Fabrication and Biomedical Applications of Functional Nanoporous Materials

Subjects: Nanoscience & Nanotechnology

Contributor: Gurvinder Singh

Functional nanoporous materials are categorized as an important class of nanostructured materials because of their tunable porosity and pore geometry (size, shape, and distribution) and their unique chemical and physical properties as compared with other nanostructures and bulk counterparts. Progress in developing a broad spectrum of nanoporous materials has accelerated their use for extensive applications in catalysis, sensing, separation, and environmental, energy, and biomedical areas.

nanoporous materials additive manufacturing dealloying nanoporosity hierarchical nanoporous

1. Introduction

Nanoporous materials are categorized as an important class of nanostructured material that possess unique surface and structural characteristics, including high surface area, tunable pore sizes, tunable pore geometries, as well as surface topographies with porous architectures. These unique characteristics of nanoporous materials underline their applications in various fields, such as ion-exchange [1], separation [2], catalysis [3], sensors [4], water purification [5], CO_2 capture and storage [6], renewable energy [7][8], targeted drug delivery [9], tissue engineering [10], and implants [11]. For example, the presence of highly active low-coordinated atoms (i.e., atoms with lower numbers of bonds such as atoms on surfaces, steps, and kinks) on interconnected curved backbones of nanoporous structures make them suitable for catalytic applications. Their extensive porous networks facilitate the mass transfer of reactants from the exterior surfaces to the interior surfaces, thus, enhancing the catalytic reaction rate, even at low temperatures. The lightweight and excellent mechanical properties of nanoporous materials make them suitable for use in medical implants. Furthermore, the design of nanoporous materials with variations in pore size can reduce the response time and improve sensitivity of sensing and microfluidic devices. Nanoporous materials can be used as a platform to understand and study guest–host reactions [12][13], chemical reactivities in confined environments [14], and chemical reactions involved in the synthesis of nanomaterials (nanoparticles, nanowires, and quantum dots) [15].

In general, nanoporous materials can be defined as any material with a pore size of nanoscale dimension (100 nm or less) in their structures. However, these nanoporous materials can be developed and classified into categories based on pore size, structure of the pores, crystallinity of the materials, and type of materials. In the case of pore size, these materials are subdivided, based on the international union of pure and applied chemistry (IUPAC) nomenclature, into three different categories: microporous (pore size <2 nm), mesoporous (pore size ~2–50 nm), and macroporous (pore size >50 nm) [16]. The classification of porous structures is generally based on disordered and ordered systems. Compared with disordered structures, ordered nanoporous materials are desirable for optoelectronic applications as they provide periodicity of pore sizes and, thus, facilitate greater control over their interactions with electromagnetic waves [17]. Furthermore, nanoporous materials can be categorized based on the crystallinity (i.e., amorphous vs. crystalline) of the materials used. Amorphous nanoporous materials have a hierarchy of pore sizes (a wide distribution of pore sizes) and are suitable for heterogenous catalytic reactions. These amorphous nanoporous materials are comprised of cross-linked polymers, carbon, and porous aromatic frameworks. Crystalline nanoporous materials have a narrow pore size distribution and are suitable for molecular sieving filtration where uniformity in pore size is important [18][19]. Zeolites, metal organic frameworks (MOFs), and covalent organic frameworks are examples of crystalline nanoporous materials [20][21][22]. Nanoporous materials can also be subdivided based on the material type, i.e., inorganic (zeolites, mesoporous silica), metal-organic frameworks (MOFs), and covalent-organic frameworks (COFs). MOFs are considered to be a new class of crystalline nanoporous materials with rigid nanopore structures. MOF-based nanoporous materials are formed by the interconnections of inorganic constituents (metal nodes) with organic molecules. The tunable chemical functionalities with well-defined nanopore size and geometries makes them suitable for several practical applications, such as gas separation [23], gas capture [24], energy storage [25], and catalysis [26][27][28].

Since the synthesis of mesoporous silica was first reported in the 1990s, significant progress has been made in developing strategies for fabricating nanoporous materials from a wide range of materials, including metal, metal oxides, and polymers [29][30]. The most common strategies adapted for fabricating such materials include dealloying, soft and hard template methods, physical vapor deposition, nonsacrificial templating, and block copolymers and colloidal self-assembly. These strategies have been used to fabricate ordered, disordered, and hierarchical nanoporous materials with tunable pore sizes, shapes, and relative orientation of pores at different length scales. In recent years, several reviews published on nanoporous materials have primarily focused on selective modification of nanoporous materials, synthesis, and characterization of specific types of nanoporous materials and their applications [8][17][30][31][32][33][34][35][36][37][38][39].

