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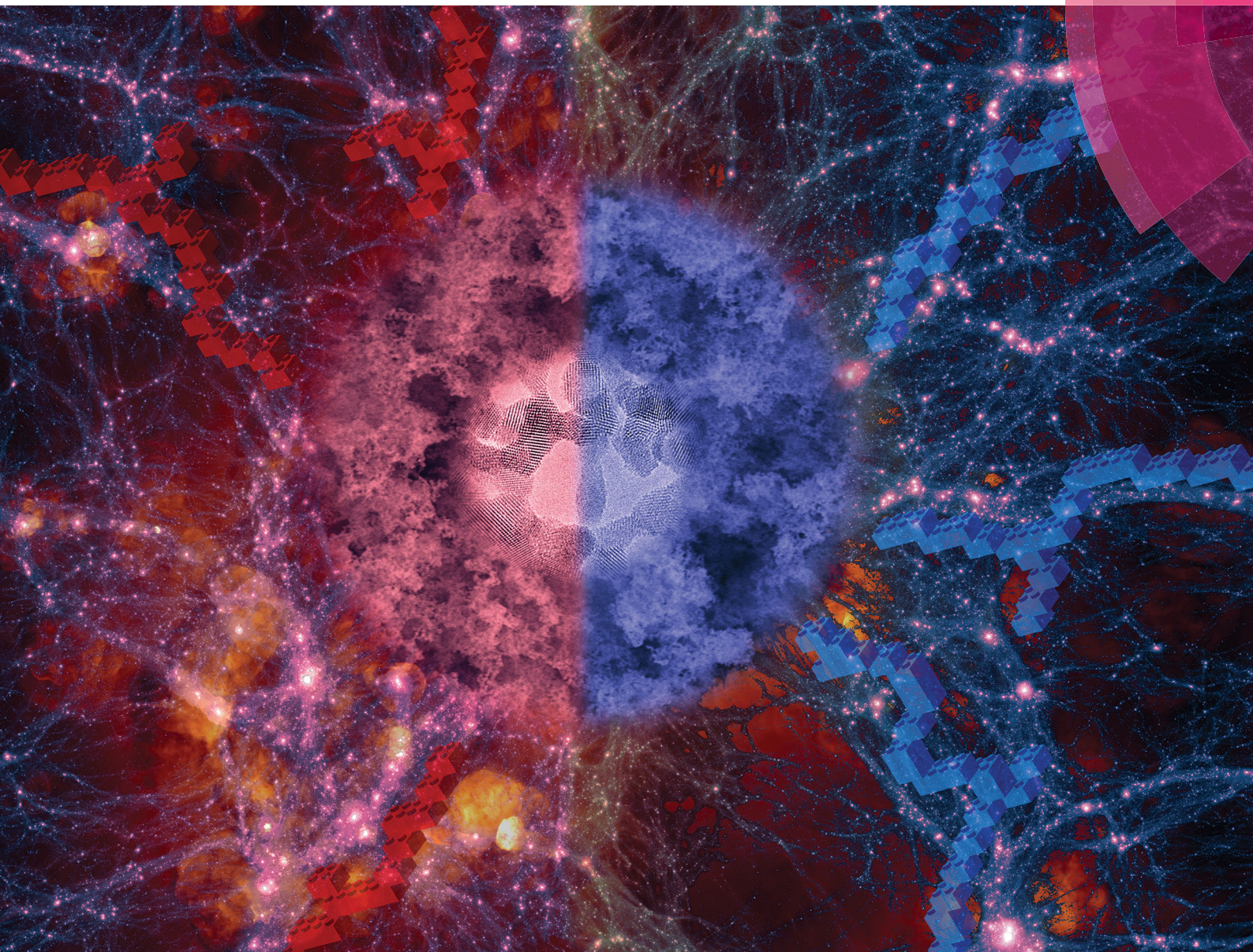
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REVIEW ARTICLE
Felix Rechberger and Markus Niederberger
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REVIEW

Synthesis of aerogels: from molecular routes to 3-dimensional nanoparticle assembly

Felix Rechberger and Markus Niederberger*

Colloidal nanocrystals are extensively used as building blocks in nanoscience, and amazing results have been achieved in assembling them into ordered, close-packed structures. But in spite of great efforts, the size of these structures is typically restricted to a few micrometers, and it is very hard to extend them into the macroscopic world. In comparison, aerogels are macroscopic materials, highly porous, disordered, ultralight and with immense surface areas. With these distinctive characteristics, they are entirely contrary to common nanoparticle assemblies such as superlattices or nanocrystal solids, and therefore cover a different range of applications. While aerogels are traditionally synthesized by molecular routes based on aqueous sol–gel chemistry, in the last few years the gelation of nanoparticle dispersions became a viable alternative to improve the crystallinity and to widen the structural, morphological and compositional complexity of aerogels. In this Review, the different approaches to inorganic non-siliceous and non-carbon aerogels are addressed. We start our discussion with wet chemical routes involving molecular precursors, followed by processing methods using nanoparticles as building blocks. A unique feature of many of these routes is the fact that a macroscopic, often monolithic body is produced by pure self-assembly of nanosized colloids without the need for any templates.

1. Introduction

The ability to create materials on different as well as over many length scales is the basis of today's technological progress.[1–11] Over thousands of years materials processing routes were

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developed with the goal to fabricate bulk materials such as ceramics, polymers, metals or composites. The major part of these processes involves engineering, *i.e.*, the desired functionality of a material is obtained by casting, shaping, joining, blending or annealing without necessarily tailoring the composition of the individual components. Chemistry, on the other hand, exactly focuses on this aspect: the synthesis of new molecules, compounds and materials, starting basically from the atoms. Somewhat oversimplified one could say that the chemist makes the material, while the engineer brings it into a specific shape that is suitable for the targeted technological application. With the advent of nanoscience however, the traditional working areas and their corresponding size regimes got blurred and chemists, physicists, engineers and materials scientists now address all length scales from the nano- to the macroscale.[7,8] At the same time, the subtleness how materials can be processed has tremendously increased. In comparison to traditional processing routes, the focus now lies on the use of well-defined building blocks (molecules, molecular assemblies or particles) and their sequential and modular arrangement into, ideally, hierarchical and complex structures.[1,2] The main challenge is to keep full control over the assembly of the building blocks including their spatial arrangement, orientation and their interaction from the nano- to the macroscale, thus bridging several orders of length scales.[12] In the best case, the final material exhibits a combination of the intrinsic properties of the building blocks as well as new properties resulting from collective or synergistic effects.[13–16] Clearly, such a materials design strategy demands the highest level of synthesis control for the building blocks including composition, crystallinity/ crystal structure, size, size distribution, shape, defect chemistry and surface functionalization.[4,17–23] Nevertheless, after several years of intense research on nanoparticle synthesis, an immense library of well-defined building blocks is available, and the next step towards their arrangement into 1-,[24,25] 2-[25] and 3-dimensional structures[26,27] has already been taken.[4,28,29] As an illustrative example, Fig. 1 summarizes the assembly behavior of aniso- tropic Mn_3O_4 nanocuboids.[30] Either 1D, 2D or 3D microarrays are formed by oriented self-assembly through evaporation of nanoparticle dispersions with different concentrations, and the orientation of the tetragonal crystals was controlled to be parallel and perpendicular to the substrate by changing the polarity of the solvent (Fig. 1a). Scanning electron microscopy (SEM) images show linear chains of cuboids aligned in the ⟨100⟩ direction (Fig. 1c), monolayers with domain sizes of about 1 μm (Fig. 1b) or 3-dimensional superlattices several microns in size (Fig. 1d).[30]

This is just one example that underlines the impressive progress in the field of particle assembly, but at the same time it also reveals the major limitation. While it is possible to produce complex/hierarchical structures,[31] quasicrystals,[32] meso- crystals,[33] supracrystals,[34] polymer-like crystals,[35] helices[36] and many others, their size is typically limited to a few micrometers, and it is very hard to translate such structures into the macro- scopic world. It is interesting to note that in most of these examples great efforts were made to arrange the particles into
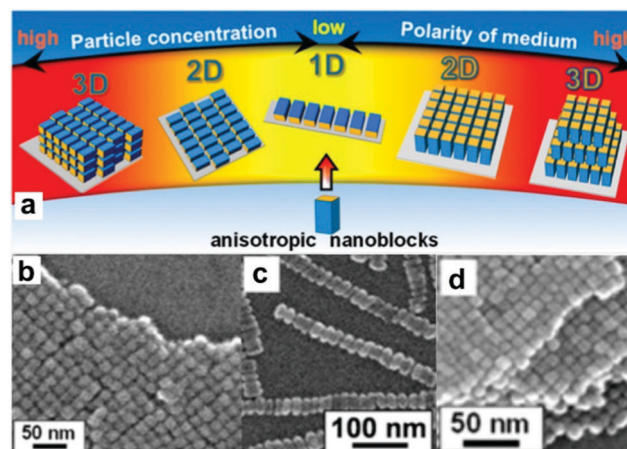

Fig. 1 (a) Schematic of the assembly behavior of anisotropic Mn_3O_4 nanoblocks in dependence of the dispersion media and the particle concentration. SEM images of (b) a monolayer (2D), (c) linear chains (1D), and (d) a superlattice (3D) of Mn_3O_4 cuboids. Adapted with permission from ref. 30, Copyright 2013, American Chemical Society.

dense and highly ordered structures, and often the degree of order is the limiting factor for their performance in a specific application (*e.g.*, photonic crystals). However, if opposing properties like low density, extended porosity and high surface areas are desired, then colloidal gels represent the materials of choice. For their synthesis, the key challenge is not only to produce the network structure over several orders of length scales, but also to be able to control the degree of order and porosity. In the case of ordered mesoporous materials, amphi- philic molecules like surfactants and block-copolymers are used to control the size and the arrangement of the pores during synthesis.[37–40] In aerogels, which are typically produced without the help of any templates or structure-directing agents, the pores are disordered and the pore size distribution is broad. Nevertheless, they offer a series of advantages when it comes to functional applications.[41,42] Because the pores are inter- connected with sizes reaching from the nano- up to the macro- porous regime, molecular diffusion is facilitated by multiple entrance and exit points. Therefore, if the pathways are locally blocked by reactants or through collapse of the pore structure, the molecular transport is not interrupted, which is impossible in systems with regular and non-percolating pores.[43]

As a matter of fact, if the building blocks are nanosized, it is essential that the 3-dimensional assembly occurs in a way that the large surface area of the nanocrystals and their size- and shape-dependent properties are preserved in the final material. This is only possible, if the whole gelation process is controlled from the primary particle level up to the macroscopic body.

In this Review, we address the self-assembly of nanoparticles into macroscopic, 3-dimensional, disordered and porous structures. Starting from a historical perspective on colloidal particles and gels, we move on to the preparation of aerogels by molecular routes and in the last section we discuss nanoparticle-based aerogels. In the last few years, this research field made immense progress and a large number of different nanoparticle-based aerogels are

available nowadays, covering almost all classes of materials. A unique feature of these routes is the macroscopic size of the final, often monolithic aerogels, which is reached by pure self-assembly without the use of any templates.

