Porous Materials

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Cluster-Based Holey Semiconductors

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The research and development carried out on porous (holey) materials with large specific surface areas has grown considerably within the last decades, and an amazing diversity of potential applications and development directions has emerged from these efforts. Materials with different pore sizes and arrangements, and a broad variety of chemical compositions, can be synthesized with a high degree of structure control. However, the network forming the matrix in most cases is based on oxides. Predominant examples of such highly porous materials include zeolites, aerogels, M41S-phases, periodic mesoporous organosilicas (PMOs), foams, and inverse opal structures.[1] With the desire to combine specific functions, for example, shape-selective electrocatalysis and redox processes or chemoselective sensing with the controlled formation of porous networks, the quest for more functional frameworks began. From the beginning of 1980s and early 1990s, researchers started to explore other framework compositions, with the synthesis of aluminophosphates in 1982 finally resulting in the first non-oxide-based zeolites.[2] This synthesis was a major breakthrough in the development of porous materials, and has been followed intensively since then.

In recent years, new porous structures with an integrated network functionality and record-breaking specific surface areas have been synthesized, such as metal–organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) and even covalent organic frameworks (COFs).[3] Looking at the synthesis procedures leading to these porous matrices, not only the level of functionality has been broadened with more complex chemistry involved, but also the way of assembling these networks has completely changed. The formation of oxidic frameworks often involves synthetic pathways based on trial-and-error experiments; however, a novel, more structured and logical way to synthesize porous networks has appeared in recent years by self-assembling preformed molecular or particulate building blocks. The open question remaining is: How far can we go in the deliberate design of porous materials beyond oxides that carry specific functions and are prepared with a high control over pore symmetries, sizes, and even macroscopic morphologies?

Semiconducting open-framework chalcogenides are a logical and very attractive extension to porous oxide-based materials (insulators or wide-band gap materials), as they combine the size and shape selectivity with the electrical function of the material. In these materials, the ability to tune the band gap of semiconducting chalcogenides throughout the whole visible region along with a chemically accessible porous architecture not only opens up possibilities for photocatalytic and sensing applications, but also for solid electrolytes, semiconductor electrodes, and so on. From a chemical point of view, the replacement of O^{2-} with other anionic species, such as S^{2-}, Se^{2-}, or Te^{2-}, is a seemingly logical progression in the research of porous materials with interesting optoelectronic properties, as chalcogenido anions should be able to enter similar condensation reactions as the corresponding oxo anions.

Krebs[4] has reviewed thoroughly the chemistry of isolated clusters of thio- or selenogermanates and -stannates, and showed that with an exact control of the pH value and the concentration ratio of the precursors, different structures can be obtained, starting from monomeric species $[GeQ_4]^{4-}$, via dimeric species consisting of two edge-sharing tetrahedral $[Ge_2Q_6]^{4-}$ moieties, to tetrameric adamantoid species of the composition $[Ge_4Q_{10}]^{4-}$ ($Q = S$, Se) as the predominant condensation product in solutions of lower pH values.[4] The generic structures of these anions are shown in Figure 1. Obviously, this type of Group 14 element–chalcogenide chemistry is closely related to the corresponding silicate chemistry. Bearing in mind the enormous success in constructing porous silicates or silica-based materials displaying virtually any pore size and arrangement, the question immediately arises as to whether analogous chalcogenides can similarly be made. To produce a hydrolytically stable material, primary building units with a tetrahedral topology, such as germanium and tin chalcogenides, seemed to be suitable candidates.

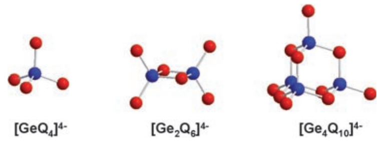

Figure 1. Generic structures of molecular germanate anions ($Q = S$, Se) that can serve as molecular building blocks in the synthesis of porous chalcogenides.