2. Dealloying for Fabricating Nanoporous Materials

Dealloying is considered to be a versatile and robust top-down approach to fabricate disordered and hierarchical nanoporous materials with tunable pore sizes with few nanometers. In this process, the selective dissolution and/or leaching of less noble metals from an alloy or composite material induces three-dimensional (3D) porosity in materials. This was first demonstrated in the Au-Ag alloy system. The selective dissolution of the less noble metal (Ag) due to acid treatment resulted in the formation of 3D nanoporous metals [40]. The technique can be applied to fabricate nanoporous materials with macro-scale dimensions and these materials can be engineered to different shapes prior to dealloying. The precursor alloys should be homogenous to fabricate nanoporous materials with desirable structural properties and minimal mechanical damage. Various dealloying approaches, such as chemical, electrochemical, liquid metal, and vapor phase dealloying have been established to create nanoporosity in both metals and metal oxides.

2.1. Chemical Dealloying

Chemical dealloying has been widely used to fabricate nanoporous metals and metal oxides by selective etching/leaching of less reactive species in an acidic or basic medium [41][42][43]. This process has been applied to fabricate homogenous and crack-free nanoporous Au from different precursor alloys, including Au-Ag [44], Au-Ni [45], and Au-Cu [46]. Nanoporosity has evolved as a result of the dissolution of the less noble metal (Ag) layer-by-layer, followed by surface diffusion and reorganization of more noble metal (Au) at the interface [47]. Therefore, the nanoporosity in materials can be associated with the surface mobility (diffusivity) of the more noble metal. However, the surface mobility of metal atoms should be optimal because a high surface diffusion rate of metal atoms can lead to coarsening of the nanoporous structure, which can cause undesirable effects, such as reducing the surface energy and/or area. This can cause the degradation of physical properties over time, even at room temperature.

2.2. Electrochemical Dealloying

Electrochemical dealloying is a process in which the selective dissolution of a more electrochemically active metal of low standard electrode potential from a homogenous alloy leads to the formation of 3D nanoporous structures. In this process, the elements involved in the precursor alloy should have different chemical reduction potentials. For example, nanoporous Ni can be fabricated by electrochemical etching of Cu from the homogenous Ni_xCu_{1-x} alloys because Cu has a lower standard electrode potential than Ni [48]. The technique has been employed to produce nanoporous Au [49], Ag [50], Pt [51], Pd [52], and Cu [53], as well as bimetallic nanoporous MnFe from Mn-Fe-Cu alloy [54] and PdAu [55].

2.3. Liquid Metal Dealloying

Liquid metal dealloying is a promising technique that has been adapted for fabricating nanoporous materials which uses metallic melts as the dealloying medium instead of acidic and basic media [37]. This technique relies on the solubilities of each element of precursor alloy into a liquid metal medium.

2.4. Vapor Phase Dealloying

Vapor phase dealloying utilizes differences in the vapor pressure of elements present in the precursor alloy to selectively evaporate and/or dealloy one component. In this technique, the precursor alloy is prepared by mechanically mixing the elements, followed by melt spinning to engineer a thin film. Vacuum heating introduces nanoporosity in the materials by the selective evaporation of an element from the precursor alloy. Although the formation of porosity under vacuum was observed by Balluffi and Alexander in the 1950s [56], this technique did not received a great deal of attention until it was used to generate 3D bicontinuous nanoporous Co by high vacuum heating of the mechanically prepared precursor Co_5Zn_{21} alloy [57].

3. Templating

Templating is considered to be a promising approach for fabricating ordered, disordered, and hierarchical nanoporous metals and metal oxides with tunable pore sizes and pore geometries from a wide range of materials. A templating method involves three processing steps: (i) designing a soft or hard template, (ii) material deposition or chemical reduction to the template, and (iii) nanoporous structure formation after the removal of the template. The desirable materials can be deposited on the template via numerous strategies, including physical vapor deposition, electrochemical/chemical plating, sputtering, sol-gel method, or electron evaporation. The templating approach must also meet three essential criteria: (i) the infiltration of materials into the template to generate a continuous nanoporous structure; (ii) the stability of the template after deposition of the desired materials, and (iii) an appropriate template removal strategy to obtain stable nanoporous structures.

3.1. Soft Template Method

The soft template method utilizes a micellar structure made from surfactants, and organic and block copolymeric molecules as a sacrificial template to fabricate nanoporous metals, metal oxides, and carbons. When these templates are exposed to precursor solution, precursor constituents interact with the template by weak noncovalent bonds, such as van der Waals interactions, hydrogen bonding, and electrostatic interactions. This approach offers great control over the geometry, pore size, and architecture of the nanoporous materials.

3.2. Hard Template Method

The hard template (nanocasting) method of fabrication involves the use of relatively rigid structures to fabricate uniform and regular nanoporous materials. Examples of hard templates include porous silica [58], zinc oxide [59], alumina [60], zeolite [20] or self-assembled colloidal crystals [61]. The hard template method provides additional support to nanoporous structures to retain stable pore geometry even after high temperature or solution treatment of the template. Significant progress has been made to develop scalable strategies based on evaporation for constructing 2D and 3D self-assembled colloidal crystals [62][63].