2. Historical overview

According to IUPAC, a gel is a "*Non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid.*"[44] As the definition already suggests, these structures are based on colloids as point of origin. These particles cover a wide range of multiphase substances of small particles (1 μm > colloids > 10 nm) dispersed in a continuous phase. Colloids occur naturally and are all but a new phenomenon. Observations by Robert Brown in 1827 were performed on the colloidal motion in pollen and spores,[45] thereby laying the foundations for the research of Einstein on atoms[46] and Perrin on Avogadro's number[47] in the beginning of the 20th century. However, these studies were not the first discoveries or even uses of colloids. In the following, we move back in time to the late Pleistocene age to start our short historical overview on the human usage and understanding of colloids.[48–51]

Dating back 17 000 years, cave paintings in Lascaux in France showed the earliest known use of human-made colloidal suspensions. By using natural oils as surface stabilizing agents, fine ground powders of iron oxide, carbon and clays were dispersed in water and used as paint. Efforts of the Chinese and Egyptians using lamp blacks in natural polymers in the form of colloidal dispersions with protective agents like gelatin or gum led to non-coagulating and therefore not-gelling inks.

The next major milestone was reached some 8000 years ago in the Atlantic age period by early examples of colloids in plaster and bricks produced through burning. At around 4000 BCE faience was produced in Egypt by firing an aqueous paste of crushed sand, binder and sodium flux, connecting silica particles together with the molten flux. In China and Mesopotamia surfaces were sealed in porous clay vessels by fusing powdered glass through glazing methods, dating back as far as 2000 BCE. First developments of concrete were based on the idea of using chemically linked particles as a matrix to form a composite with other colloidal materials in Iran 700 BCE. The Romans improved this process between 200 BCE and 400 CE, and the British, French and Germans continued the work until the 18th century. Later, Alchemists made gold and silver in colloidal form in stained glass for church windows. A significant development was the discovery of "water glass" by van Helmont in 1644.[52] Silicates were dissolved in alkali and formed a precipitate upon acidification of the liquid. In 1779 Bergman described the gelation of silicates upon addition of a dilute acid.[53] Following this discovery, many materials were prepared from hydroxide gels, such as zirconium or uranium oxide gels.[49] Shortly before Faraday reported his studies on the optical properties of colloidal gold solutions in his famous Bakerian lecture in 1857,[54] Ebelmen prepared the first silicon alkoxide in 1846 through the reaction of silicon tetrachloride in alcohol.[55] Upon exposure to atmosphere with normal humidity,

the product gelled, laying the basis for future discoveries in the field of colloidal gels. Hydrolysed derivatives of silicon alkoxides and silicic acid were discovered between 1876[56] and 1884.[57] Important work towards processibility of gels was performed by Graham, showing that the porous water in silica gels could be exchanged to organic solvents.[58] This observation led Kistler in 1931 to the conclusion that a gel (once it is formed) is independent of the pore fluid[59] and this fluid could very well be a gas rather than a liquid.[60] At that time, gels were dried by simply evaporating the liquid in ambient conditions, which was accompanied by large shrinkage. Liquid–vapour interfaces within the network of the gel resulted in strong surface tensions, which destroyed the network and caused the structure to collapse. In order to preserve the macroscopic body of the wet gel after drying, Kistler worked out the following idea: "*Obviously if one wishes to produce an aerogel, he must replace the liquid with air by some means in which the surface of the liquid is never permitted to recede within the gel. If a liquid is held under pressure always greater than the vapour pressure, and the temperature is raised, it will be transformed at the critical temperature into a gas without two phases having been present at any time. [...] Accordingly, it becomes possible to take a gel filled with a liquid, transform the liquid gradually into a gas, allow the gas to expand above the critical temperature, and end with the gel filled with gas of low density without at any time having subjected the gel to compressive forces. This, in general, is the procedure [...]*"[59] of supercritical drying.[61–64] Supercritical drying is obviously able to avoid capillary forces present during ambient drying, thus making it possible to produce aerogels as a representative of ultralight materials.[59,61]

Further insight in the structure of silica gels was gained in the late 1930s, when Hurd showed the percolating polymeric skeleton of silicic acid containing a continuous liquid phase.[65] In the 1970s, significant research efforts were conducted on gels and colloidal particles mainly by nuclear industry for fuel cells in nuclear reactors[49] and by the mining industry for Bingham fluids in waste clay disposal.[66] Further interest was generated by food and cosmetic industry on reversible aggregation of colloids, leading to features like yield stress and thixotropy observed *e.g.* in Ketchup or shampoo.[67] From the 1980s on, there was a big push in gel research, mainly generated by the progress in the synthesis routes and the discovery of fractal structures within gelled colloids. Meakin and Weitz became the pioneers in understanding fractal aggregates (Fig. 2) and their ramifications in gels.[68–70] The development of a wide range of characterization techniques based on light,[71] X-ray[72] and neutron[73,74] scattering and confocal microscopy techniques[75,76] has allowed a deep insight into the structure and mechanics of gels and how they are influenced by the aggregation kinetics. Application of simulation techniques in gel research allowed a detailed view on the interaction models within the colloidal network.[77–79]

The concept of gels is related to that of glass. Therefore, the differences and similarities in the rheological signatures of these materials were elaborated.[80–87] Recently, the focus has shifted towards depletion gels, which were actually discovered many years ago.[88] These systems allow the systematic study of "sticky" colloids by varying the strength of the depletion potential.[75,76,85,86,89]
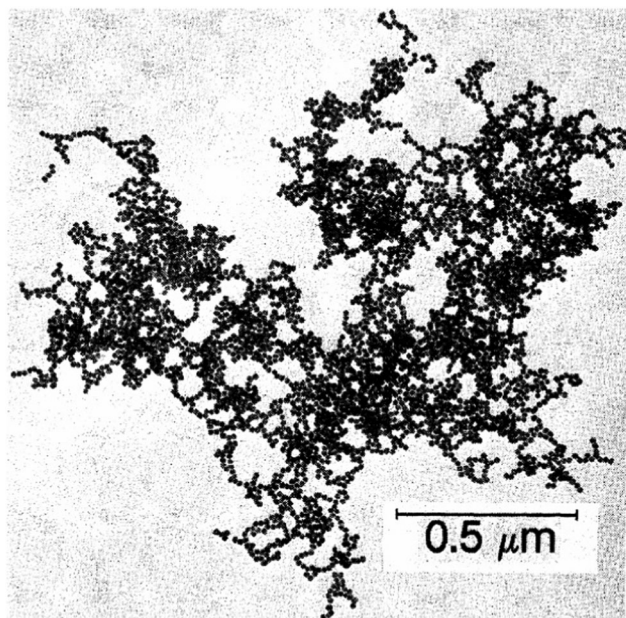
Fig. 2 Transmission electron microscope (TEM) image of a fractal gold colloid aggregate. Reproduced with permission from ref. 69, Copyright 1984, American Physical Society.

Without any doubts, research in the field of sol–gel processes has undergone immense progress until today with significant impact on the development of synthesis routes to nanoparticles, gels and ceramics. Many of today's known sol–gel techniques have their historical origin in decorative and constructional materials, sometimes discovered by serendipity, sometimes rationally developed. Applied in art in ancient times, then implemented in technology, colloids and gels also became science. Although research on wet gels remains a "hot topic", we change our focus now towards the preparation of their self-supporting, supercritically dried counterparts: aerogels.

3. Terms and definitions

Before we discuss the preparation of aerogels, we begin with the definition of a few terms used throughout the Review. Gelation has been defined in different ways, but the most common definition is often associated with percolation.[90] The colloids are linked together, forming branched fractal chains, thereby filling the entire volume homogenously with a coherent network of particles. Once there is a sample-spanning arrangement of particles in the reaction container, the percolation threshold, also called the gelling point, is reached. Percolation is clearly related to "connectedness" and therefore can also be applied to other physical properties such as electrical conductivity. However, percolation alone is not sufficient for defining a gel state, but simply a necessary prerequisite, as often the associated bonds are not permanent (yet) and can still break and reform ("hopping").[91] Further aging of the gel beyond the percolation point increases the stiffness and leads to a rigid structure with a permanent stress bearing capacity.[92] Unfortunately, a clear definition of when the "gelled state" is reached is still missing and part of ongoing discussions.[92]

Flocculation also involves the linking of colloidal particles to a three-dimensional network. However, the formed flocks do not span the entire sample volume. Depending on gravitational settling, flocculation leads to sedimentation. Highly concentrated dispersions undergoing a phase separation either by gelation or flocculation cannot be distinguished from each other, because the single flocks can form bridges, leading to percolation and gel formation.[50,93]

Kistler's work on supercritical drying made use of a reactor able to sustain pressures of 300 bars and temperatures of over 250 °C to reach and hold the supercritical state of organic solvents without crossing the liquid–gas phase boundary, before the pressure is reduced at constant temperature to ambient pressure to remove the sample.[59] Apart from the obvious safety risks, these harsh conditions might damage the cell structure of the gel through surface modifications or accelerated aging and ripening.[63] The development of milder supercritical drying with CO_2 solved this problem, but introduced another time consuming step. Solvent exchange to an intermediate liquid miscible with liquid CO_2, e.g. ethanol or acetone, is required, because water is immiscible. In addition, a considerable amount of time for diffusion and substitution of this intermediate liquid with CO_2 within the gel is needed in the pressure reactor. After increasing the temperature to reach the supercritical state, it is kept for a certain period of time to ensure a homogeneous distribution of the supercritical state within all pores of the gel. As the critical conditions of CO_2 (31 °C and 74 bar) are relatively moderate compared with other organic solvents, structural changes in the gel are marginal. Recently, suggestions for alternatives such as aerosol gelation[94] or freeze dried aerogels from aqueous[95] or organic solvent dispersions[96] have been published. Freeze drying is however often accompanied by shrinkage or destruction of the fine gel structure due to slow freezing rates.

In this Review we will focus on supercritically dried gels. Contrary to their ambient dried counterparts (xerogels),[97] where pores collapse due to capillary forces present during evaporation, aerogels show a preserved percolating microstructure which is often fractal and with open porosity. Fractals are self-similar structures with objects looking similar even when viewed at different length scales, i.e. at different magnifications. Thus, the structure on the length scales of a few particles resembles the microstructure of the aerogel. Interestingly, the word 'aerogel' itself is not clearly defined throughout the literature. Hüsing et al. used a definition closest associated to the necessary supercritical drying step: "*materials in which the typical structure of the pores and the network is largely maintained [. . .] while the pore liquid of a gel is replaced by air are called aerogel.*"[63] The authors of this Review believe that aerogels are increasingly recognized as materials with special structures and characteristics, while the specific drying technique or preparation procedure is less important. Therefore, we prefer a structural definition similar to Fricke et al.:[98] aerogels are open-celled porous solid materials composed of a network of interconnected nanostructures with the majority of pore sizes below 100 nm and a porosity of over 80%.

