

Metal-Based Aerogels and Porous Composites as Efficient Catalysts: Synthesis and Catalytic Performance

Ran Du ^{1,*} and Alexander Eychmüller ^{2,*}¹ School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China² Physical Chemistry, Technische Universität Dresden, Bergstr. 66b, 01069 Dresden, Germany

* Correspondence: rdu@bit.edu.cn (R.D.); alexander.eychmueller@tu-dresden.de (A.E.)

Faced with the threat of energy shortage and environment pollution in modern society, the development of efficient and cost-effective catalytic systems is becoming increasingly important. Among diverse material systems, metals stand out for both their high intrinsic catalytic activity and high electrical conductivity, which benefit their applications in both non-electro- and electrocatalysis. To further improve their performance, the pores must be made smaller and the characteristic size of the metals should be reduced. When the size is down to nanoscale, a large fraction of active surface atoms can be generated, accessible surfaces can be increased, and abundant pores can be created, which thereby endow the resulting porous materials with excellent catalytic performance. For example, although gold was considered to be inert in its bulk state in ancient times, the development of nanotechnology has enabled the production of various nanostructured gold [1] as highly active catalysts for, e.g., the oxidation of carbon monoxide and methanol [2,3].

Among various porous metals, metal aerogels (MAs) are of particular interest. Discovered in 2009 by Eychmüller's and Leventis's group [4,5], MAs are a new member of the family of porous materials. Featuring nanostructured building blocks, 3D conductive pathways, a number of catalytically/optically active sites, and a self-supporting open network, MAs have unique advantages in catalysis due to their efficient mass/electron transfer, good structural stability, and high activity [6]. These features are particularly advantageous in electrocatalysis, as they allow for the elimination of inactive binder and less stable carbon supports. Therefore, the development of porous metals, especially MAs, may lead to a revolution in the field of catalysis, solving problems in energy- and environment-related applications.

Inspired by their unlimited potential, MAs have been widely explored in the last fourteen years. From a synthesis point of view, MAs are dominantly prepared via the sol-gel processing of nanoparticle solutions, followed by supercritical or freeze drying. The composition of MAs has been extended from Au, Ag, Pd, and Pt to Ru, Rh, Os, Cu, Ni, and various alloys using newly developed destabilization strategies [4,7–12]. Furthermore, the ligament size and multiscale structure of MAs have been successfully tuned by applying new initiating methods, tuning ionic-nanoparticle interactions, designing ligand chemistry, and manipulating temperature fields [9,13–18]. In terms of practical production, rapid synthesis has been achieved through the use of elevated temperatures, high concentrations, special initiators, non-water solvents, and force fields, enabling the production of metal gels within minutes [19–22]. On the other hand, application possibilities have also been explored in detail. Electrocatalysis is the most studied application direction, with palladium aerogels being investigated first in 2012 for the catalytic oxidation of ethanol [23]. Currently, the electrocatalytic use of MAs has been extended to a variety of reactions, including the alcohol oxidation reaction, the oxygen reduction reaction, the oxygen evolution reaction, the hydrogen oxidation reaction, the hydrogen evolution reaction, the nitrate reduction reaction, and the carbon dioxide reduction reaction [9,24–30]. Compared to conventional catalysts, MAs have the advantage of long-term stability and high activity. Liu et al. [31]



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recently reported the growth of MAs on commercial melamine foams, which enables the non-destructive use of MAs for electrocatalysis and thus greatly promotes methanol oxidation. The success in electrocatalysis has prompted researchers to further their use for electrocatalytic sensing, such as for glucose sensing and ethanol detection [32–34]. In addition to electrocatalysis, MAs based on Au, Ag, Pd, and Cu have also been applied for non-electro catalysis, which can be divided into the catalytic degradation of organic contaminants, the use of “nanozymes”, and other areas (e.g., hydrogenation and carbon monoxide oxidation) [8,35–41]. Considering their optical properties, Au- and Ag-based aerogels were used as 3D substrates for surface-enhanced Raman scattering [42–45]. Furthermore, recently, the photoelectrocatalytic properties of MAs were studied and put forward by Du et al., further expanding the scope of their application [15,21].

Despite the aforementioned advances, MAs are still far from being completely developed and the related research are facing many challenges, ranging from controlled synthesis to smart applications. In this Special Issue, “Metal-Based Aerogels and Porous Composites as Efficient Catalysts: Synthesis and Catalytic Performance”, five papers were accepted for publication. Here, new synthesis designs and novel applications in the field of MAs are presented [45–47] to gain new insights, to advance development, and to draw more attention to metal-based aerogels and metal-based porous materials for catalytic applications. The contributions of this collection are summarized below.

Georgi et al. systematically investigated the synthesis of Au-Cu aerogels using different solvents. Compared to water, which is widely used, the use of ethanol can accelerate the gelation process and suppress the formation of the CuO phase, which is advantageous for the rapid preparation of pure transition metal aerogels.

Cai et al. succeeded in the one-step synthesis of nanoparticles from a high-entropy FeCoNiCuIr alloy. The cocktail effect and the synergistic effect between the individual elements enabled excellent performance in the electrocatalytic oxygen evolution reaction. Pan et al. reported Pt-Pd aerogels for the detection of hydrogen peroxide. The electrochemical sensor based on Pt₅₀Pd₅₀ aerogels showed the best performance, exhibiting both a wide linear range from 5.1 to 3190 μM ($R^2 = 0.9980$) and high sensitivity of 0.19 $\text{mA mM}^{-1} \text{cm}^{-2}$. Shi et al., on the other hand, focused on solving environmental problems. By developing a $\text{UV/C}_2\text{O}_4^{2-}/\text{Fe}^{3+}$ system, the reduction of nitrate to gaseous nitrogen was achieved with high efficiency, good selectivity, and low cost.

Li et al. provided an overview of the history of the application of MAs for electrocatalysis and summarized the current status of the development of efficient MA-based electrocatalysts for energy and environment applications.

In conclusion, this compilation of articles is intended to highlight new synthetic routes and new applications of metal-based porous materials, particularly MAs. Although porous materials are receiving more and more attention and have shown promising development, challenges exist, and there are many potential future directions worth thinking about. We would like to see if the knowledge of the evolution of elemental distributions in bi- and multi-metallic gels, especially under operating conditions, could be utilized to develop better electrocatalysts. More investigations into gas storage (e.g., hydrogen) in MAs, as the corresponding structure/composition–performance correlation may also point in an interesting direction. In addition, with regard to the recently reported 2D metal gels [48], it is intriguing to know whether they can serve as electrodes (especially flexible electrodes) for neuroscience and wearable electronics.

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