4. Microwave-Based Fabrication of Nanoporous Materials

Microwave-based techniques has been used to fabricate nanoporous materials from various materials, such as polymers, metal oxides, silica, zeolites, and metal-organic frameworks. When microwave irradiation is exposed to a precursor material, the temperature increases upon microwave penetration (conversion of microwave energy to heat). The origin of microwave heating is caused by two mechanisms: ionic conduction (oscillation of cations or anions back and forth) and dipolar polarization (fluctuations/rotations of dipoles) [33]. Microwave heating increases the temperature of the reaction mixture (not vessel) uniformly as compared with conventional methods of heating, which are slow and nonuniform. In addition, the microwave approach can fabricate nanoporous materials with high yield, purity, and selectivity. Low energy microwave heating has been employed to synthesize highly crystalline mesoporous silica [64]. In the synthesis, microwave irradiation of 120 W was applied to precursors consisting of

CTAB and sodium silicate, which led to the fabrication of highly ordered mesoporous silica of uniform pore size (~4 nm) in 30 min. The wall thickness of silica could be tuned from 0.34–0.36 nm to 0.78–0.90 nm by changing the microwave power, 120 W and 80 W, respectively (thinner nanoporous backbone at high microwave power). Attempts have also been made to fabricate heteroatom-doped mesoporous silica structures, thus, offering an avenue to alter their physical properties [65][66][67].

5. Additive Manufacturing of Nanoporous Materials

Additive manufacturing involves a layer-by-layer deposition of material to design mechanically robust 3D physical objects from digital information. In recent years, additive manufacturing has revolutionized the design 3D materials of complex architectures and customized shapes because of low production cost. Three-dimensional printing technology has been used during the recent COVID-19 pandemic to meet the demands of the healthcare industry, from personal protection equipment to medical and testing devices, personal accessories, and isolation wards [68]. Progress has also been made to use additive manufacturing in combination with traditional nanoporous fabrication methods, such as dealloying, to produce a broad spectrum of ordered or hierarchical nanoporous materials with uniform porosity. Additive manufacturing offers several benefits, including low fabrication of nanoporous materials with tunable architecture, ability to produce materials over multiple lengths from meso- to macroscale, high level of reproducibility, industrial scalability, and mechanical robustness. The 3D printing approach also has the capability to fabricate compositional gradient hierarchical porous materials by changing the composition of relative ink during the printing process, thus, providing additional structural control with new functionality.

6. Ion Beam-Induced Fabrication of Nanoporous Materials

Progress has been made to fabricate nanoporous materials by ion beam irradiation on bulk materials or 3D self-assembled crystals made from nanoparticles. The ion beam technique is a top-down destructive technique involving the irradiation of high-energy ion beams, such as Ga^+, He^+, O^+, Ar^+, or Xe^+. The proposed mechanism involved in the formation of nanopores using this method can be explained based on the combined effect of milling and sintering while being exposed to high-energy ion beam. The ion beam technique offers several advantages as compared with other fabrication strategies adapted for nanoporous materials, such as fine control over pore size distribution and an interconnected pore network by ion beam acceleration voltage, independent of material choices; no use of toxic chemicals; and no need for additional steps, such as chemical dealloying. Since the technique operates in a vacuum, air and water sensitive materials can also be used to fabricate nanoporous materials. Ion beam exposure to the materials may contaminate the backbone of nanoporous structures. However, the use of inert gas-based ion beams or thermal annealing can be used to remove ion contamination. Bischoff et al. used focused ion beam (Bi^+) to fabricate amorphous porous germanium (Ge) [69]. They showed that the porosity and porous structure could be varied by changing the accelerating voltage of ion beams (30 kV and 60 kV) and the angle of incidence. In another work, the fabrication of nanoporous indium antimonide (InSb) was demonstrated by using focused ion (Ga^+) beam [70]. The results showed a linear increase in the pore size by increasing the ion dose.

However, nonporous InSb surface with pillar structures formed at a high ion dose instead of the porous structure. Therefore, the ion dose plays a vital role in controlling the porosity.

7. Laser-Induced Fabrication of Nanoporous Materials

Laser techniques have widely been employed to generate micro- and nanopatterned surfaces [71], microfluidic channels [72], and tiny photonic waveguide structures [72]. Laser irradiation in combined with dealloying strategies have been explored for fabricating nanoporous materials. In the work of Gu et al., the fabrication of nanoporous manganese was demonstrated by laser cladding, followed by selective electrochemical dealloying [73]. Mn-Cu precursor alloy of thickness 1 mm was prepared by mixing Mn and Cu elemental powder and depositing it on the mild steel substrate. Laser power of 1.2 kW and scanning speed of 6 mm/s were used to achieve low diffusion cladding. The electrochemical dealloying of the laser processed specimen led to the formation of nanoporous MnCu. The pore size and backbone size of porous structures could be tuned by changing the electrochemical dealloying time from 30 min to 150 min. Additionally, strategies such as chemical oxidation and femtosecond laser ablation have been demonstrated to fabricate nanoporous anatase TiO_2 on a microstructured Ti-based substrate [74]. Firstly, a femtosecond laser was used to generate a primary microarray patterned Ti surface. In the next step, nanoporous TiO_2 was produced by the chemical oxidation (H_2O_2) of femtosecond laser-treated Ti surface. Finally, the nanoporous surface was thermally annealed to form anatase TiO_2 without significant change in the morphology. The annealed anatase TiO_2 showed improved photocatalytic activity and excellent stability under ultraviolet-visible (UV-Vis) light irradiation.