4. Molecular routes to aerogels

The vast majority of publications are dedicated to aerogels based on silica and carbon. Silica was the first material produced as aerogel and it became the most extensively studied system in the community. For the synthesis of silica aerogels, mostly alkoxides are used as molecular precursors in sol–gel reactions, because the chemistry and the reaction kinetics are well known and controllable for these systems, and silica offers extensive potential for surface functionalization.[99,100] For carbon aerogels, which have gained a lot of attention in the past years, the typical synthesis involves polymerization of resorcinol and formaldehyde (RF), followed by pyrolysis.[100,101] Compared to silica, carbon aerogels are not necessarily prepared by sol–gel processes, but can even be produced from other carbon sources like nanotubes.[102] There is extensive literature on carbon and silica aerogels, and therefore a detailed discussion of these materials and their composites goes far beyond the scope of this Review. The interested reader is referred to other publications and reviews covering the recent advances in carbon and silica aerogel research.[100,103–106]

In this section, we focus on different wet-chemical molecular routes to non-siliceous and non-carbon aerogel materials,[107] which mainly include metal oxides and chalcogenides.[108] Metal oxides and metal chalcogenides offer a great variety of diverse and distinctive properties in many fields of materials science. Their synthesis in form of aerogels results in highly multifunctional materials with properties well beyond those of a simple support or scaffold material as it is often the case for silica and carbon.

Metal alkoxides are the most widely used precursors in aqueous sol–gel chemistry for the synthesis of metal oxides. Their chemical transformation basically involves two reactions: hydrolysis and condensation (Scheme 1). These two types of reactions are fundamental for all metal alkoxides, although of course coordination numbers, oxidation states, reaction rates and finally the materials properties are different for each metal ion. Further information on the specific reactions leading to metal oxides can be found somewhere else.[109,110] During hydrolysis, the alkoxide groups (–OR) are (partly or completely) substituted by hydroxyl groups (–OH) through a nucleophilic attack of water. In the second step, condensation reactions occur between two M–OH species under the release of water (oxolation) or between M–OH and M–OR under release of an alcohol (alkoxolation), resulting in the formation of bridged M–O–M bonds.[97] Through nucleation and growth these hydrolysis and condensation reactions produce an often amorphous oxidic sol, a dispersion of colloids in a liquid (Scheme 2).[109] Further condensation and crosslinking beyond the so-called sol-to-gel transition results in a percolating, open-porous network enclosing a continuous liquid phase throughout the sample.[97] The main issue of sol–gel chemistry is that, even though the chemical reactions are well-known, the hydrolysis and condensation rates are fast and hard to control, making it difficult to adjust the gelling behaviour and to tailor the final porosity. However, there are a number of strategies to influence the reaction kinetics of the sol–gel process, such as using precursors with bulky non-reacting side chains (which do not participate in the condensation reactions), concentration of precursors, addition of surfactants, variation of solvents, regulation of pH and many more.[48] Similar modifications and tricks are also adapted for particle synthesis to achieve control over morphology and size.[97] However, as the system is constantly changing, controlling the kinetics especially related to gel formation remains a major challenge and slight deviations from the optimal conditions has a detrimental effect on the gelling behavior.[40] Accordingly, after sol formation, gelation is the second and fundamental step en route to an aerogel, as Kistler postulated: "*the ability to form an aerogel is a general property of gels.*"[59] It is important to note that upon formation of the gel network, the chemical reactions are not terminated. Structural changes within the gels due to condensation reactions of neighbouring –OH and –OR groups and thermodynamically driven rearrangements like Ostwald ripening of the still flexible network lead to a mechanically more stable scaffold. Therefore, gels are often aged and ripened after synthesis before supercritical drying.[100]
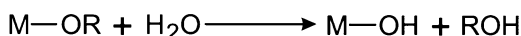
Although research efforts on aerogel materials have been ongoing since nearly a century, their characterization is not yet fully established. The mechanical properties are quite poor and the structure covers several orders of magnitude. A detailed description of possible characterization techniques goes beyond our Review, but is readily available in dedicated literature.[100,111–113]
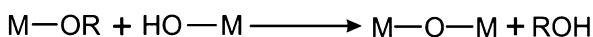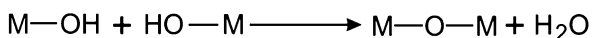
Sol–gel approaches

In this section, the most prominent examples of non-siliceous oxides and chalcogenide aerogels produced by sol–gel synthesis are presented. The aerogels are grouped into paragraphs according to their compositions, and additionally we briefly discuss selected applications.

In 1975, Yoldas found a method to fabricate Al_2O_3 'aerogels' from alkoxides. Although their porosity does not completely fit to the definition of aerogels, they are one of the first examples of highly porous non-siliceous structures (Fig. 3).[114–117] Different attempts were made to study the intermediate species during formation[118] and to improve the mechanical[119] and thermal[120] stability. Al_2O_3 aerogels are interesting for applications as catalysts and catalyst supports,[121–126] and they are also used for the removal of mustard gas[127] or for silica alternatives in capturing cometary fragments.[128]
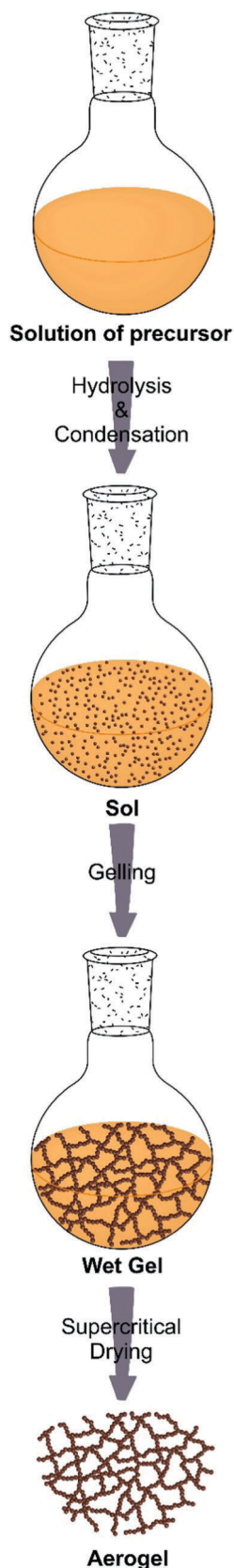
Hydrolysis

$$M-OR + H_2O \longrightarrow M-OH + ROH$$

Condensation

$$M-OH + HO-M \longrightarrow M-O-M + H_2O$$

$$M-OR + HO-M \longrightarrow M-O-M + ROH$$

Scheme 1 Main reactions of the sol–gel process using metal alkoxides (represented by M–OR) in aqueous solutions: hydrolysis and condensation involving both oxolation (elimination of water) and alkoxolation (elimination of an alcohol ROH).

Scheme 2 Overview of an aerogel synthesis by the sol–gel route from molecular precursors undergoing hydrolysis and condensation reactions. The wet gel, formed by the sol-to-gel transition, is supercritically dried to obtain the final aerogel.
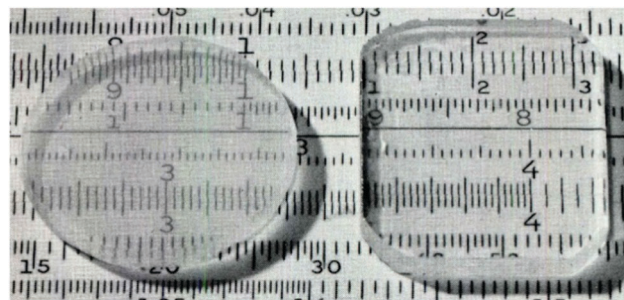

Fig. 3 Transparent alumina 'aerogels' with 4.8 mm thickness heat treated at 1000 °C. Right specimen is impregnated with benzyl alcohol to improve transparency. Reprinted from ref. 116, Copyright 1975, with permission of The American Ceramic Society.

A lot of attention has been directed towards the synthesis of titania aerogels.[63,100,129] These materials are usually synthesized from the corresponding ethoxide,[130] isopropoxide[131–136] or butoxide[137,138] by classical sol–gel approaches in aqueous alcohol or ketone mixtures. After calcination, the TiO_2 aerogels are mainly used for applications in catalysis,[129,132,134] dye-sensitized solar cells[136] and in monolithic form as columns for chromatography.[133] In order to offer a rare possibility to modify the porosity, TiO_2 aerogels are co-gelled with SiO_2.[139–143] Doping with Eu,[144] Fe[145] and Pt improved the photocatalytic activity.[146] By using gold nanoparticles as "guests" during gelling of a TiO_2 "host", the electron scavenging properties of gold could be introduced in the TiO_2 aerogel composite.[147] Producing mixed oxides of CeO_2,[148] RuO_2,[149] MnO_x/V_2O_5[150] and ZrO_2[151] with TiO_2 presents another approach to tune the photocatalytic activity.

Vanadium oxide is a promising cathode material in lithium ion batteries due to its capability to intercalate Li ions. For such an application, the porous structure of an aerogel should be highly beneficial. Several groups investigated the electrochemical properties of V_2O_5 aerogels for energy storage.[152–165] Apart from Li^+, these aerogels showed great potential to host other ions such as Na^+, K^+, Mg^{2+}, Ba^{2+}, Al^{3+} and Zn^{2+}.[166,167] The electrochemical performance was modified by doping V_2O_5 with copper or zinc,[168] by fabricating nanocomposites with RuO_2[169] or with polypyrrole[170] and by introducing $Ba_{0.25}V_2O_4$ whiskers as 1D electron conducting additive.[171] By nitridation of V_2O_5, various degrees of nitrogen enrichments were achieved with different vanadium valence states. These vanadium oxynitrides were tested in sensor devices.[172] In combination with TiO_2, V_2O_5 also showed excellent photocatalytic activity.[150,173–181]

Zirconia aerogels were prepared by different traditional sol–gel syntheses with alkoxides or salts as precursors and subsequent calcination.[100,182–187] Baiker *et al.* investigated the effect of acids and solvents on the structural properties.[188,189] The short range order and the fractal properties of zirconia aerogels were investigated by Zeng *et al.* with X-ray diffraction (XRD)[190] and small angle X-ray scattering (SAXS) measurements.[191] SAXS allowed analysis of the morphological changes by local surface diffusion, leading to fragmentation during thermal relaxation.[192] Zirconia aerogels find applications in catalysis,[193–195]

phosphopeptide enrichment[196] and thermal insulation.[197] Doping enhanced the catalytic activity, especially through the impregnation with sulphur.[198–205] Furthermore, ZrO_2 aerogels stabilized with Y_2O_3,[206,207] doped with Rh,[206] Ni,[202,204] Fe,[208] Cu[209] and Co,[203] and mixed oxides with Al_2O_3,[210] TiO_2[211] or WO_x[198] were reported.

