, which affect the establishment of the corresponding models for directing material design/optimization toward certain applications. Therefore, vital challenges and equally immense opportunities coexist in both fundamental research and practical applications, some of which are summarized below.

1. Arbitrary control of material parameters. Despite a wide spectrum of available fabrication strategies, as-obtained NMFs often suffer from limited composition diversity (only Au, Ag, Pd, Pt, and alloys), less-tunable feature sizes and pore sizes, inhomogeneous structures, and less-controlled assembling modes of the nanosized building blocks. Additionally, single-atom doped NMFs, such as the gold foams that are decorated with isolated iridium single atoms, might be a promising direction that can afford large-scale production of high-performance and stable catalysts. The realization of the above conceptions calls for creative fabrication approaches with a deep understanding and systematic studies of precursors chemistry, ligand chemistry, reductant chemistry, initiator chemistry, etc.

2. Formation mechanism in the sol–gel method. As the most prevalently adopted method, the core issue lies in the ambiguous understanding of the gelation process, thus affecting facile synthesis and material manipulation. Aside from more efforts required by delicate experimental design, theoretical support with combined molecular dynamics and quantum mechanics calculations is highly desired.

3. Characterization. Certain basic characterizations for NMFs are problematic or missing, such as inappropriate density calculations, missing production yield, etc. New techniques to probe the mechanical properties of fragile NMAs as well as time-lapse techniques for in-depth understanding of the fabrication/application mechanisms remain to be developed.

4. Mechanical properties. The mechanical strength is always a problem for NMFs, which can be either too rigid (e.g., dealloying-derived foams) or too fragile (for NMAs), retarding not only applications but also fundamental characterizations. The creation of all-noble-metal-constructed foams with desirable mechanical properties has been a big unsolved challenge so far.

5. Applications. It is not uncommon to find very high-performance NMFs in the literature. However, the overemphasis on performance leads to few insightful advances, especially for the establishment of the relationship between material parameters and performance for guiding material design. Additionally, endeavors are needed to find the killer applications that embody the uniqueness and maximize the performance-to-price ratio of NMFs.
challenges and opportunities reside in fundamental studies, including the further development of the fabrication methods, investigations of the fabrication mechanisms, flexible manipulation of structures/compositions, and the establishment of composition/structure–property/performance correlations. Therefore, joint efforts from interdisciplinary scientists are desired to not only make a difference in NMFs, but also wield these promising materials to address practical demands for clean energy, environment remediation, and beyond.

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Conflict of Interest

The authors declare no conflict of interest.

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