8. Biomedical Applications of Nanoporous Materials

Nanoporous materials have several biological and medical applications including biosensing, delivery of biological molecules, antimicrobial properties, dialysis, developing novel medical devices for orthopedics, and neural implants [75]. It has been shown that nanostructured materials can facilitate and increase cell growth, tissue remodeling, angiogenesis, and antimicrobial properties. Xu et al. demonstrated that Ti-based alloys modified by nanoporous oxidation to form nanopores and nanotubes on the substrates could facilitate enhanced cell adhesion, proliferation, and matrix deposition as compared with unmodified substrates, providing favorable conditions for tissue growth and osseointegration [76]. Furthermore, He et al. developed nanoporous surfaces by anodizing of Ti surface to generate the titania nanotubular structure to investigate the effects of nanotopography on osteogenesis. It was shown that the nanotopographical features promoted macrophage recruitments around the implants and inhibited osteoclast activity. The nanoporous Ti implants facilitated the secretion of cytokines that promoted mineralization, inhibited the activity of osteoclasts through the integrin signaling pathway, and regulated improved implant osseointegration [77].

9. Conclusions

The dealloying approach has been extensively investigated to produce nanoporous metals and metal oxides with controlled pore sizes, porous structures, and chemical composition. Although dealloying is very simple and yields mechanically robust nanoporous materials, the approach cannot be considered to be a generic technology to fabricate a wide range of materials, including soft materials. Moreover, the use of toxic chemicals used during fabrication, careful preparation of alloy, and limitations with industrial scalability restrict applying the technique to a range of applications. Templating methods can be considered to be an alternative method to dealloying approaches because of their capability to produce nanoporous inorganic, polymers, or composite materials. However, the mechanical stability of nanoporous structures is compromised and hinders their broader practical applications, since the removal of template can destabilize the nanoporous structures.

Nanoporous materials truly encompass an ever-expanding list of applications, ranging from agriculture to biosensing, tissue engineering, biomedical implants, energy, and environmental applications. Advanced fabrication technologies have allowed for growth in these areas due to their tailorability, highlighting the fact that different applications require different sets of criteria out of nanoporous materials (i.e., pore size, pore structure, crystallinity, and ordered vs. disordered structures). For example, ordered nanoporous materials prove much more efficient for optoelectronic applications because the interaction of electromagnetic waves with ordered nanopore structures can be controlled by the periodicity of nanopores. Ordered nanoporous materials are desirable for membrane and separation applications over disordered nanoporous materials. However, the disordered nanoporous materials are mechanically robust as compared with ordered nanoporous materials and, thus, can be used for the applications requiring excellent mechanical stability. Microporous materials are suitable for catalysis, sensing, and drug delivery applications. However, mesoporous materials can be used as adsorbents to remove pollutants from water and storages of gases. When nanoporous materials are exposed to harsh environments, their physical and chemical properties can degrade over time. To protect these nanoporous from degradation or aging, a coating of stable metal or doping of metal into the nanoporous structures is required to enhance the resistance towards aging.

Further work is necessary to maximize the potential benefits offered by additive manufacturing. In particular, the challenges associated with generic and environmentally friendly fabrication technology (capability to produce nanoporous materials independent of material choice without the use of toxic chemicals and materials recycling) and industrial-scale manufacturing are yet to be addressed. To minimize the environmental impact, new nanoporous manufacturing technologies should be designed and optimized to reduce the reliance on toxic and harsh solvents.

References

1. Noori, Y.; Akhbari, K. Post-synthetic ion-exchange process in nanoporous metal–organic frameworks; an effective way for modulating their structures and properties. RSC Adv. 2017, 7, 1782–1808.