Klabunde *et al.* synthesized and investigated the formation of magnesia aerogels.[212–215] Another group slowed down the gelation by adding glycerol and acetic acid to produce large and crack-free samples.[216] Recently, the influence of structure directing agents (Pluronic 123) was investigated by Hüsing *et al.*[217] The potential applications for MgO are in catalysis or in the removal of toxic gases.[218] The catalytic activity could be improved by loading gold particles onto the surface,[219] by co-gelling with VO_x[220,221] or by producing Mg–Zr mixed oxides.[222]

The influence of organics on the properties of chromia aerogels was investigated by Skapin *et al.*[223] Furthermore, the fluorination effects on Cr_2O_3 were studied,[224] which was later also adapted to alumina aerogels.[225–227] But the metal oxides were only partially fluorinated on the surface, while deep bulk fluorination led to the complete loss of the aerogel structure.[228] More chromium based materials were synthesized by Landau[229,230] and co-workers including α-Cr_2O_3, α-CrOOH and other compounds as catalysts supports.[231] Younes *et al.* combined Cr_2O_3 with Al_2O_3 to catalyse the nitroxidation of toluene to benzonitrile.[232]

In addition to the metal oxide aerogels described above, which are among the most studied ones, there are also examples, for which the literature is much more limited, *e.g.* Fe–Cr–Al mixed oxides,[233,234] gold–iron oxides,[235] MoO_3,[236–238] WO_3,[239,240] $Li_2O\cdot B_2O_3$,[241] GeO_2,[242] ZnO[243] and V doped ZnO,[244–247] SnO_2,[248–250] Sn–Al oxides,[251] Nb_2O_5,[252] Pd doped CeO_2,[253] MnO_2,[254,255] Ta_2O_5[256] and more complex compositions like $MgFe_2O_4$,[257] $BaTiO_3$,[258–260] $SrTiO_3$,[260] $PbTiO_3$,[261] $Li_4Ti_5O_{12}$,[262] $VOHPO_4\cdot0.5H_2O$,[263] $La_2Mo_2O_9$[264] and CuO–$Zr_xCe_{1-x}O_y$.[265]

For some applications, chalcogenides are preferred over oxides. Analogous to classical aqueous sol–gel synthesis it is possible to produce amorphous or poorly crystalline sulfide gels through thiolysis, where H_2O is replaced by H_2S gas, resulting in sulfur-linked gels. Similar to metal oxide gels, the relative reaction kinetics of thiolysis and condensation play a major role for gel formation.[100] Another reaction towards sulfide gels is metathesis, a partner-switching polymerization reaction.[266] Here, soluble chalcogenide clusters are linked by metal ions leading to a three dimensional network.[267]

Pioneering work on chalcogels was performed by Stanić *et al.* starting in 1996 on sulfides such as ZnS,[268] WS_x[269] and GeS_2.[270,271] Doping GeS_2 with Er^{3+} increased the thiolysis rate and consequently led to a more grainy gel.[272] The group of Kanatzidis later on developed the expertise to synthesize various sulfide chalcogels, many of which show interesting ion-exchange properties[273–275] and high efficiencies towards adsorption of heavy metals.[274–276] The same group investigated the improvement of the selective adsorption of gases on inorganic networks with high surface polarizability.[277] Especially $CoMo_xS_x$[278,279] based chalcogels showed excellent results.[280] An example of a hierarchical architecture involved one dimensional chains of chalcogenide clusters, which were then used as building blocks for three dimensional chalcogenide gels.[281,282] Recently, chalcogels with biomimetic functionalities produced by a controlled metathesis reaction between precursor clusters were reported, leading to a bottom-up assembly of redox-active species linked in between a network of tin sulfide clusters. These structures were then used as hybrid systems, combining both biomimetic and porous properties of heterogeneous catalysts. The chalcogels showed good photochemical conversions of nitrogen[283] and production of solar fuels.[284–288] Furthermore, these tin sulfide based chalcogels also showed promising properties for the remediation of radionuclides and could possibly solve problems in nuclear waste treatments.[289–292]

Recently, Rothenberger *et al.* reported polysulfides such as $KFe_xM_xS_x$ (M = Sb, As, Co, Y, Eu)[293,294] and $CuSb_2S_4$.[295] Additionally, they prepared the first telluride based quaternary aerogel ($KFeSbTe_3$).[296] All these materials showed great potential in gas adsorption for the purification of gases.

For the sake of completeness, we conclude this section with selected aerogels beyond oxides and chalcogenides, and which were produced by special methods. Zettl *et al.* used a carbothermal reduction of boron oxide and simultaneous nitridation to obtain BN aerogels.[297,298] These aerogels could then be loaded with platinum nanoparticles for gas sensing applications.[299] Furthermore, the first carbide aerogels consisting of TiC and NbC were synthesized from a carbon aerogel network by using a low temperature pseudomorphic carbidization approach with volatile metal compounds.[300] Recently, the direct preparation of fluorides from sol–gel processes has been shown for luminescent EuF_3 compounds[301] and for AlF_3 synthesized in the presence of methanol.[302]

Epoxide addition methods

Despite the respectable collection of metal oxide and chalcogenide aerogels, the fast reaction kinetics of the sol–gel process remains an issue for many oxidic materials. Even under ideal conditions, hydrolysis and condensation of the precursors generally lead to dense hydroxide or oxide sediments. To obtain porous gels, the hydrolysis and condensation rates need to be significantly slowed down.[100] An interesting study was published by Gash *et al.* in 2001 in the context of Fe_2O_3[303] and Cr_2O_3[304] aerogels. They used inorganic salts and epoxides (epoxide addition: EA method) to induce gelation. This method was introduced for the formation of lanthanide(–silicate) aerogels with erbium and praseodymium.[305] The group of Gash investigated the influence of different types of epoxides (see Fig. 4) on the microstructural properties of iron oxides.[306] In the following years, the EA method allowed the formation of many different materials, which were not accessible until then, significantly expanding the range of possible monolithic aerogel materials.

Propylene oxide (PO) is the most frequently used epoxide for gel formation by the EA method, and therefore we discuss its reaction mechanism in more details. In a first step, the oxygen in the epoxide is protonated by an acid HA, as depicted in Fig. 5a. In a second step, the acid anion A^- undergoes a nucleophilic attack, leading to a ring opening reaction (Fig. 5b). Therefore, the epoxide acts as proton scavenger, thus slowly raising the pH. This pH change induces hydrolysis and
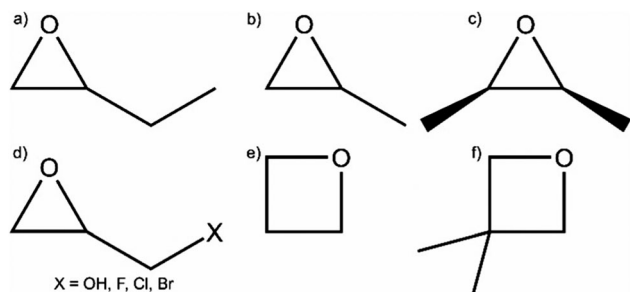
Fig. 4 Examples of epoxides used in different EA methods for the formation of gels. (a) 1,2-Epoxybutane, (b) propylene oxide, (c) cis-2,3-epoxybutane, (d) glycidol (X = OH) and epihalohydrines (X = F, Cl, Br), (e) trimethylene oxide, and (f) 3,3-dimethyloxetane.
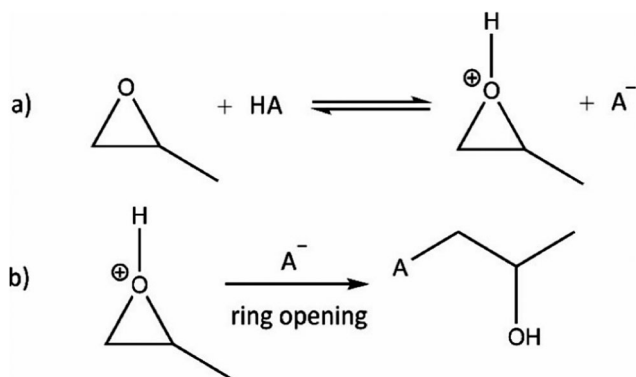

Fig. 5 Reaction schematics for propylene oxide as proton scavenger. In a first step, (a) propylene oxide gets protonated by the acid HA and (b) in a second step the acid anion induces a ring opening reaction through a nucleophilic attack.

condensation of the inorganic salts and more importantly slows down the condensation rate, which is highly beneficial to form an inorganic oxide framework.

This type of reaction worked for transition and main group metal oxides as long as the formal oxidation state of the metal in the precursor is larger or equal to 3+.[304] The work on Fe_2O_3[303] by Gash et al. was then gradually extended to Fe_3O_4,[307,308] β-FeOOH,[306] Fe_3C,[309] Pd[310] and K[311] doped iron oxide and iron–chromium mixed oxides gels.[312] Gash et al. were also the first to synthesize a metal oxide based aerogel with a divalent metal ion through the EA method.[313] However, the formation of divalent metal containing aerogels remained difficult until the discovery of the dispersed inorganic method (DIS), which will be covered later in this Review. Hu et al. expanded the EA method to binary spinel nickel cobaltite aerogels, which were crystallized already at a calcination temperature of 200 °C and which were tested as capacitor materials.[314] Also Al_2O_3 was synthesized,[315,316] and by addition of poly(ethylene oxide), the pore size could be modified.[317] Heterogeneous catalysts based on Al_2O_3 with CuO and ZnO for methanol synthesis were obtained by Epple et al.,[318] while Hope-Weeks et al. later on showed the co-gelation of aluminium and nickel nitrate salts.[319]

Combined with non-alkoxide chemistry, the EA method allowed the synthesis of yttria stabilized zirconia.[320] The formation

mechanism, role of cyclic ether,[321] solvents[321] and PO[322] on surface area and morphology were investigated thoroughly, and alternative synthesis routes were found with different salts and alkoxides.[323] Recently, monolithic zirconia aerogels were obtained by a nitric acid assisted EA method.[324]

High surface area SnO_2[325] and ZnO[326–328] aerogels were synthesized by different groups. Their combination as nano-composite ZnO–SnO_2 showed an efficient degradation of RhB.[329]

Doping of tin oxide is a widely used strategy towards con-ducting materials, which are often used as transparent electro-des in LCD,[330] LED[331] and solar cells.[332] Through traditional sol–gel chemistry the synthesis of well-crystalline conducting aerogels is difficult, while the demand for porous conducting networks in battery materials[333] and fuel cells[334] continuously grows. With the synthesis of indium doped tin oxide aerogels through the EA method with glycidol, this gap could be closed.[335] Agrios et al.[336] produced transparent conducting aerogels through the EA route with antimony doped tin oxide as electron scavenger in dye sensitized solar cells.[337]

Until today, the family of accessible materials for aerogels through the EA method has grown a lot. It is possible to gel materials including TiO_2,[338] V_2O_5,[339] Co_3O_4,[340] UO_3,[341] Gd_2O_3,[342] many different lanthanide oxides,[343] mixed oxides from chloride precursors,[344] Ta_2O_5,[345] Mn_3O_4,[346] Y_2O_3[347] and Eu doped Y_2O_3,[348] ThO_2,[349] and more complex materials such as nickel alumina composites,[350] $ZnFe_2O_4$,[351,352] VFe_2O_x,[353] $La_{0.85}Sr_{0.15}MnO_3$,[354] $MnFe_2O_4$,[355] $NiFe_2O_4$[356] and recently simonkolleite.[357]

Despite all the improvements that came along with the EA method, crack-free monolithic materials from bivalent metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, etc....) were still not easily accessible. Further progress was achieved with the development of the DIS route, a modification of the EA procedure, by Du et al.,[358] which involves the addition of polyacrylic acid (PAA) and PO to inorganic salt solutions. PAA acts as both dispersant through its steric hindrance and also as template for gel formation. The carboxyl group is an active nucleation site for the sol, which grows along the PAA backbone and links the colloids together to build a three dimensional network (Scheme 3).