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Over the last years, several achievements in the development of porous materials based on chalcogenides have been made.[5–7] Not only are variable pore sizes and arrangements now accessible, but also completely new synthetic procedures have been developed (Figure 2). In 1989, Bedard et al. patented a new class of microporous metal germanium sulfides, prepared hydrothermally from the respective elements.[8] Yaghi et al. subsequently showed that these open framework materials could be prepared also at room temperature by using the well-known adamantoid $[Ge_4Q_{10}]^{4-}$ clusters ($Q = S$) combined with manganese acetate in water and tetramethylammonium ions for charge balancing.[9] In this case, the clusters are assembled by coordination reactions with a divalent metal cation as the key element, which is in contrast to oxides, which are normally formed by polycondensation reactions. Many microporous materials that are isostructural to $((CH_3)_4N)_2MnGe_4S_{10}$ with other divalent metals ions (Fe, Co, Cu, Hg, Cd) have been prepared by this modular approach, and even numerous templates have been applied.[10]

These syntheses of microporous chalcogenides stimulated further research in the preparation of mesoporous and mesostructured analogues. Aqueous and non-aqueous synthetic procedures have been published, leading to chalcogenide materials that display a framework with disordered worm-hole like arrangements or even periodically aligned mesostructures.[11,12] For these materials with a periodic arrangement of the pores, the construction of non-oxide analogues of, for example, MCM-41 or MCM-48 materials, presents a considerable challenge, mainly arising from difficulties in removing the supramolecular organic templates. Periodic platinum germanium chalcogenides and platinum tin selenide and telluride analogues of MCM-41 and MCM-48 have however been reported.[13] The frameworks of these structures are formed by self-assembly of $[Ge_4Q_{10}]^{4-}$, ($Q = S$, Se) and $[Sn_4Se_{10}]^{4-}$ adamantoid clusters or binuclear Zintl clusters $[Sn_2X_6]^{4-}$ ($X = Se$, Te) with long-chain cationic surfactants as the structure-directing agents. Transition-metal ions, in this case Pt^{2+} or Pt^{4+} ions, act as crosslinkers, but many more are possible, such as Zn^{2+} or Cd^{2+}. Both tetrahedral as well as square planar coordination is in principle possible. However, the templates could not be removed completely. These materials are highly periodic nanocomposites that have an important advantage over most oxide systems for optoelectronic applications in that their range of band gaps can be tuned between 0.6 and 3.4 eV depending on the exact chemical composition. However, their macroscale morphology is more or less limited to powders, and only recently were Tolbert et al. able to synthesize thin films.[14]

Not only micro- or mesoporous materials are of interest, but also the general ability to control and tune the density of the final network and thus the extent of porosity, as it allows the bulk physical properties in the material to be designed. Aerogels are a class of lightweight materials with a 3D nanoarchitecture and intriguing properties that result from their customizable porosity and pore size.[1d] Chalcogenide-based mesoporous aerogels have previously been prepared by Brock and co-workers by applying either the oxidative condensation of preformed metal chalcogenide nanoparticles to three-dimensional networks or thiolysis/condensation chemistry, in analogy to the sol–gel approach (hydrolysis/condensation) that leads to the oxidic counterparts.[15]