2. Li, Z.; Zhang, X.; Tan, H.; Qi, W.; Wang, L.; Ali, M.C.; Zhang, H.; Chen, J.; Hu, P.; Fan, C.; et al. Combustion Fabrication of Nanoporous Graphene for Ionic Separation Membranes. Adv. Funct. Mater. 2018, 28, 1805026.
3. Sharma, S.; Saxena, V.; Baranwal, A.; Chandra, P.; Pandey, L.M. Engineered nanoporous materials mediated heterogeneous catalysts and their implications in biodiesel production. Mater. Sci. Energy Technol. 2018, 1, 11–21.
4. Wong, T.S.B.; Newman, R. Nanoporous Gold as a VOC Sensor, Based on Nanoscale Electrical Phenomena and Convolutional Neural Networks. Sensors 2020, 20, 10.
5. Wang, Z.; Wu, A.; Colombi Ciacchi, L.; Wei, G. Recent Advances in Nanoporous Membranes for Water Purification. Nanomaterials 2018, 8, 2.
6. Sneddon, G.; Greenaway, A.; Yiu, H.H.P. The Potential Applications of Nanoporous Materials for the Adsorption, Separation, and Catalytic Conversion of Carbon Dioxide. Adv. Energy Mater. 2014, 4, 1301873.
7. Lang, X.; Hirata, A.; Fujita, T.; Chen, M. Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. Nat. Nanotechnol. 2011, 6, 232–236.
8. Fu, J.; Detsi, E.; De Hosson, J.T.M. Recent advances in nanoporous materials for renewable energy resources conversion into fuels. Surf. Coat. Technol. 2018, 347, 320–336.
9. Kapruwan, P.; Ferré-Borrull, J.; Marsal, L.F. Nanoporous Anodic Alumina Platforms for Drug Delivery Applications: Recent Advances and Perspective. Adv. Mater. Inter. 2020, 7, 2001133–2001150.
10. Davoodi, E.; Zhianmanesh, M.; Montazerian, H.; Milani, A.S.; Hoorfar, M. Nano-porous anodic alumina: Fundamentals and applications in tissue engineering. J. Mater. Sci. Mater. Med. 2020, 31, 60.
11. Guo, T.; Oztug, N.A.K.; Han, P.; Ivanovski, S.; Gulati, K. Influence of sterilization on the performance of anodized nanoporous titanium implants. Mater. Sci. Eng. C 2021, 130, 112429.
12. Wonanke, A.D.D.; Bennett, P.; Caldwell, L.; Addicoat, M.A. Role of Host-Guest Interaction in Understanding Polymerisation in Metal-Organic Frameworks. Front. Chem. 2021, 9, 559.
13. Ritter, H.; Ramm, J.H.; Brühwiler, D. Influence of the Structural Properties of Mesoporous Silica on the Adsorption of Guest Molecules. Materials 2010, 3, 8.
14. Grommet, A.B.; Feller, M.; Klajn, R. Chemical reactivity under nanoconfinement. Nat. Nanotechnol. 2020, 15, 256–271.
15. Liu, J.; Wang, N.; Yu, Y.; Yan, Y.; Zhang, H.; Li, J.; Yu, J. Carbon dots in zeolites: A new class of thermally activated delayed fluorescence materials with ultralong lifetimes. Sci. Adv. 2017, 3, 1603171–1603179.

16. Rouquerol, J.; Avnir, D.; Fairbridge, C.W.; Everett, D.H.; Haynes, J.H.; Pernicone, N.; Ramsay, J.D.F.; Sing, K.S.W.; Unger, K.K. Recommendations for the Characterization of Porous Solids. Pure Appl. Chem. 1994, 66, 1739–1758.
17. Ron, R.; Haleva, E.; Salomon, A. Nanoporous Metallic Networks: Fabrication, Optical Properties, and Applications. Adv. Mater. 2018, 30, 1706755.
18. Sayari, A. Catalysis by Crystalline Mesoporous Molecular Sieves. Chem. Mater. 1996, 8, 1840–1852.
19. Barton, T.J.; Bull, L.M.; Klemperer, W.G.; Loy, D.A.; McEnaney, B.; Misono, M.; Monson, P.A.; Pez, G.; Scherer, G.W.; Vartuli, J.C.; et al. Tailored Porous Materials. Chem. Mater. 1999, 11, 2633–2656.
20. Na, K.; Jo, C.; Kim, J.; Cho, K.; Jung, J.; Seo, Y.; Messinger Robert, J.; Chmelka Bradley, F.; Ryoo, R. Directing Zeolite Structures into Hierarchically Nanoporous Architectures. Science 2011, 333, 328–332.
21. Kushwaha, R.; Kaleeswaran, D.; Haldar, S.; Chakraborty, D.; Mullangi, D.; Borah, A.; Vinod, C.P.; Murugavel, R.; Vaidhyanathan, R. Nanoporous Covalent Organic Framework Embedded with Fe/Fe3O4 Nanoparticles as Air-Stable Low-Density Nanomagnets. ACS Appl. Nano Mater. 2020, 3, 9088–9096.
22. Yang, X.; Jiang, X.; Huang, Y.; Guo, Z.; Shao, L. Building Nanoporous Metal–Organic Frameworks “Armor” on Fibers for High-Performance Composite Materials. ACS Appl. Mater. Inter. 2017, 9, 5590–5599.
23. Jeong, H.-K. Metal–organic framework membranes: Unprecedented opportunities for gas separations. AIChE J. 2021, 67, e17258.
24. Liu, X.; Wang, M.; Zhou, S.; Wang, J.; Xin, H.; Wei, S.; Liu, S.; Wang, Z.; Lu, X. Tracking CO2 capture and separation over N2 in a flexible metal–organic framework: Insights from GCMC and DFT simulations. J. Mater. Sci. 2021, 56, 10414–10423.
25. Chakraborty, D.; Bej, S.; Sahoo, S.; Chongdar, S.; Ghosh, A.; Banerjee, P.; Bhaumik, A. Novel Nanoporous Ti-Phosphonate Metal–Organic Framework for Selective Sensing of 2,4,6-Trinitrophenol and a Promising Electrode in an Energy Storage Device. ACS Sust. Chem. Eng. 2021, 9, 14224–14237.
26. Noor, T.; Pervaiz, S.; Iqbal, N.; Nasir, H.; Zaman, N.; Sharif, M.; Pervaiz, E. Nanocomposites of NiO/CuO Based MOF with rGO: An Efficient and Robust Electrocatalyst for Methanol Oxidation Reaction in DMFC. Nanomaterials 2020, 10, 8.
27. Ahmad, R.; Iqbal, N.; Baig, M.M.; Noor, T.; Ali, G.; Gul, I.H. ZIF-67 derived nitrogen doped CNTs decorated with sulfur and Ni(OH)2 as potential electrode material for high-performance supercapacitors. Electrochim. Acta 2020, 364, 137147.