Compared to the EA approach, this method yields aerogels with less shrinkage and a stronger scaffold. Especially for bivalent metal ions the difficulties of three dimensional crosslinking could be solved.[358,359] The DIS method allowed the synthesis of oxidic aerogels from inorganic salts (selected examples are visualized in Fig. 6).[358–360] Later, Zhang et al. adapted the DIS method to amorphous nickel oxide based aerogels with enhanced firmness compared to the EA method.[361]
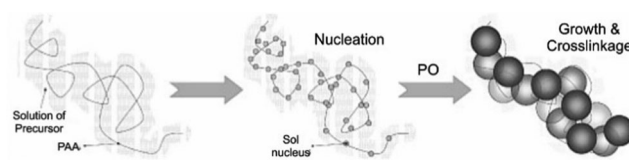
Scheme 3 Nucleation and growth of the sol along the PAA chain via DIS method. Adapted from ref. 358, Copyright 2008, with permission from Elsevier B.V.
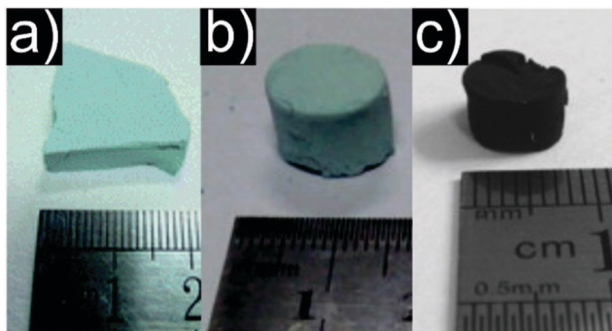
Fig. 6 Representative photographs of aerogels produced by the DIS method: (a) chromia, (b) Cu containing (c) CuO. (a) Adapted with permission from ref. 359, Copyright 2011, The Royal Society of Chemistry and the Centre National de la Recherche Scientifique. (b and c) Adapted from ref. 358, Copyright 2008, with permission from Elsevier B.V.

So far, we only discussed materials with metal ions in oxidation states larger than 0. To our knowledge, there is no direct synthesis route available so far for pure metallic aerogels.[362] However, there are several other routes to porous metal architectures available in literature.[9,363] In a typical sol–gel process, the formation of the metal oxide is often favoured, and to obtain a metal, the oxide needs to be further reduced.[364,365]

Hope-Weeks et al. showed an elegant solution to this problem by first gelling copper oxide,[366] CuO–NiO[367] or ZnO–CuO.[368] After calcination in an atmosphere containing 5% hydrogen and 95% nitrogen, the copper oxide was reduced to Cu_2O and metallic Cu.[369] Zhang et al.[370–372] managed to obtain pure metallic copper aerogels after annealing under reducing atmosphere.[373] Leventis et al. produced pig iron aerogels, an intermediate product of smelting pure iron from ore, by nanosmelting interpenetrated networks of carbon and iron oxide aerogels.[374] Recently, the same group introduced a new route to pure metallic iron aerogels by simultaneously gelling iron precursors with a polybenzoxazine network as template. After carbonization and removal of the carbon network a porous metallic iron structure with 7% relative bulk density was achieved.[375,376] The group of Zhou et al. recently showed the formation of metallic titanium aerogels by using TiO_2 aerogels as template and subsequent magnesiothermic reduction and etching with HCl.[377]

To sum up, a large variety of aerogels have been produced by molecular approaches. Properties such as high surface area and extremely low density make aerogels promising candidates for applications as catalysts,[378,379] supports for catalysts,[380] sensors,[63] filters,[381] cosmic dust collectors,[100,382] detectors in particle physics,[103,383] thermal insulators,[384] interlayer dielectrics,[103] optical applications,[63] and many others.[98,385–388] As a conductive matrix, aerogels could be potentially applied in battery materials, capacitors and components in fuel- or solar cells.[389] But despite their enormous application potential, the great morphological features of aerogels are still far from being fully exploited mainly due to their low crystallinity and the difficulties to access compositions with particularly broad functionalities. The reasons for these drawbacks can be found in the underlying sol–gel process, which is still the most popular route to such aerogels.

On the one hand, some precursors are not commercially available or only at high costs, and on the other hand their chemistry is not understood and thus not controllable. Additionally, gels obtained through the sol–gel route are most often amorphous and calcination at high temperatures is necessary for crystallization. However, annealing is accompanied by loss of many properties typical for aerogels. Particle growth and coalescence lowers the surface area and the porosity, leading to the collapse of the structure and destruction of the monolithic body. Additionally, phase separation and loss of stoichiometry might occur at high temperatures. Many metal oxides, especially mixed oxides,[390] are hard to synthesize in gel form as adjusting and controlling the hydrolysis and condensation rates of the molecular precursors remains a major challenge. With the development of the EA and DIS methods, the range of available materials could be expanded significantly, but the crystallinity has not yet been satisfactorily resolved. Furthermore, pure metallic aerogels cannot directly be synthesized through molecular routes without thermal treatment in reducing atmospheres.

An elegant and likewise powerful method to overcome these drawbacks is to use preformed nanoparticles as building blocks and assemble them into aerogels.[391] The difficulty here is to control the assembly behavior of the nanoparticles into a three-dimensional percolating network stable enough to allow further processing without the use of any templates. This approach is covered in the next section of this Review.

5. Particle based aerogels

The availability of an immense library of nanoparticles with different sizes and shapes offers a great opportunity to control and combine the distinct and versatile properties and functionalities by using them as building blocks. Assembling nanoparticles in a bottom-up process, similar to connecting LEGO bricks,[29] into aerogel monoliths opens up the possibility to conserve their properties in a truly nanostructured macroscopic bulk material. Such aerogels not only show high porosity, high surface area and low density, but due to the intrinsic properties of their building blocks also new functionalities such as super-para-magnetism,[392] ferroelectricity,[393] luminescence,[394] (photo)catalytic activity[99,395] or electrical conductivity[389,396] can be introduced to the whole framework. Especially for batteries,[397] fuel[398] or solar cells[337] such porous conducting networks are of high interest. The next part of this Review is dedicated to a general overview of the different steps of assembling preformed nanoparticles into aerogels (Scheme 4).

In a first step, the building blocks need to be synthesized. In most cases, wet chemical processes are applied, because they offer good control over particle size, size distribution and shape. Most importantly, solution approaches enable control over the surface chemistry, which is essential to prevent or minimize agglomeration for good redispersibility in the next step. Nowadays a broad variety of synthesis methods for defined nanoparticles is available, including aqueous[109] and nonaqueous sol–gel processes,[399,400] polyol route,[401] hot-injection,[402]
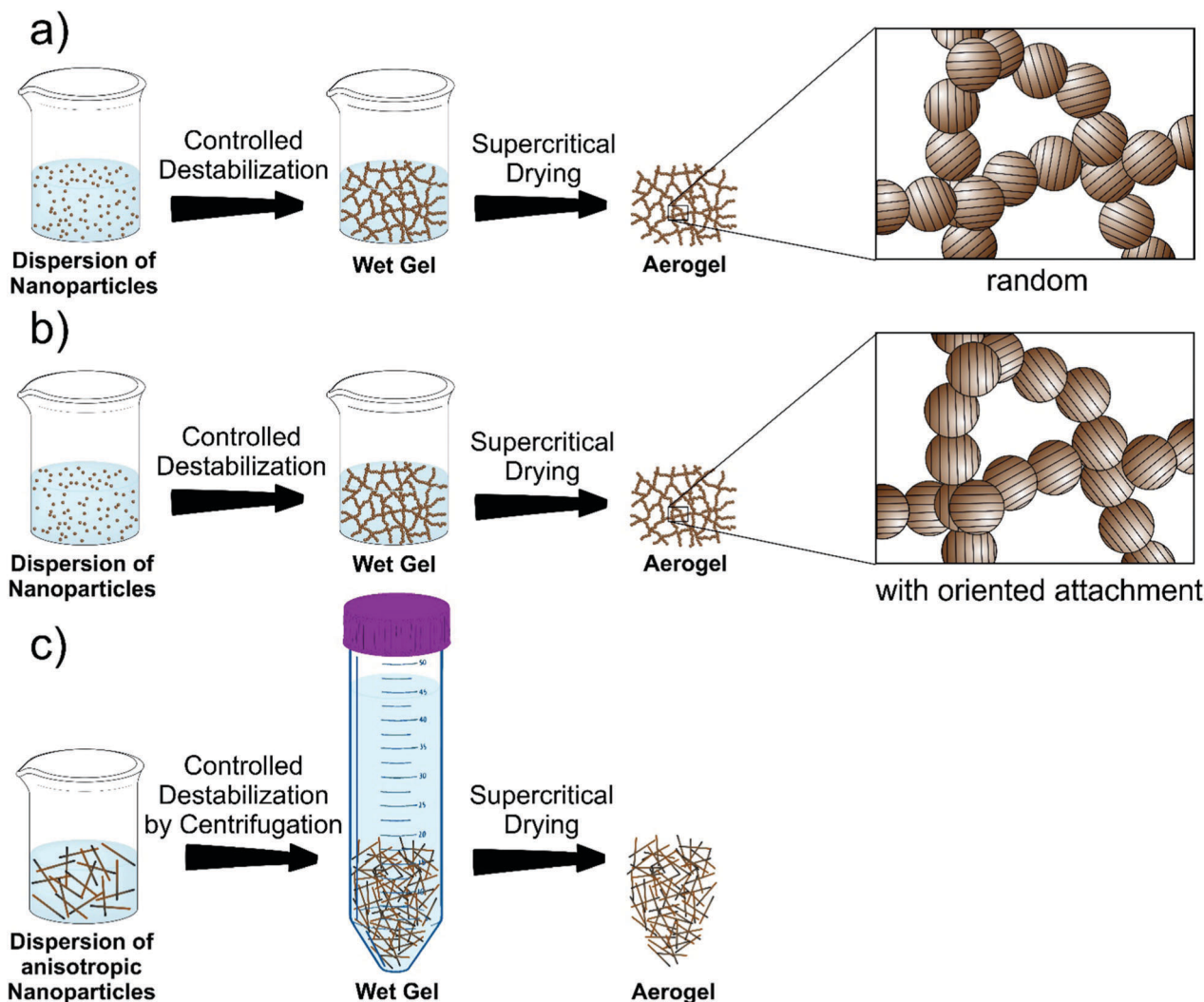
Scheme 4 Overview of the gelation of preformed nanocrystal building blocks into three dimensional macroscopic aerogel monoliths. After dispersing the nanoparticles in high concentration, the controlled destabilization leads to gelation. (a) In most systems the assembly of the nanoparticles occurs at random crystallographic orientation (*e.g.* chalcogenides, metals,…). (b) Selected systems assemble through an oriented attachment mechanism (*e.g.* TiO$_2$ and SnO$_2$). (c) Dispersions of anisotropic building blocks can often be destabilized through mild centrifugation (*e.g.* WO$_x$, Y$_2$O$_3$,…).

heating-up method,[403] hydro- and solvothermal processing[404] and many others.