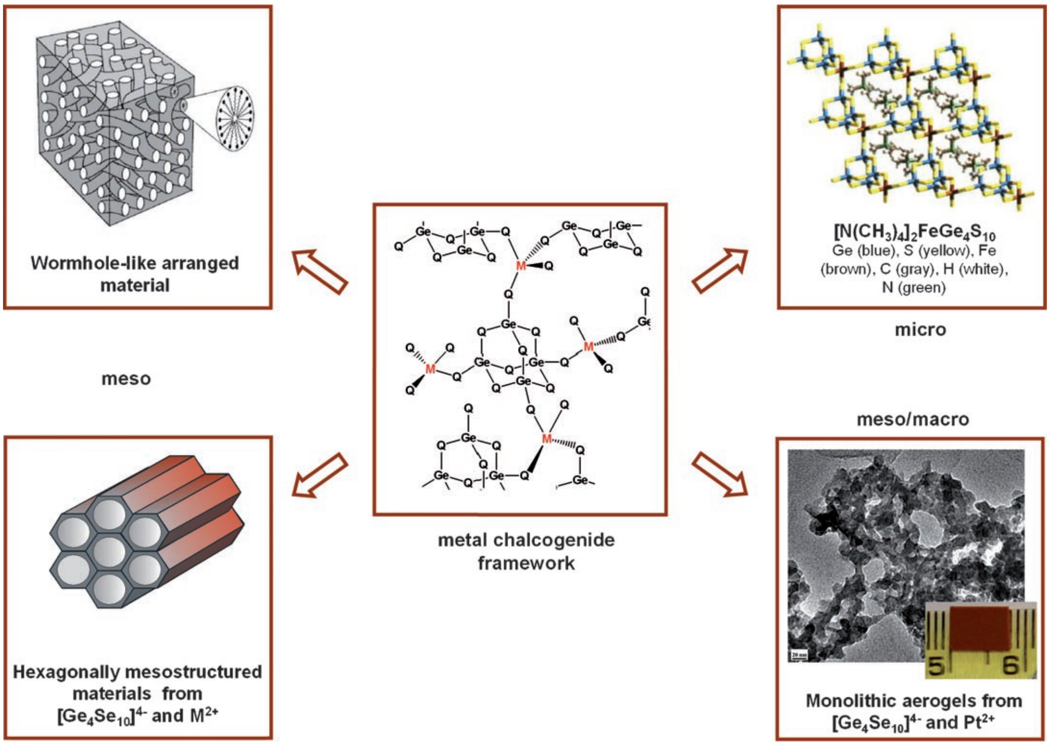

Figure 2. Porous structures that are accessible by linking chalcogenide clusters with transition metals.

In a recently published article,[16] Kanatzidis et al. have shown that the general modular approach of linking chalcogenido clusters with metal ions can also be applied in the synthesis of highly porous chalcogenide aerogel monoliths. By linking molecular building blocks, such as $[Ge_4Q_{10}]^{4-}$ or $[Sn_2Q_6]^{4-}$ clusters, as well as tetrahedral $[SnQ_4]^{4-}$ units ($Q = S$, Se) in a metathesis reaction by Pt^{2+} ions, monolithic gels of low density were obtained after drying with supercritical carbon dioxide. This template-free synthetic strategy allows the synthesis of a highly porous solid, which has an internal surface area of up to 327 $m^2 g^{-1}$ and pores in the meso- and macroscopic regime. This is the first example of a porous chalcogenide material in which the integration of cluster chemistry with the molding into monolithic form was performed, and it clearly demonstrates the huge potential of this approach. Moreover, the material was not only characterized with respect to its structure, but Kanatzidis et al. could also impressively show that absorption of Hg^{2+} ions from contaminated water in the porous network is possible with a high capacity, and that the material exhibits exceptional optoelectronic properties. The band gap can be easily tuned from 2.0 to 0.8 eV by changing the type and concentration of building block.

The various research efforts devoted to porous semiconductors based on chalcogenido clusters are an impressive example that the work of chemists can really be understood as nanoscopic architecture. A thorough understanding of the underlying chemistry, together with a toolbox of inorganic clusters that can easily be linked, allows a deliberate control and design of more or less any particular network structure and kind of functionality desired. A wide variety of open-framework non-oxidic solids with controllable and regular pore structure and interesting electronic and ion–exchange properties has now been achieved. A fascinating playground of novel structures, synthetic methods, and functional nanostructures is available. Kistler stated for aerogels 70 years ago (and it still applies today for these new materials): “There is no reason why this list should not be extended indefinitely”.[17]

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