28. Rizvi, S.A.M.; Iqbal, N.; Haider, M.D.; Noor, T.; Anwar, R.; Hanif, S. Synthesis and Characterization of Cu-MOF Derived Electrocatalyst for Oxygen Reduction Reaction in PEMFC. Catal. Lett. 2020, 150, 1397–1407.
29. Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. The Preparation of Alkyltrimethylammonium–Kanemite Complexes and Their Conversion to Microporous Materials. Bull. Chem. Soc. Jpn. 1990, 63, 988–992.
30. Alothman, Z.A. A Review: Fundamental Aspects of Silicate Mesoporous Materials. Materials 2012, 5, 12.
31. Luc, W.; Jiao, F. Synthesis of Nanoporous Metals, Oxides, Carbides, and Sulfides: Beyond Nanocasting. Acc. Chem. Res. 2016, 49, 1351–1358.
32. Fechete, I.; Vedrine, J.C. Nanoporous Materials as New Engineered Catalysts for the Synthesis of Green Fuels. Molecules 2015, 20, 4.
33. Glowniak, S.; Szczesniak, B.; Choma, J.; Jaroniec, M. Advances in Microwave Synthesis of Nanoporous Materials. Adv. Mater. 2021, 33, e2103477.
34. Malgras, V.; Tang, J.; Wang, J.; Kim, J.; Torad, N.L.; Dutta, S.; Ariga, K.; Hossain, M.S.A.; Yamauchi, Y.; Wu, K.C.W. Fabrication of Nanoporous Carbon Materials with Hard- and Soft-Templating Approaches: A Review. J. Nanosci. Nanotechnol. 2019, 19, 3673–3685.
35. Wu, L.; Li, Y.; Fu, Z.; Su, B.L. Hierarchically structured porous materials: Synthesis strategies and applications in energy storage. Natl. Sci. Rev. 2020, 7, 1667–1701.
36. Yin, J.; Zhang, W.; Alhebshi, N.A.; Salah, N.; Alshareef, H.N. Synthesis Strategies of Porous Carbon for Supercapacitor Applications. Small Methods 2020, 4, 1900853.
37. Guo, X.; Zhang, C.; Tian, Q.; Yu, D. Liquid metals dealloying as a general approach for the selective extraction of metals and the fabrication of nanoporous metals: A review. Mater. Today Commun. 2021, 26, 102007.
38. Chuang, A.; Erlebacher, J. Challenges and Opportunities for Integrating Dealloying Methods into Additive Manufacturing. Materials 2020, 13, 17.
39. Thommes, M.; Schlumberger, C. Characterization of Nanoporous Materials. Ann. Rev. Chem. Biomol. Eng. 2021, 12, 137–162.
40. Erlebacher, J.; Aziz, M.J.; Karma, A.; Dimitrov, N.; Sieradzki, K. Evolution of nanoporosity in dealloying. Nature 2001, 410, 450–453.
41. Zhang, Z.; Wang, Y.; Qi, Z.; Zhang, W.; Qin, J.; Frenzel, J. Generalized Fabrication of Nanoporous Metals (Au, Pd, Pt, Ag, and Cu) through Chemical Dealloying. J. Phys. Chem. C 2009, 113, 12629–12636.