The next step is to immerse the building blocks in a highly concentrated dispersion. The concentration needs to be high enough to reach a percolation threshold during gelling. However, it is vital that the particles remain separated without aggregation. Dispersion forces such as van der Waals interactions are omnipresent sources of attraction and depend strongly on the nature of the particles within the medium and are seldom practical to modify.[92] Therefore, in an unstable system, the colloids tend to form aggregates and sediment. In colloidal science the objective in this step is to turn the particles into so-called ''hard spheres''. This model involves impenetrable spheres that experience an extremely strong repulsion at very close distances but otherwise do not interact which each other. They are subjected to the Brownian motion, but at close proximity van der Waals forces are not able to cause aggregation due to the strong repulsion.[92]

For a dispersion to remain stable, the nanoparticles typically need to be stabilized sterically by brushes, surfactants or electronic charges to avoid spontaneous aggregation. For any specific system, the balance of attractive and repulsive forces between particles governs the behaviour of the particles, *i.e.*, whether they form a stable dispersion or undergo coagulation.[405–407] Each system is a unique combination of stabilizing strategies and solvents used. A generally applicable recipe or unifying concept to prepare concentrated colloidal nanoparticle dispersions is still missing and part of intense research.

The third step towards aerogel formation is the controlled and efficient destabilization of the dispersions. Obviously, the dispersions should not be too stable, otherwise the gelation is not possible anymore. Usually, strategies for destabilization involve photochemical treatment,[408] temperature change,[396] sonication,[393] adding chemicals[394] or additional solvents[396] for the removal of stabilizing ligands from the surface of the

nanoparticles[395] or neutralizing surface charges by changing the ionic strength[409] or pH[410] of the media. As the subtle balance between attractive and repulsive forces is sufficiently disturbed, the attractive interactions gain the upper hand and the dispersed colloids are no longer sterically or electrostatically well separated.[92] As a result, the particles become more "sticky" and do not act like hard spheres anymore, but collide and fuse together.[411] Due to the large number of colloids in a concentrated dispersion, rapid aggregation occurs. Although van der Waals forces are very weak and thus easily broken, irreversible strong interactions can still be formed upon contact through diffusion of atoms to reduce the surface free energy.[412,413] In any case, it is crucial to control the rate of the destabilization process.[414,415] If it is not efficient enough, the nanoparticles do not gel but flocculate and, depending on gravitational settling, simply sediment. Under optimal conditions, the colloidal aggregates form a percolating network throughout the entire volume of the sample and a gel is formed.[92] In most systems, the nanoparticles fuse upon contact at random orientations and atom diffusion can occur (Scheme 4a). However, TiO_2 and SnO_2 are among the few systems undergoing oriented attachment upon controlled destabilization (Scheme 4b). This mechanism and the destabilization of anisotropic building blocks (Scheme 4c) will be discussed later in this Review. Finally, in the last step, the wet gel is supercritically dried to obtain the nanoparticle based aerogel.

The assembly of building blocks of just a few nanometres in size to centimetre sized macroscopic structures looks particularly impressive, if we consider that such a process bridges seven orders of magnitude in length scale.

Chalcogenides

The first and presumably best understood example of a particle based aerogel made use of chalcogenide quantum dot semi-conductor nanocrystals as building blocks. Boilot *et al.* investigated the sol to gel transition through oxidative surface ligand removal in capped CdS[416–418] colloids with ^{19}F NMR measurements.[419] The group of Brock *et al.* studied the bottom up assembly of chalcogenide nanocrystals into macroscopic aerogels extensively and with great success, laying the foundations for the particle based approach to aerogels. The first results on CdS (Fig. 7a),[394,420]
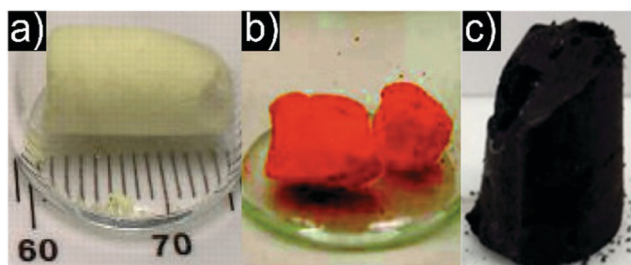
Fig. 7 Representative photographs of aerogel monoliths consisting of (a) CdS, (b) CdSe, and (c) Ni_2P nanoparticles. (a) From ref. 394, Copyright 2005, adapted with permission from AAAS. (b) Adapted with permission from ref. 425, Copyright 2008, American Chemical Society. (c) Adapted with permission from ref. 446, Copyright 2014, American Chemical Society.
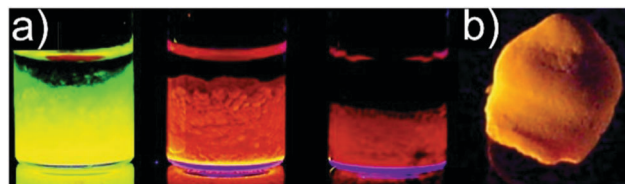
Fig. 8 Representative photograph of luminescent gels under UV illumination: (a) wet CdSe/ZnS core/shell nanoparticle based gels, (b) CdTe nanoparticle based aerogel. (a) Adapted with permission from ref. 428, Copyright 2007, American Chemical Society. (b) Adapted with permission from ref. 408, Copyright 2008, Wiley-VCH Verlag GmbH & Co.

ZnS,[394] PbS[394] and $CdSe$[394] (Fig. 7b) aerogels showed optical properties (*i.e.*, blue-shift) characteristic for quantum confined nanocrystals even in the bulk aerogel.[421] Later, also GeS_x aerogels were produced.[422] The optical properties were related to the pore structure and could be tuned by changing the network density[423] through different concentrations of the primary particles,[424] their morphology[425,426] and subsequent heat treatments.[427] However, these aerogels only showed weak emissions due to the large number of trap states leading to nonradiative recombination. This drawback was resolved by the development of CdSe/ZnS core/shell nanoparticle based aerogels (Fig. 8a), where the structural dependence of the optical properties could be bypassed.[428] Furthermore, the aggregation kinetics of these core/shell nanoparticles was investigated by time resolved dynamic light scattering,[429] and transparent conducting xerogel films were produced directly from the same dispersions.[430] Progress and perspective of this emerging field was summarized in several reviews.[266,267,431–433] Meanwhile, the family of available aerogels includes selenides (Ag_2Se[434] and $PbSe$[435]) and tellurides ($PbTe$,[436] $CdTe$,[437] Bi_2Te_3[438] and $Bi_{2−x}Sb_xTe_3$).[438] The gelation mechanism of the selenides (and tellurides analogously) involved oxidation of the surface attached thiolates (*e.g.* by H_2O_2), leading to the release of Cd^{2+} ions from the surface of the particles and to the formation of a selenide rich surface. Excess oxidizing agents then oxidized the surface selenide groups, resulting in cross-linked di- or polyselenide species. The mechanism of linking particles through selenide and telluride bonds, respectively, was confirmed by Raman and XPS measurements,[437,439] and the pore structure of the aerogels was analysed by [129]Xe NMR measurements.[440] These chalcogenide aerogels are promising for applications in optoelectronic devices,[441] optical sensing,[442] remediation of polluted water[443] and for quantum dot based photovoltaic devices.[444] Recently, the same group managed to synthesize InP[445] and Ni_2P[446] aerogels with similar gelling mechanisms (Fig. 7c).

The success of the method developed by Brock *et al.* inspired other groups to investigate other systems suitable for gelation. Hope-Weeks *et al.* studied the influence of gold[447] and silver[448] coatings on CdS on the aerogel morphology and porosity. Yunfeng *et al.* used different carbohydrates as ligands for the formation of PbTe nanoparticle networks.[449] Extremely high exciton lifetimes and large fluorescence quantum yields were achieved by Bigall *et al.* through the combination of CdSe and CdS nanorods.[450] Recently, they synthesized aerogel monoliths

from CdSe and CdSe/CdS core/crown nanoplatelets with solely (111) as the exposed facet, strong quantum confinement and high photoluminescence quantum yields.[451] Capped CdTe nanocrystals were used by Eychmüller *et al.* and assembled through a photochemical treatment[408] or metal salt addition (Fig. 8b).[452,453] Later, this assembly method was extended to CdTe/Au mixed aerogel structures.[454,455] Furthermore, the optical properties could be controlled by using different types (ZnSe, CdTe) and different sized semiconductor quantum dots in a single hybrid network. Due to different energy levels and non-radiative transfers from donor to acceptor levels of the different colloids, the emission of the aerogel could be finally tuned to achieve white photoluminescence.[456] In another work, enzymes were encapsulated within the gels, resulting in multifunctional hybrids with a sensing and signalling unit in the same spatially confined structure.[457] Recently the group showed the removal of the native long-chain organic ligands from a variety of synthesized nanocrystals, replacing them by different inorganic ionic or complexing ligands. Subsequently, the nanoparticle dispersions could be destabilized by the addition of acetate salts with the appropriate coordinating cations such as Cd^{2+}, Pb^{2+} and Zn^{2+}. The resulting gels showed a complete lack of organic residues with strong linking of the nanocrystals through bridging of the cations.[458]

Metals

Previously in this Review, the difficulties to synthesize metal aerogels directly from molecular precursors have been shown. However, the use of preformed nanoparticles as building blocks represents a viable alternative, especially because metal nanoparticles are readily available in a large variety.[459]

Although low-density metal foams are sometimes regarded as the first examples of metal aerogels,[460] we want to highlight instead the pioneering work of Eychmüller *et al.*, who in 2009 reported the synthesis of metallic aerogels based on colloidal assembly.[461,462] Various noble metal nanoparticles were gelled into single (Ag, Au, Pt, see Fig. 9a) and bimetallic (Ag–Au and Ag–Pt) aerogels. For the formation mechanism they proposed the initial metal nanoparticles to coalesce upon contact by atom diffusion occurring between the connected particles.[463] Later, they prepared pure Pd,[464] bimetallic as well as alloyed

Fig. 9 TEM images of aerogels consisting of (a) pure metallic platinum and (b) bimetallic platinum–palladium nanoparticles. Scale bars: 50 nm. (a) Adapted with permission from ref. 461, Copyright 2009, Wiley-VCH Verlag GmbH & Co. (b) Adapted with permission from ref. 463, Copyright 2014, American Chemical Society.

Pt_xPd_y aerogels (Fig. 9b) with excellent electrocatalytic and bioelectrocatalytic activities using enzyme electrodes.[465–467]

The formation of the Pd gel involved the assembly of the nanoparticles into short nanowires, followed by the formation of a nanowire network and finally the Pd gel.[468] For the enzyme composites a Ca^{2+} induced assembly of citrate coated Pd nanoparticles was applied.[466,467] With the availability of Pd aerogels, another possibility for bi- or even trimetallic noble metal aerogels was opened.[463,469] Among their latest results, the group of Eychmüller *et al.* showed the dopamine-induced assembly of metallic Au nanoparticles into aerogels with high surface area and promising applications in electrocatalysis.[470] The group showed the bottom-up design of functional aerogels by assembling alloyed PdNi nanospheres to aerogels for electrocatalysis[471] and Pd/ZnO aerogels, which were transferred into ZnPd/ZnO aerogels as catalytic material for methanol steam reforming.[472]

The group of Arachchige *et al.* reported the self-assembly of noble metal nanoshells through salt mediation[409] and oxidative removal of surface thiolates.[473] In a next step, they combined the metal (Ag) and semiconductor (CdSe) colloids to form hybrid aerogels through oxidative surface ligand removal.[474] This method allowed the tuning of interfacial reactions leading to different optical properties.