42. Wang, J.; Liu, X.; Li, R.; Li, Z.; Wang, X.; Wang, H.; Wu, Y.; Jiang, S.; Lu, Z. Formation mechanism and characterization of immiscible nanoporous binary Cu–Ag alloys with excellent surface-enhanced Raman scattering performance by chemical dealloying of glassy precursors. Inorg. Chem. Front. 2020, 7, 1127–1139.
43. Rosen, J.; Hutchings, G.S.; Jiao, F. Ordered Mesoporous Cobalt Oxide as Highly Efficient Oxygen Evolution Catalyst. J. Am. Chem. Soc. 2013, 135, 4516–4521.
44. Hu, L.-W.; Liu, X.; Le, G.-M.; Li, J.-F.; Qu, F.-S.; Lu, S.-Y.; Qi, L. Morphology evolution and SERS activity of the nanoporous Au prepared by dealloying sputtered Au-Ag film. Phys. B Cond. Matter 2019, 558, 49–53.
45. Cheng, C.; Lührs, L. Robust Metallic Actuators Based on Nanoporous Gold Rapidly Dealloyed from Gold–Nickel Precursors. Adv. Funct. Mater. 2021, 31, 2107241.
46. Mahr, C.; Schowalter, M.; Mitterbauer, C.; Lackmann, A.; Fitzek, L.; Mehrtens, T.; Wittstock, A.; Rosenauer, A. Nanoporous gold dealloyed from AuAg and AuCu: Comparison of structure and chemical composition. Materialia 2018, 2, 131–137.
47. McCue, I.; Benn, E.; Gaskey, B.; Erlebacher, J. Dealloying and Dealloyed Materials. Ann. Rev. Mater. Res. 2016, 46, 263–286.
48. Sun, L.; Chien, C.-L.; Searson, P.C. Fabrication of Nanoporous Nickel by Electrochemical Dealloying. Chem. Mater. 2004, 16, 3125–3129.
49. Lu, X.; Yu, T.; Wang, H.; Qian, L.; Lei, P. Electrochemical Fabrication and Reactivation of Nanoporous Gold with Abundant Surface Steps for CO2 Reduction. ACS Catal. 2020, 10, 8860–8869.
50. Luo, J.; Han, P.; Dan, Z.; Qin, F.; Tang, T.; Dong, Y. Bimodal nanoporous silver fabricated from dual-phase Ag10Zn90 precursor via electrochemical dealloying for direct ammonia-borane electrooxidation. Micropor. Mesopor. Mater. 2020, 308, 110532.
51. Steyskal, E.-M.; Qi, Z.; Pölt, P.; Albu, M.; Weissmüller, J.; Würschum, R. Electrochemically Tunable Resistance of Nanoporous Platinum Produced by Dealloying. Langmuir 2016, 32, 7757–7764.
52. Shi, S.; Markmann, J.; Weissmüller, J. Actuation by hydrogen electrosorption in hierarchical nanoporous palladium. Philos. Mag. 2017, 97, 1571–1587.
53. Zhang, Q.B.; Abbott, A.P.; Yang, C. Electrochemical fabrication of nanoporous copper films in choline chloride–urea deep eutectic solvent. Phys. Chem. Chem. Phys. 2015, 17, 14702–14709.
54. Zeng, Y.; Gaskey, B.; Benn, E.; McCue, I.; Greenidge, G.; Livi, K.; Zhang, X.; Jiang, J.; Elebacher, J. Electrochemical dealloying with simultaneous phase separation. Acta Mater. 2019, 171, 8–17.

55. Chiu, H.-Y.; Liu, Y.-C.; Hsieh, Y.-T.; Sun, I.W. Some Aspects on the One-Pot Fabrication of Nanoporous Pd–Au Surface Films by Electrochemical Alloying/Dealloying of (Pd–Au)–Zn from a Chlorozincate Ionic Liquid. ACS Omega 2017, 2, 4911–4919.

56. Balluffi, R.W.; Alexander, B.H. Development of Porosity during Diffusion in Substitutional Solid Solutions. J. Appl. Phys. 1952, 23, 1237–1244.

57. Lu, Z.; Li, C.; Han, J.; Zhang, F.; Liu, P.; Wang, H.; Wang, Z.; Cheng, C.; Chen, L.; Hirata, A.; et al. Three-dimensional bicontinuous nanoporous materials by vapor phase dealloying. Nat. Commun. 2018, 9, 276.

58. Liang, H.-W.; Wei, W.; Wu, Z.-S.; Feng, X.; Müllen, K. Mesoporous Metal–Nitrogen-Doped Carbon Electrocatalysts for Highly Efficient Oxygen Reduction Reaction. J. Am. Chem. Soc. 2013, 135, 16002–16005.

59. He, S.; Zhang, C.; Du, C.; Cheng, C.; Chen, W. High rate-performance supercapacitor based on nitrogen-doped hollow hexagonal carbon nanoprism arrays with ultrathin wall thickness in situ fabricated on carbon cloth. J. Power Source 2019, 434, 226701.

60. Fang, Y.; Lv, Y.; Che, R.; Wu, H.; Zhang, X.; Gu, D.; Zheng, G.; Zhao, D. Two-Dimensional Mesoporous Carbon Nanosheets and Their Derived Graphene Nanosheets: Synthesis and Efficient Lithium Ion Storage. J. Am. Chem. Soc. 2013, 135, 1524–1530.

61. Saito, Y.; Matsuno, T.; Guo, Q.; Mori, T.; Kashiwagi, M.; Shimojima, A.; Wada, H.; Kuroda, K. Preparation of Ordered Nanoporous Indium Tin Oxides with Large Crystallites and Individual Control over Their Thermal and Electrical Conductivities. ACS Appl. Mater. Inter. 2021, 13, 15373–15382.

62. Zhang, Z.; Yi, G.; Li, P.; Zhang, X.; Wan, Z.; Wang, X.; Zhang, C.; Zhang, Y. Recent Advances in Binary Colloidal Crystals for Photonics and Porous Material Fabrication. J. Phys. Chem. B 2021, 125, 6012–6022.

63. Håkonsen, V.; Singh, G.; Normile, P.S.; De Toro, J.A.; Wahlström, E.; He, J.; Zhang, Z. Magnetically Enhanced Mechanical Stability and Super-Size Effects in Self-Assembled Superstructures of Nanocubes. Adv. Funct. Mater. 2019, 29, 1904825.

64. Ergün, A.N.; Kocabaş, Z.Ö.; Baysal, M.; Yürüm, A.; Yürüm, Y. Synthesis Of Mesoporous Mcm-41 Materials With Low-Power Microwave Heating. Chem. Eng. Commun. 2013, 200, 1057–1070.

65. Dündar-Tekkaya, E.; Yürüm, Y. Synthesis of palladium incorporated MCM-41 via microwave irradiation and investigation of its hydrogen storage properties. Int. J. Hydrogen Energy 2016, 41, 9828–9833.

66. Wang, S.; Shi, Y.; Ma, X. Microwave synthesis, characterization and transesterification activities of Ti-MCM-41. Micropor. Mesopor. Mater. 2012, 156, 22–28.

67. Nguyen, T.T.; Qian, E.W. Synthesis of mesoporous Ti-inserted SBA-15 and CoMo/Ti-SBA-15 catalyst for hydrodesulfurization and hydrodearomatization. Micropor. Mesopor. Mater. 2018, 265, 1–7.

68. Choong, Y.Y.C.; Tan, H.W.; Patel, D.C.; Choong, W.T.N.; Chen, C.-H.; Low, H.Y.; Tan, M.J.; Patel, C.D.; Chua, C.K. The global rise of 3D printing during the COVID-19 pandemic. Nat. Rev. Mater. 2020, 5, 637–639.

69. Bischoff, L.; Pilz, W.; Schmidt, B. Amorphous solid foam structures on germanium by heavy ion irradiation. Appl. Phys. A 2011, 104, 1153–1158.

70. Miyaji, T.; Nitta, N. Nanoporous Structure Formation on the Surface of InSb by Ion Beam Irradiation. Nanomaterials 2017, 7, 8.

71. Yang, L.; Wei, J.; Ma, Z.; Song, P.; Ma, J.; Zhao, Y.; Huang, Z.; Zhang, M.; Yang, F.; Wang, X. The Fabrication of Micro/Nano Structures by Laser Machining. Nanomaterials 2019, 9, 12.

72. Liao, Y.; Cheng, Y. Femtosecond Laser 3D Fabrication in Porous Glass for Micro- and Nanofluidic Applications. Micromachines 2014, 5, 4.

73. Gu, Y.; Dong, C.; Zhong, M.; Ma, M.; Li, L.; Liu, W. Fabrication of nanoporous manganese by laser cladding and selective electrochemical de-alloying. Appl. Surf. Sci. 2011, 257, 3211–3215.

74. Huang, T.; Lu, J.; Zhang, X.; Xiao, R.; Yang, W.; Wu, Q. Femtosecond Laser Fabrication of Anatase TiO2 Micro-nanostructures with Chemical Oxidation and Annealing. Sci. Rep. 2017, 7, 2089.

75. Adiga, S.P.; Jin, C.; Curtiss, L.A.; Monteiro-Riviere, N.A.; Narayan, R.J. Nanoporous membranes for medical and biological applications. Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol. 2009, 1, 568–581.

76. Xu, Z.; Jiang, X. Osteogenic TiO2 composite nano-porous arrays: A favorable platform based on titanium alloys applied in artificial implants. Colloids Surf. A Physicochem. Eng. Asp. 2022, 640, 128301.

77. He, Y.; Li, Z.; Ding, X.; Xu, B.; Wang, J.; Li, Y.; Chen, F.; Meng, F.; Song, W.; Zhang, Y. Nanoporous titanium implant surface promotes osteogenesis by suppressing osteoclastogenesis via integrin β1/FAKpY397/MAPK pathway. Bioact. Mater. 2022, 8, 109–123.