Using amyloid fibers as templates, Mezzenga *et al.* recently obtained metallic gold aerogels.[475]

Metal oxides

In spite of significant efforts, for a long time the compositions of nanoparticle based aerogels remained mostly limited to metal chalcogenides,[267] noble metals[468] and combinations thereof.[455] The gelation of colloidal manganese oxide into gels reported by Brock *et al.* in 2001 remained the only example for metal oxides for about ten years.[476] One of the reasons lies in the difficulty to synthesize well-defined, crystalline and dispersible metal oxide nanoparticles. A generally applicable synthesis method was developed by the group of Niederberger. The so-called benzyl alcohol route gave access to a large library of metal oxide nanoparticles covering a broad range of properties including electronic conductivity, ferroelectricity or magnetism.[97,477] As these nanomaterials are typically obtained in the form of powders, they lose a major part of their surface area. Assembled into an aerogel, however, the immense surface area of the nanoparticles can be retained. In comparison to aqueous routes, the use of benzyl alcohol as solvent results in nanoparticles with high crystallinity and small crystal sizes due to the stabilizing effect of benzyl alcohol. As a matter of fact, the solvent plays manifold roles as reaction medium, oxygen source, and surface modifying agent. As a result, the non-aqueous sol–gel method represents an ideal tool for the synthesis of nanocrystalline oxidic building blocks for aerogels.[97,478]

In 2011 the Niederberger group made use of the tendency of titania nanoparticles functionalized with 2-amino-2-(hydroxymethyl)-1,3-propanediol (Trizma, see Fig. 10a) to undergo oriented attachment for the formation of macroscopic aerogels (Scheme 4b and Fig. 11a), finally opening a sustainable
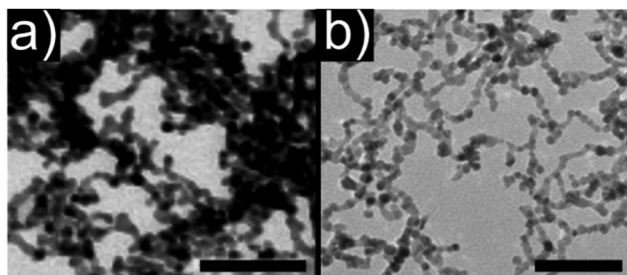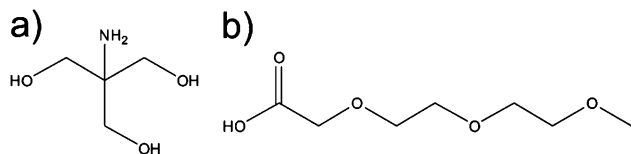
Fig. 10 Chemical structure of (a) 2-amino-2-(hydroxymethyl)-1,3-propanediol (Trizma) and (b) 2-[2-(2-methoxyethoxy) ethoxy] acetic acid (MEEAA).

approach to metal oxide particle based aerogels.[395] The aqueous dispersion was destabilized by a simple heat treatment. Addition of ethanol improved the transparency of the aerogels.[392]

Co-assembly of different types of nanoparticles in the same dispersion enabled the formation of multicomponent aerogels. The concept of introducing guests to a host, thereby combining the properties potentially even in a synergistical way, has already been shown for catalytically active sol–gel derived aerogels,[147] but is also known for silica aerogels.[479–482] In the latter case, however, the silica matrix always represents an amorphous (and typically not very functional) host, whereas in the nanoparticle approach introduction of additional functional materials within a crystalline matrix is possible.

The addition of gold nanoparticles (Fig. 11b, high resolution TEM (HRTEM) image in Fig. 11h) improved the photocatalytic dye degradation of rhodamine B by acting as electron sinks, reducing the recombination rate of the electron–hole pairs and thus resulting in longer lifetimes of the charge carriers.[395] The photocatalytic properties can be tailored further through incorporation of WO_x nanowires and gold nanoparticles into titania (Fig. 11c).[483] The addition of gold led to a higher performance in OH radical generation, whereas the addition

of WO_x increased the degradation rate of methylene blue. Together the two types of building blocks gave rise to an overall increased activity of both OH radical production and MB degradation, thereby combining their beneficial effects.[483]

Addition of negatively charged silica particles, obtained by the Stöber method, to a dispersion of positively charged Trizma functionalized titania nanoparticles resulted after gelling in an interconnected titania–silica framework (Fig. 11i).[484] Such a composite combines the photocatalytic activity of the anatase particles with the extensive possibilities of silica surface functionalization.

Furthermore, it turned out that the ternary composite aerogel consisting of a titania matrix, Pt nanoparticles and reduced graphene oxide is well suited for photocatalytic hydrogen production.[485]

The use of superparamagnetic Fe_3O_4 nanoparticles as building blocks offers several interesting possibilities. Incorporated in a non-magnetic host such as titania they enable contactless manipulation of the aerogel monolith by a magnet.[392] Different dispersion concentrations and magnetic fields during gelation gave rise to anisotropic aerogels such as layered monoliths with gradients in Fe_3O_4 concentration (Fig. 11d) or with magnetic texture (Fig. 11e) along the magnetic field lines.

Common to all these systems is the destabilization of aqueous dispersions of the Trizma stabilized anatase nanoparticles, which builds up the matrix. The selective removal of Trizma from {001} facets by water induces oriented attachment in a preferential direction over several length scales (Fig. 11f).[486,487] Due to imperfect assembly events, this process allows branching and by increasing the particle concentration in the initial dispersion, a 3-dimensional and percolating network forms,
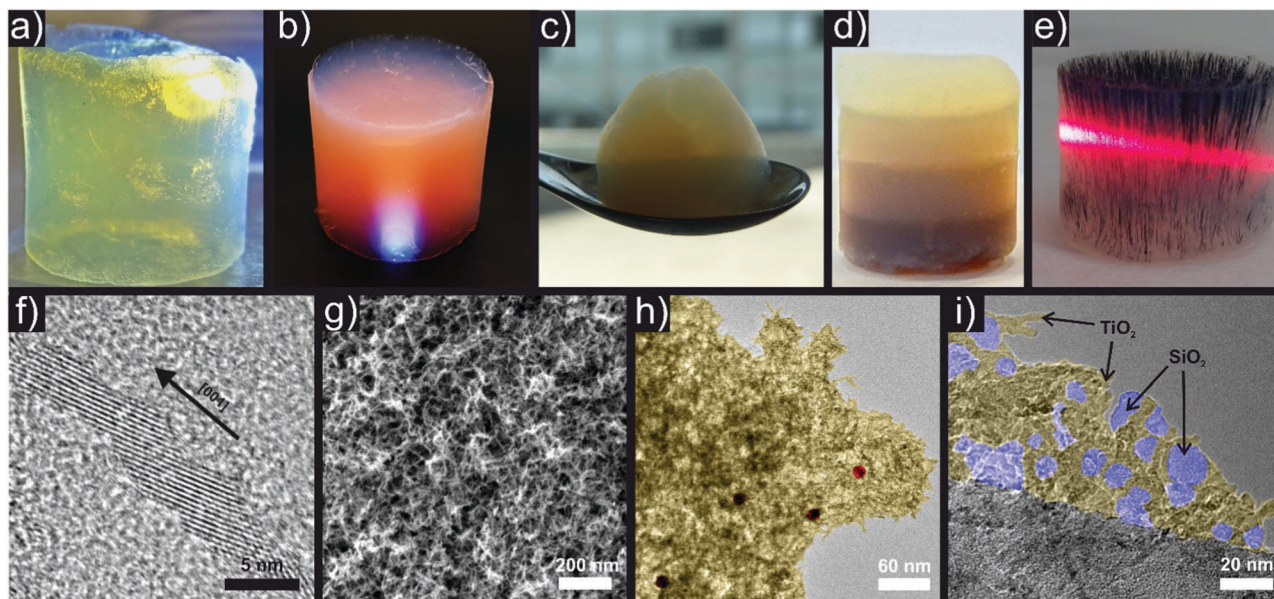

Fig. 11 Representative examples of titania based aerogels with the incorporation of different functional nanocrystals. Photographs of aerogels based on (a) pure anatase, (b) anatase with Au nanoparticles, (c) anatase – WO_x nanowires – Au, (d) layered anatase with four different concentrations of magnetite increasing from top to bottom and (e) magnetically textured anatase – magnetite with a laser beam passing through the aerogel. Selected electron microscopy images: (f) HRTEM of oriented attached anatase building blocks, (g) SEM of a pure anatase aerogel, (h) HRTEM of anatase (yellow) – Au (red) aerogel, (i) anatase (yellow) – silica (blue) composite aerogel. (a) Adapted with permission from ref. 487, Copyright 2005, Wiley-VCH Verlag GmbH & Co. KGaA.

resulting in a gel (Fig. 11g). In this case, the tendency of titania to undergo oriented attachment greatly facilitates the formation of porous gels (Scheme 4b).

Another system, which undergoes oriented attachment is SnO$_2$, when exposed to hydrothermal conditions.[488–490] SnO$_2$ is a wide-band-gap material, but it can be made conductive by doping. By traditional aqueous sol–gel synthesis it is challenging to produce aerogels of crystalline conducting oxides. However, they are readily available as nanoparticles with high crystallinity.[331,491] Therefore, antimony doped tin oxide (ATO) nanoparticles were used as building blocks for conductive aerogels.[396] Destabilization of concentrated dispersions by heat treatment led to the gelation of the building blocks with partial oriented attachment.[396] After annealing, conductivity over the whole monolithic body (Fig. 12a) could be induced without destroying the integrity and micro-structure of the aerogel (HRTEM image in Fig. 12e before and
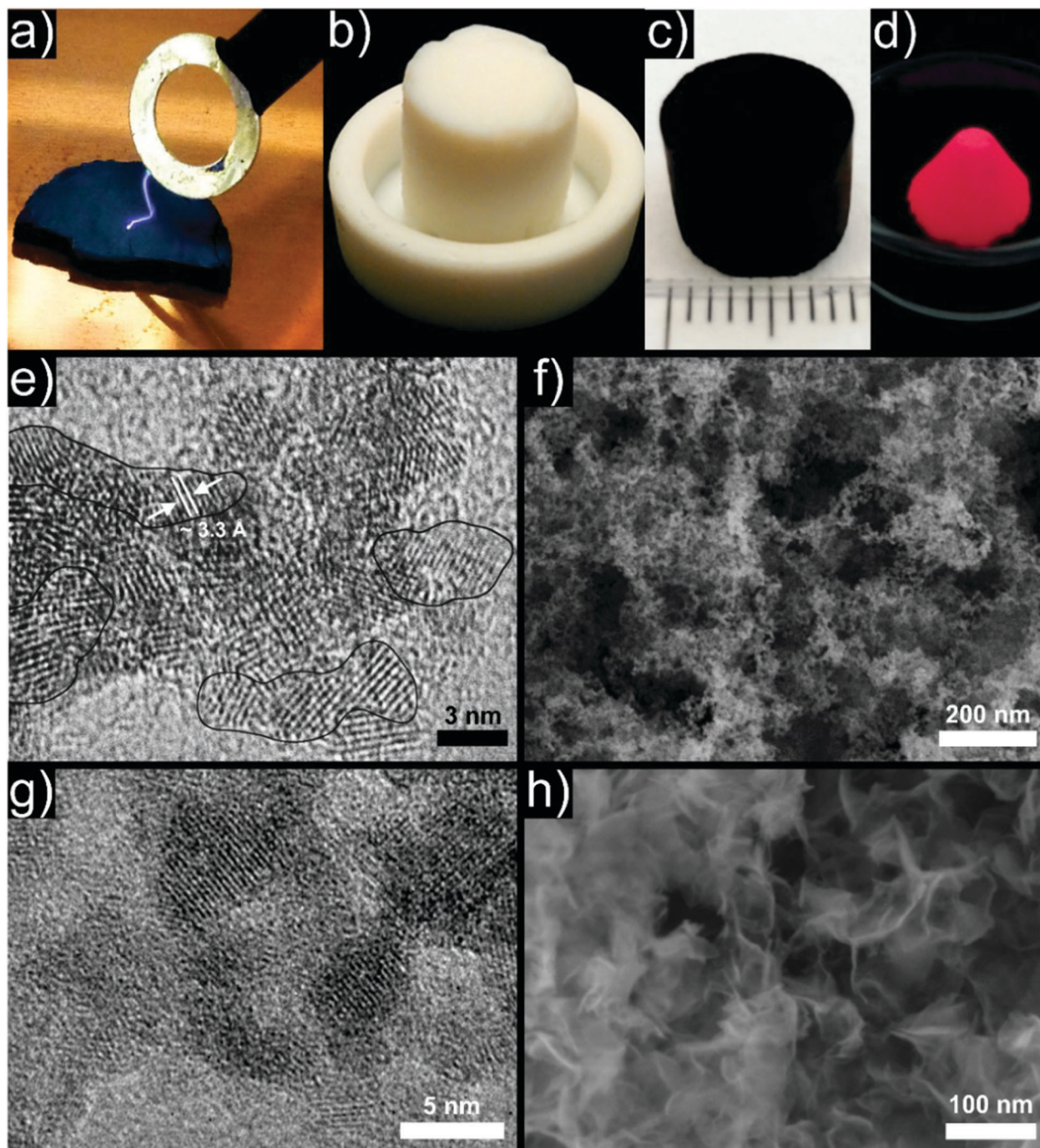

Fig. 12 Representative photographs of particle based aerogel monoliths composed of (a) conducting ATO, (b) BaTiO$_3$, (c) Cu$_3$N and (d) Eu^{3+} doped Y$_2$O$_3$. Electron microscopy images of (e) ATO aerogel before and (f) after heat treatment. (g) HRTEM image of BaTiO$_3$ nanoparticles and (h) SEM image of Y$_2$O$_3$ nanosheets in the corresponding aerogels.

SEM image in Fig. 12f after annealing). Recently, different strategies were developed to improve the electrical conductivity of these conducting aerogels without losing the porous microstructure.[492]

With the observation that 2-[2-(2-methoxyethoxy)ethoxy] acetic acid (MEEAA, Fig. 10b) functionalized nanoparticles[493] synthesized by the benzyl alcohol route can easily be dispersed in different organic solvents in high concentration,[393] another very versatile route to aerogels was discovered. A first example with this method included the formation of ferroelectric barium titanate aerogels (Fig. 12b), introducing a new type of functionality. The addition of water and heat to a concentrated ethanolic dispersion of $BaTiO_3$ nanocrystals of about 5 nm in size led to an effective destabilization process and eventually to a gel.[393] HRTEM investigations indicated another gelation mechanism than oriented attachment, as the lattice fringes of adjacent nanocrystals are randomly distributed and no oriented attachment is observed (Scheme 4a and Fig. 12g). In both systems water plays a decisive role as destabilizing agent. In case of $BaTiO_3$, it leads to a nonselective removal of MEEAA from the surface and subsequent fusion of colliding nanocrystals. Although $BaTiO_3$ is just one example of such a rapidly induced destabilization process beyond oriented attachment, the method with MEEAA functionalization is straightforward. Considering that nanoparticles prepared by the benzyl alcohol route often have a comparable surface chemistry,[477] this method could potentially be applied to other metal oxide nanoparticles, laying the foundation for a general synthesis strategy to crystalline oxide aerogels with broader compositional and functional variety.

Using a different method, many monolithic perovskite gels have been fabricated by another group.[494]

Recently, the family of aerogels was expanded to another class of materials. Starting from very small Cu_3N nanoparticles,[495] the Niederberger group presented a transition metal nitride aerogel (Fig. 12c). Here, no surface functionalization nor chemical crosslinkers were needed to gel the samples.[496]

Anisotropic building blocks

Up to here we mainly discussed aerogels made of spherical nanoparticles as building blocks. But nanocrystals are of course available in an immense variety of sizes and shapes. Especially anisotropic building blocks[497–500] such as nanowires (1D) or nanosheets (2D) are attractive, and therefore the question arises, whether it is possible to form aerogels based on building blocks of reduced dimensionality. Jung et al. reported the assembly of nanowires (Ag, Si, CNT, MnO_2) into 3D networks, if the critical concentration of the anisotropic colloidal dispersions was reached during solvent evaporation.[501] Furthermore, copper nanowires were freeze-casted in water and after subsequent vacuum drying a monolithic copper aerogel could be produced.[502] A simple approach to alumina based aerogels was carried out by Hayase et al. by aggregating boehmite nanofibers through a pH change from acidic to weakly basic.[410] Recently, Niederberger et al. used ultrathin tungsten oxide nanowires with very high aspect ratio as building blocks to synthesize monolithic aerogels (Scheme 4c).[503] Jung et al. also investigated the assembly of 2D nanosheets (MoS_2, h-BN) into macroscopic aerogels.[501]

Recently, another approach for BN aerogels was found involving freeze drying of an aqueous dispersion of BN nanosheets obtained by an urea assisted ball milling process and subsequent exfoliation.[504] Furthermore, MoO_2 nanosheets were assembled by freeze drying. Contrary to most nanocrystal based systems, no organic stabilizers were needed and therefore no organic impurities could be found in the resulting aerogel.[505] These aerogel architectures showed excellent performance in applications for lithium–air battery materials.[506]

The Niederberger group recently published a method to produce flexible hybrid aerogels based on spinel-type metal oxides and reduced graphene oxide sheets as anode materials for lithium ion batteries with greatly enhanced rate capability and long-term stability.[397] Moreover, they introduced a centrifugation assisted gelation method to produce monolithic Y_2O_3 aerogels from nanosheets (Scheme 4c). By doping and co-doping with Eu^{3+} and Tb^{3+}, luminescent aerogels with tunable color emissions from red to green under UV excitation were fabricated (Fig. 12d and h). Moreover, the as-prepared gels and aerogels exhibit excellent adsorption capacities for organic dyes.[507] Recently, WS_2 and MoS_2 aerogels were produced by freeze-drying and thermal decomposition of the metal chalcogenide precursors resulting in aerogels with layered morphologies.[508]

These examples show that the synthesis of aerogels from preformed nanocrystals is not limited to isotropic particles, offering a completely new aspect in aerogel research not accessible by molecular sol–gel routes. However, the gelling mechanisms and the various forces involved in the assembly process of anisotropic particles differ significantly and remain to be explored.

6. Conclusions & outlook

Nanoparticles are the ideal building blocks for the creation of materials. They show physical properties, which vary systematically as a function of size, but also depending on their mutual arrangement enable collective or synergistic properties. Most of the efforts were dedicated to the assembly of nanoparticles into ordered and dense structures. But in spite of all the progress, it is not yet possible to produce such assemblies with macroscopic dimensions. Aerogels, on the other hand, are nanostructured bulk materials, however with completely contrary properties: they have a low density, high porosity, large surface area and are completely disordered. But these characteristics are advantageous in terms of molecular diffusion.[41,42] One gram of TiO_2 aerogel combines the surface area of more than a tennis field with a percolating pore system for molecular transport.[483] All these properties make aerogels unique candidates for applications involving transport of matter and charges on the nanoscale.[43]

After a short historical perspective on colloidal particles and the pioneering work of Kistler on supercritical drying, we discussed the preparation of a broad range of aerogel materials (however excluding silica and carbon), starting from molecular sol–gel routes involving hydrolysis and condensation reactions, which allow for the formation of highly multifunctional materials

with distinctive intrinsic properties. The major issue for these materials is their typically amorphous nature, which is also a characteristic of silica aerogels. With the discovery of new approaches like the EA and DIS methods, the range of accessible compositions was significantly expanded by facilitating control over the hydrolysis and condensation rates and by introducing steric guidance by the polyacrylic acid.

A major advancement on the way to further increase the compositional variety and architectural complexity and to overcome the amorphous nature can be achieved by switching from molecular precursors to the assembly of preformed, nanocrystalline colloids. Since the early example of quantum dots, many different nanoparticles have been processed into crystalline aerogels including metals, metal oxides and mixtures thereof. Most recently, also anisotropic nanostructures such as nanowires or nanosheets were assembled into monolithic aerogels of macroscopic sizes.

In spite of all the progress on nanoparticle based aerogels, it is clear that we are still just at the beginning. On an incredible pace new nanoparticles with different compositions, sizes, and shapes are synthesized and published, and only a minor fraction of them has been processed into aerogels. The possibilities to use and combine these nanoparticles as a large toolbox of building blocks are only limited by imagination, and many new complex aerogel architectures will be produced in the coming years.

But in spite of all the enthusiasm for these disordered and porous materials, there are several challenges to overcome not only on the synthesis side, but also on the application side. For example, a great deal of efforts has been dedicated to the preparation of monolithic aerogels. But because most of the studied applications were performed in liquid medium,[464–466] the monolithic bodies irreversibly disintegrate into aggregates with micron size once in contact with a liquid.[395,485] Although the fragments typically still showed enhanced photocatalytic activity compared to a mixture of the corresponding nanopowders, all the benefits of a monolithic body, especially hierarchical porosity, close interaction between the different nanoparticle building blocks of the aerogels, simple isolation of the photocatalyst after the reaction, large contact area between photocatalyst and reactant are fully, or at least partly lost. Although a careful thermal treatment increases the mechanical stability of aerogel monoliths, they typically remain rather fragile, and it is hardly possible to use them in liquid media without destroying their monolithic shape.

One promising application of monolithic aerogels is in gas phase reactions. As a matter of fact, for reactions such as the production of solar fuels it seems to be even more promising to focus on gas phase solar fuel (*e.g.* fuels from CO_2 with the use of sunlight) reactions, or, as Geoffrey Ozin wrote in his recent perspective: "*It is becoming increasingly apparent that the solar refinery of the future cannot be limited to the historical approach of aqueous-phase biomimetics, which is often characterized by low […] conversion efficiencies. A shift to gasphase heterogeneous catalysis is occurring and looks promising in terms of its ability to deliver high […] conversion efficiencies with the added advantage of being able to interface seamlessly with existing chemical and petrochemical industrial infrastructure.*"[509] The development of aerogels as all-active highly porous gas-phase catalysts without the need of an inactive catalyst support (*e.g.* silica-based aerogel catalysts)[479] will allow for very efficient conversion rates. We expect that results in this direction will lead to a breakthrough in the field of aerogel research and will have a significant impact.

Acknowledgements

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